

Experimental aspects of molecular electronics''

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Chapter 2

Reminder to Solid State Physics

2.1 Electronic states and their occupation

2.1.1 Excitation spectrum, dispersion relations

Schrödinger Equation

$$\left(-\frac{\hbar^2}{2m}\Delta + V(\vec{r})\right)\Psi = E\Psi$$

$V(\vec{r})$ periodic $\rightarrow \Psi_{n,\vec{k}}$ Bloch states

Excitation spectrum splits up into *bands* $E_n(\vec{k})$.

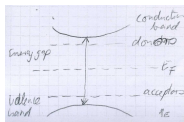
Group velocity

$$\vec{v}_n(\vec{k}) = \frac{\partial}{\partial \hbar \vec{k}} E_n(\vec{k})$$

Semiconductors

all bands either completely occupied or completely empty

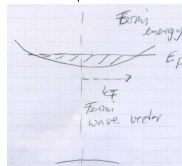
$\rightarrow$ excited states are separated from ground state by an energy gap



Metals

partially occupied bands

$\rightarrow$ excitations with arbitrarily small energy



For small excitation

energies the excitation spectrum is characterized by a small number of parameters.

parabolic approximation of $E_n(k)$

effective mass for one band

$$(m_n^*)^{-1} = \frac{\partial^2 E_n(k)}{\partial \hbar k^2}$$

example GaAs

m^*/m

0.07 Conduction band

Valence band:

0.12 light holes

0.68 heavy holes

linear approximation of $E_n(k)$

Fermi velocity

$$\vec{v}_F = \left. \frac{\partial E_n(\vec{k})}{\partial \hbar \vec{k}} \right|_{\vec{k}=\vec{k}_F}^{-1} = \frac{v_F}{\hbar k_F}$$

If interactions are neglected, m^* contains no additional information

In general metals have high electron density, i.e. electron-electron interaction (eei) becomes important.

The simplest description of eei is given by Landau's theory of Fermi liquids.

Main result: eei moves energy levels $\rightarrow$ renormalization of the effective mass

$$(m^*)^{-1} = \left. \frac{\partial^2 E^{free}}{\partial \hbar k^2} \right|_{k=0} \cdot (1 + \lambda)$$

λ : material dependent. Can achieve values up to ≈ 1000 "heavy fermions"

For simplicity we treated here the 1dim case. In general m_n^* is a tensor.

2.1.2 Effective mass approximation

Assumption: The electrons within one band behave like free particles with mass m^*

Hamiltonian

$$H = \sum_n \frac{1}{2m_n^*} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

Eigenstates are plane waves with

$$E_n(\vec{k}) = \frac{\hbar^2}{2m_n^*} \vec{k}^2,$$

$$\Psi_{n\vec{k}} = e^{i\vec{k} \cdot \vec{r}}$$

We consider periodic boundary conditions and a volume $\Omega = L^d$ (with $d = 1, 2, 3$: dimensions of the system; L : length)

For simplicity we deal with the 1d case and suppress indices

$\Psi(x) = \Psi(x + L) \rightarrow k_i = n_i \frac{2\pi}{L} \rightarrow$ discrete values for k_i . The volume of one state in k -space is $(2\pi)^d / L^d$.

Electrons carry the spin $s = 1/2 \rightarrow 2$ states per volume element $\rightarrow$

Density of states in k -space: $\rho_k = \frac{2}{(2\pi)^d}$

All electrons in the system have to find a state in the energy range from zero to E_F

$\rightarrow$ electron density:

$$n(E_F) = \sum_{\text{all occupied states}} \frac{2}{(2\pi)^d} \underbrace{\rightarrow}_{\substack{\text{L big} \rightarrow \text{many states} \\ \text{k-states quasi} \\ \text{continuous}}} \frac{2}{(2\pi)^d} \int d^d k \rightarrow \int_0^{E_F} dE \rho_d(E)$$

with the density of states (DOS) $\rho_d(E)$ in d dimensions.

States are filled up to the Fermi energy E_F , i.e. up to the Fermi wave vector k_F .

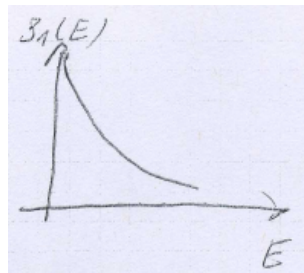
2.1.3 Density of states

$$\rho(E) = \frac{d}{dE} n(E) \text{ with } E = E_n(\vec{k})$$

- DOS appears in equations whenever one moves from a sum over discrete values (e.g. wave vectors) to a continuous variable (e.g. energies)
- DOS denotes the number of states available per energy range of a given energy and per volume
- DOS depends on the dimension of the system

We first consider "sharp" dimensions, i.e. strictly 1d, strictly 2d, strictly 3d systems.

Strictly 1 dimensional systems



$$n_1(E_F) = \frac{1}{\pi \hbar} \sqrt{2m^* E_F} = \frac{1}{\pi} k_F$$

(lin. effective mass approximation with $E = \frac{\hbar^2 k^2}{2m^*} \rightarrow k = \frac{1}{\hbar} \sqrt{2m^* E}$)

$$\rightarrow \rho_1(E) = \frac{1}{\pi \hbar} \sqrt{\frac{m^*}{2E}}$$

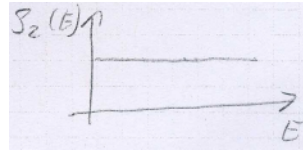
square-root singularity at $E = 0$

For many physical properties the value $\rho(E_F)$ at the Fermi energy is important

$$\rho_1(E_F) = \frac{1}{\pi \hbar} \sqrt{\frac{m^*}{2E_F}}$$

Strictly 2 dimensional systems

$$n_2(E_F) = \frac{1}{2\pi^2} \int_{\text{Fermi circle}} d^2k = \frac{1}{2\pi} \int_0^{k_F} d|k| 2\pi k = \frac{1}{\pi \hbar^2} m^* E_F = \frac{1}{2\pi} k_F^2$$

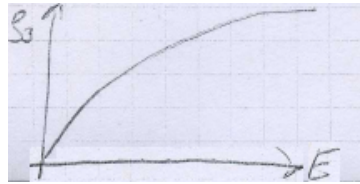


$$\rightarrow k_F = \sqrt{2\pi n_2(E_F)}$$

$$\rho_2(E) = \frac{m^*}{\pi \hbar} = \rho_2(E_F) = \text{constant}$$

Strictly 3 dimensional systems

$$n_3(E_F) = \frac{1}{4\pi^3} \int_{\text{Fermi sphere}} d^3k = \frac{1}{4\pi^3} \int_0^{k_F} d|k| 4\pi k^2 = \frac{1}{3\pi^2} k_F^3 = \frac{1}{3\pi^2 \hbar^3} (2m^* E_F)^{3/2}$$



$$\rightarrow k_F = (3\pi^2 n_3(E_F))^{1/3}$$

$$\rightarrow \rho_3(E) = \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \sqrt{E}$$

square-root function

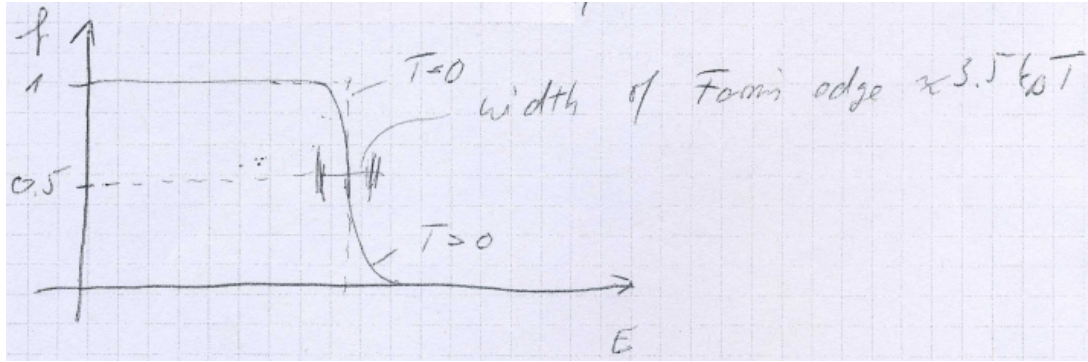
2.1.4 Occupation probability, distribution function

The thermodynamic properties of quantum systems are determined by occupation probabilities of quantum states.

For fermions (e.g. electrons) the equilibrium occupation (or distribution) function of a temperature T is:

$$f(E, T, \mu) = \frac{1}{1 + e^{(E - \mu)/k_B T}}$$

Fermi distribution function with μ : electrochemical potential, k_B : Boltzmann constant



Position and sharpness of Fermi edge are determined by the chemical potential μ and the temperature T .

Important relations:

$$\text{particle density } n(T, \mu) = \frac{\partial \phi(T, \mu)}{\partial \mu} = \int_0^{\infty} \rho(E) f(E, T, \mu) dE$$

$$\text{entropy density } s(T, \mu) = \frac{\partial \phi(T, \mu)}{\partial T} = \int_0^{\infty} \rho(E) \{f \ln f + (1-f) \ln(1-f)\} dE \quad (\text{Boltzmann's principle})$$

μ and n , and T and s are thermodynamically conjugated variables.

ϕ : thermodynamic potential (here $\phi = p$ pressure)

Insertion: Reminder of Thermodynamics of Solids

Euler's Theorem:

$$\underbrace{E}_{\text{Energy}} = \underbrace{T}_{\text{Temperature}} \cdot \underbrace{S}_{\text{Entropy}} - \underbrace{p}_{\text{Ppressure}} \cdot \underbrace{V}_{\text{Volume}} + \underbrace{\mu}_{\text{Chemical Potential}} \cdot \underbrace{N}_{\text{Particle Number}}$$

$$dE(S, V, N) = TdS - pdV + \mu dN$$

complete Legendre transformation

$$\rightarrow 0 \equiv U - TS + pV - \mu N \rightarrow -SdT + Vdp - Nd\mu = 0$$

eliminate one extensive variable. Solids are almost incompressible $\rightarrow$ eliminate V

$$\rightarrow dp = \frac{S}{V}(T, \mu)dT + \frac{N}{V}(T, \mu)d\mu = s(T, \mu)dT + n(T, \mu)d\mu$$

$$\Omega(T, V, \mu) = V \cdot p(T, \mu) \text{ grand canonical potential}$$

$\rightarrow$ description via densities.

Chemical potential is of central importance for transport processes, because it links changes of densities to changes of the energy:

$$d\left(\frac{E}{V}\right) = \mu d\left(\frac{N}{V}\right) = \mu dn \text{ if } S, V = \text{const.}$$

If μ and n are spatially inhomogeneous, $\text{grad}\mu(\vec{r})$ defines direction of particle in order to minimize the energy $\rightarrow \text{grad}\mu(\vec{r})$ drives transport processes.

Charged particles (e.g. electrons) $n(\vec{r})$ and $\vec{j}$ (currents) are additionally driven by electrical fields (gradients of the electrostatic potential) $\rightarrow$ electrochemical potential η

$$\eta = \mu + q\Phi$$

q : charge

Φ : electrostatic potential $\vec{E} = -\text{grad}\Phi$

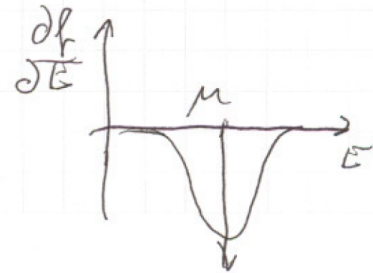
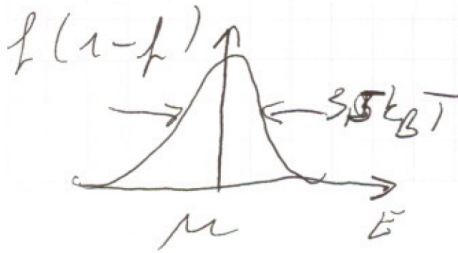
A voltmeter measures differences of η

In solid state physics often μ is written when η is meant i.e. η enters the Fermi function.

Nomenclature: We use μ for electrochemical potential
 " μ_0 for chemical potential
 Low temperatures: $k_B T \ll E_F$
 E_F and μ almost identical

$$\mu(T, n) \xrightarrow{T \rightarrow 0} E_F(n)$$

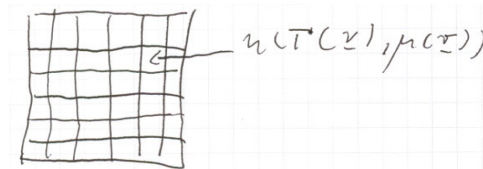
Useful relations:



$$f(E)(1 - f(E)) = -k_B T \frac{\partial f}{\partial E} = \frac{1}{4 \cosh^2 \left(\frac{E - \mu}{2k_B T} \right)}$$

$$\lim_{T \rightarrow 0} \frac{\partial f}{\partial E} \rightarrow -\delta(E - \mu)$$

Weak non-equilibrium



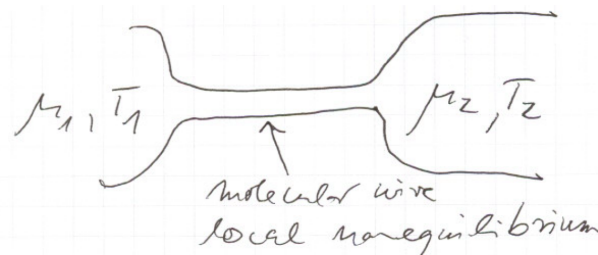
Description via densities is useful for spatially inhomogeneous systems like molecular junctions
 → segmentation into small cells. If $\text{grad} T$ and $\text{grad} \mu$ are small, the cells are in local equilibrium.

Strong non-equilibrium

Distribution function f differs from Fermi function

→ computing f from Boltzmann equation

Definition Reservoir: Area in local thermodynamic equilibrium



Calculation of currents (in bulk solid state physics)

$$\vec{I}_n = \frac{2}{(2\pi)^d} \int d^d \vec{k} f(\vec{k}) \vec{v}(\vec{k}) \quad \text{particle current}$$

$$\vec{I}_E = \frac{2}{(2\pi)^d} \int d^d \vec{k} f(\vec{k}) \vec{v}(\vec{k}) E(\vec{k}) \quad \text{energy current}$$

$$\vec{I} = e \vec{I}_n \quad \text{electrical (charge) current}$$

During this course we will see several other formulations of current formulae that we adapted to molecular electronics problems.

Classical current formula (school physics)

$$\underbrace{\vec{j}}_{\text{current density}} = \underbrace{e}_{\text{charge}} \underbrace{n}_{\text{electron density}} \underbrace{\vec{v}}_{\text{velocity}}$$

Cf $\rightarrow$ electron density is replaced by integral over distribution function

2.2 Reduced Dimensions

- If the dimensionality is not strictly fulfilled, but a transitional region is achieved, also the density of states takes up an intermediate character. The electrodes in use for molecular electronics often lie in these intermediate regimes (2d to 3d or 1d to 2d). The molecular systems themselves may be of intermediate character between 1d and 0d (see below). A characteristic new concept in reduced dimensions is the appearance of subbands.
- Approach: Boundary conditions for solving the Schrödinger equation are different in varying directions. E.g. localization of the wave-function in a confinement potential.

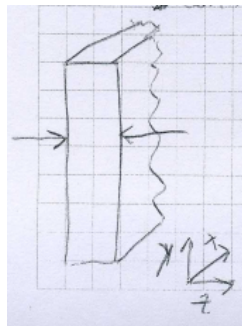
2.2.1 Confinement from 3D to 2D

"Quantum Well", "Quantum film"

Model: Confinement potential $U(z)$ in one direction (z), periodic boundary conditions in x, y .

$$H = \frac{\hbar^2}{2m^*} \Delta + U(z)$$

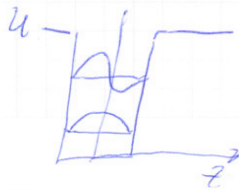
Separation ansatz for Schrödinger equation



$$\Psi(\vec{r}) = \varphi(z) \cdot e^{i(k_x x + k_y y)}$$

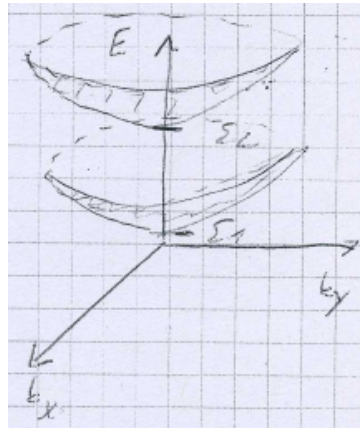
$\varphi(z)$ solves 1d Schrödinger equation

$$\left(\frac{\hbar^2}{2m^*} \frac{\partial}{\partial z^2} + U(z) \right) \varphi(z) = \mathcal{E}_n \varphi(z)$$



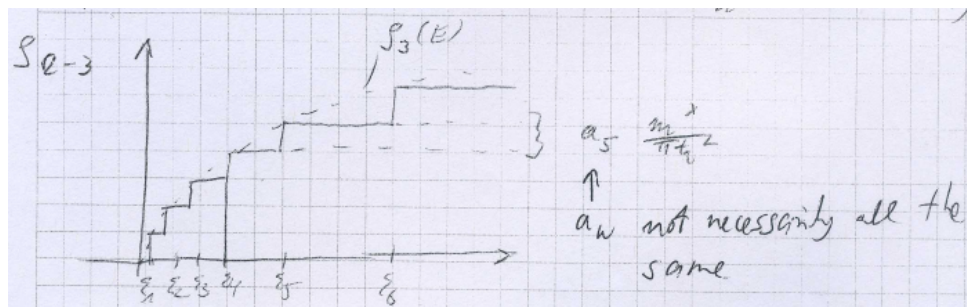
Eigenvalues $\mathcal{E}_n$ depend on functional form of $U(z)$

Energy spectrum: $E_n(k_x, k_y) = \mathcal{E}_n + \frac{\hbar^2(k_x^2 + k_y^2)}{2m^*}$
 2 dim subbands, rotational paraboloids



DOS: Superposition of 2d-DOS at varying threshold energies $\mathcal{E}$ given by $U(z)$

$$\rho_{2-3}(E) = \sum q_n^{(2)} \theta(E - \mathcal{E}_n)$$



2.2.2 Confinement from 2D to 1D

(Waveguides, quantum wires)

2 dimensional confinement potential $U(y, z)$:
 propagating waves in x -direction

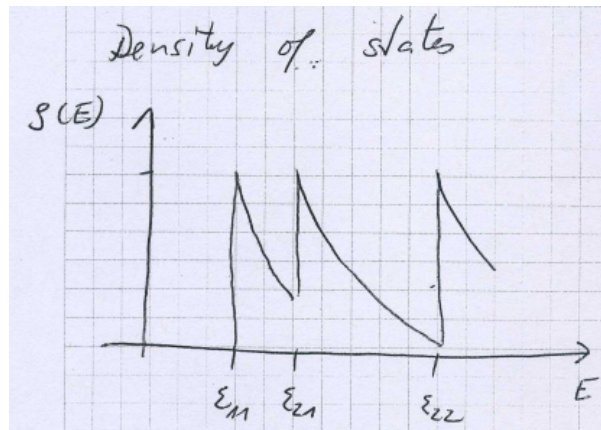
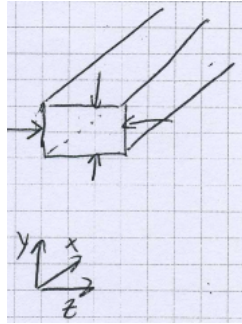
$$\Psi(\vec{r}) = \Phi_{nm}(y, z) \cdot e^{ik_x x}$$

$$E_{n,m}(\vec{k}) = \mathcal{E}_{nm} + \frac{\hbar^2 k_x^2}{2m^*}$$

→ 1 dim subbands

Series of square-root-stepped singularities

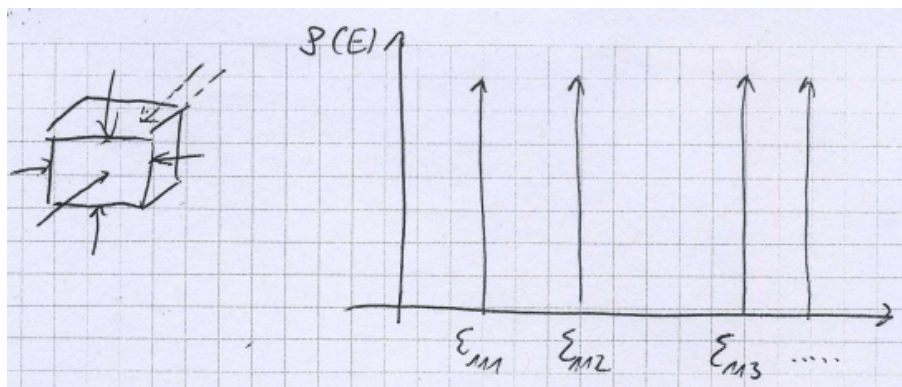
$$\rho(E) = \sum a_{nm}^1 (E - \mathcal{E}_{nm})^{-1/2}$$



2.2.3 Confinement from 1D to 0D

Quantum dots, artificial atoms

3 dim confinement potential $\rightarrow$ discrete energy spectrum like electrons bound in an atom $\rightarrow$ "artificial atoms" and molecules



$$\rho(E) = \sum_{n,m,l} \delta(E - \epsilon_{n,m,l})$$

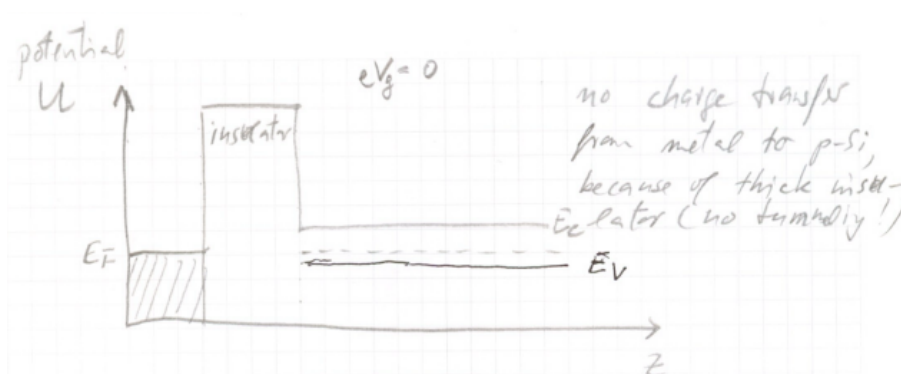
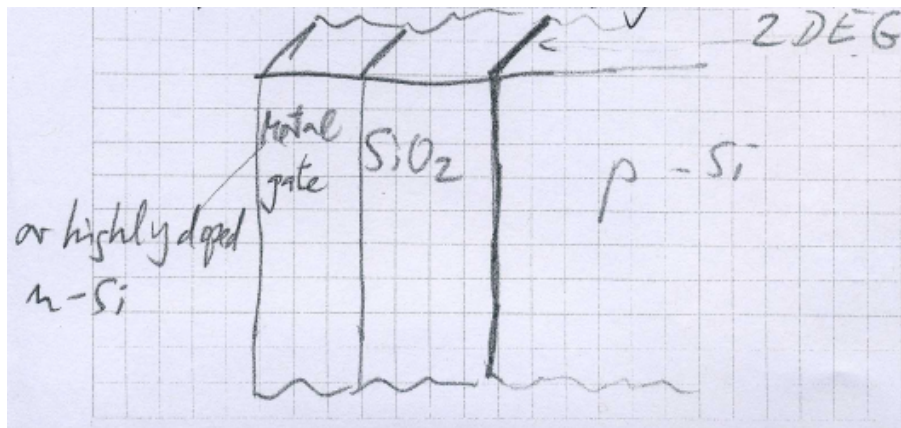
Chapter 4

Realization of reduced dimensions

a.) Two dimensional electron gases (2DEGs)
standard systems for microelectronic circuits

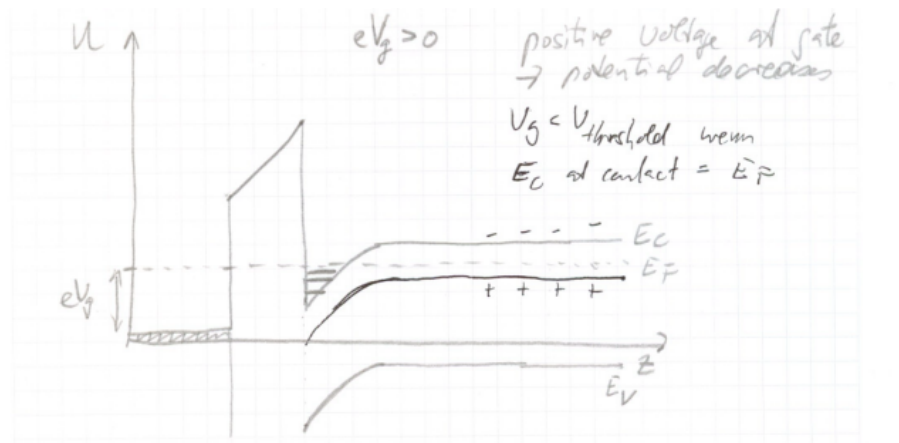
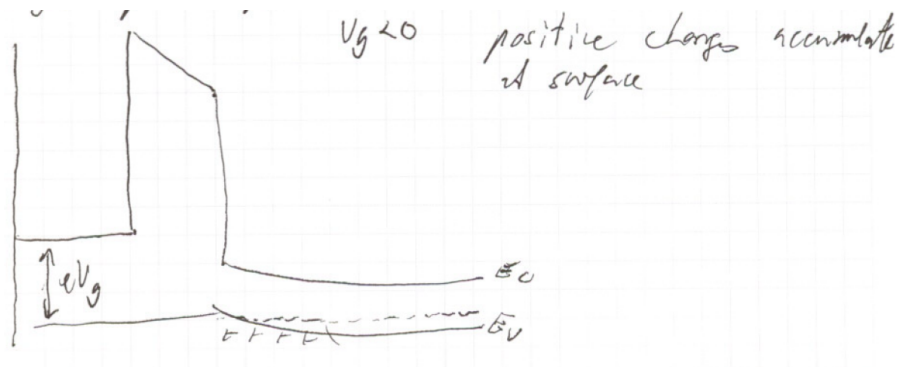
- 1.) Si inversion layers $\rightarrow$ MOSFET (metal oxide semiconductor field-effect transistor)
- 2.) GaAs-AlGaAs hetero structures $\rightarrow$ HEMT (high electron mobility transistor)

4.1 Si inversion layers



"Inversion", because surface of Si is negatively charged although the bulk is p-doped.

electron concentration linearly dependent on V_g (because $\rho(E) = \text{const.}$ in 2 dim)



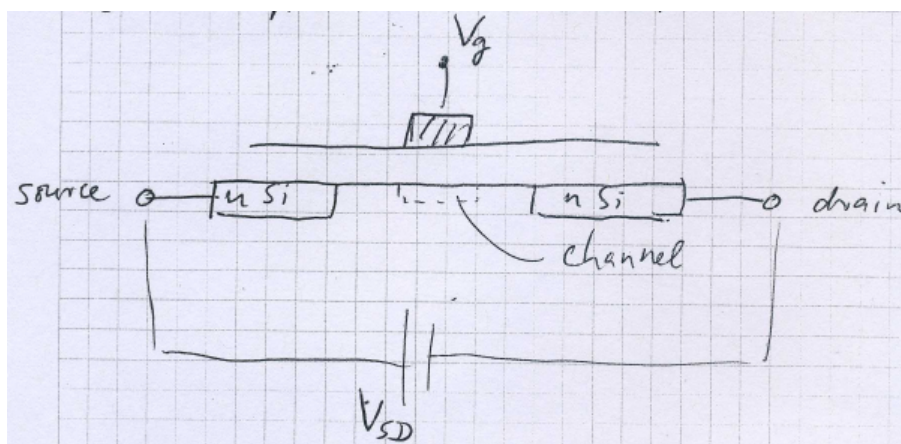
Assume geometry of a planar capacitor

$$\underbrace{n_s}_{\substack{\text{surface} \\ \text{density} \\ \text{of } e^-}} \cdot e = Q = C \cdot U = \frac{\epsilon_0 \epsilon_{SiO_2}}{d_{SiO_2}} \cdot (V_g - \underbrace{V_{thresh}}_{\substack{\text{threshold voltage} \\ \text{for populating the} \\ \text{first state of the} \\ \text{potential well}}})$$

d_{SiO_2} : thickness of oxide ≈ 50 nm

ϵ_{SiO_2} : dielectric constant of SiO_2

Technical application: MOSFET



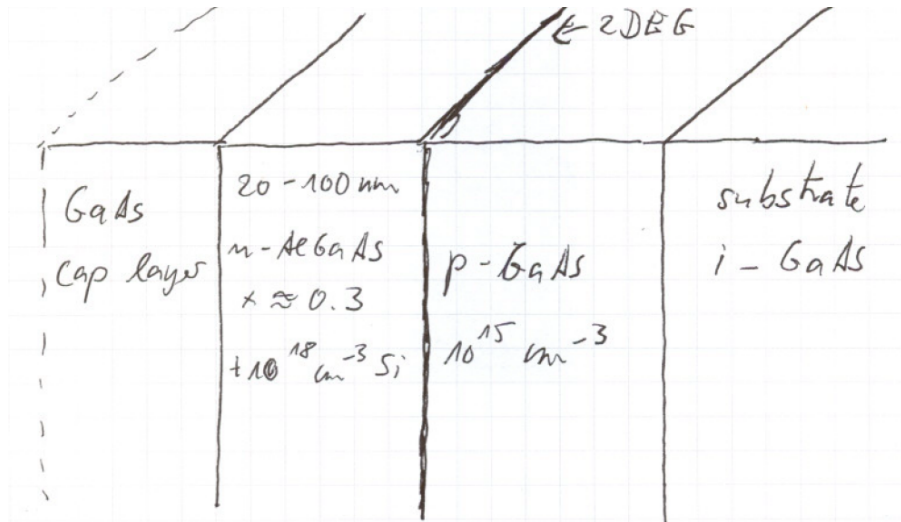
4.2 Semiconductor hetero structures

"modulation doping" Störmer *et al.*

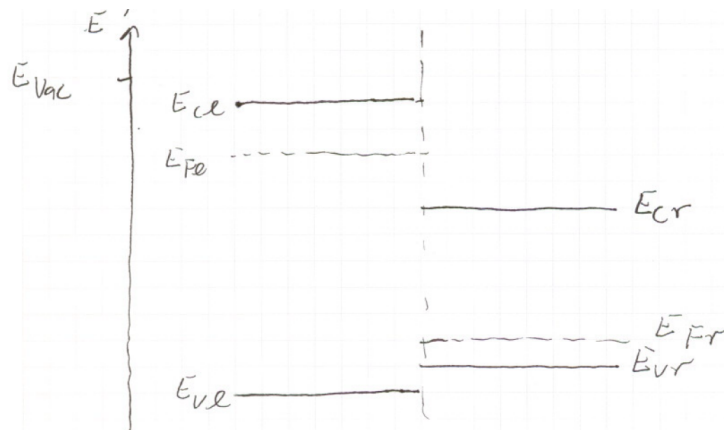
AlAs: $E_g = 2.16\text{eV}$

GaAs: $E_g = 1.424\text{eV}$, very similar lattice constant

$\text{Al}_x\text{Ga}_{1-x}\text{As}$: E_g variable, $x \leq 0.4$ direct E_g
 $x > 0.4$ indirect E_g

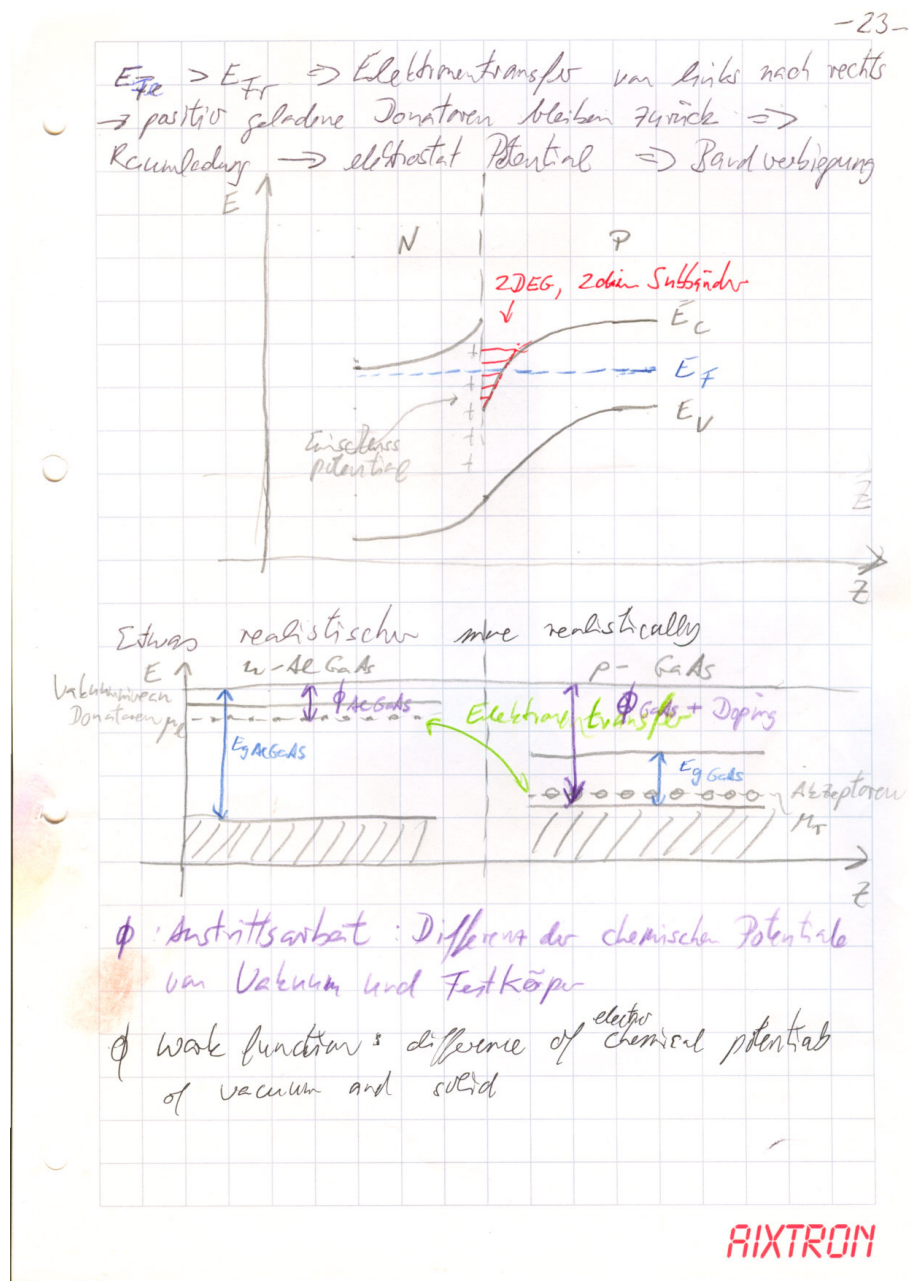


Energy diagram, when layers in contact, but no charge transfer occurred

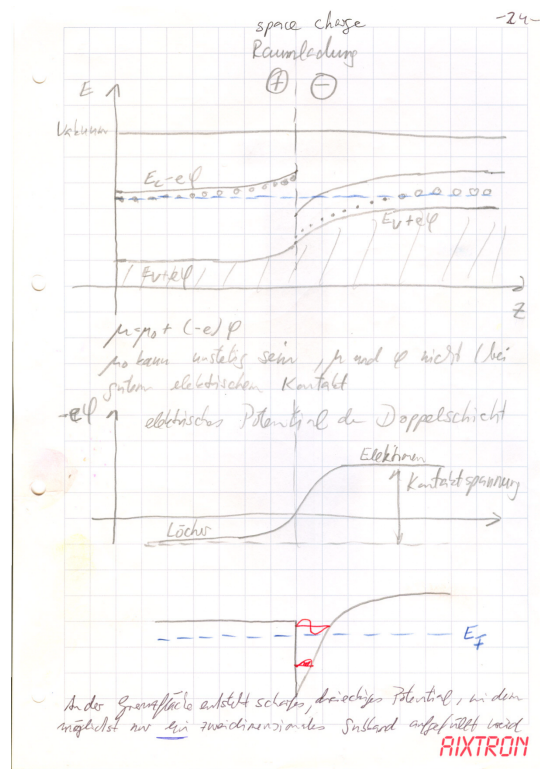


$E_{Fl} > E_{Fr}$ and transparent interface

- electron transfer from left to right
- positively charged donors left behind
- space charge zone → electrostat. potential
- band bending



- Why **HEMT** (high mobility)?
 2DEG forms on the "clean side" of the interface within the GaAs: almost perfect crystal, few defects
 $\rightarrow$ high electron mean free path
 $\mu \sim 10^6 - 10^7 \text{ m}^2/\text{Vs}$
 $n \approx 10^{10} - 10^{12} \text{ cm}^{-2}$
- 2DEG at surface: InAs
- growth of semiconductor hetero structures:
 molecular beam epitaxy $\rightarrow$ lab course
 MBE



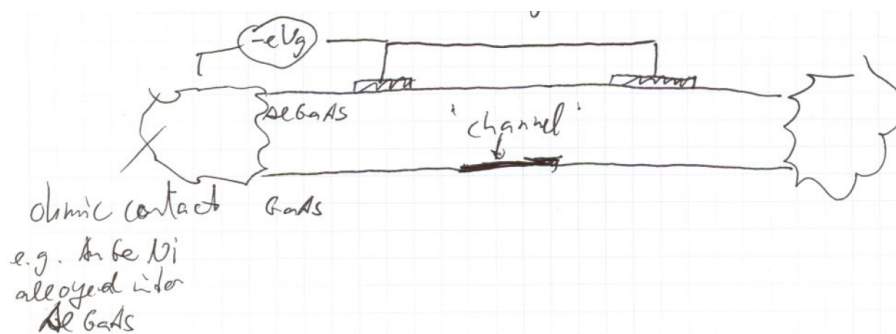
4.3 Gates

a) Gates at Si-inversion layers:

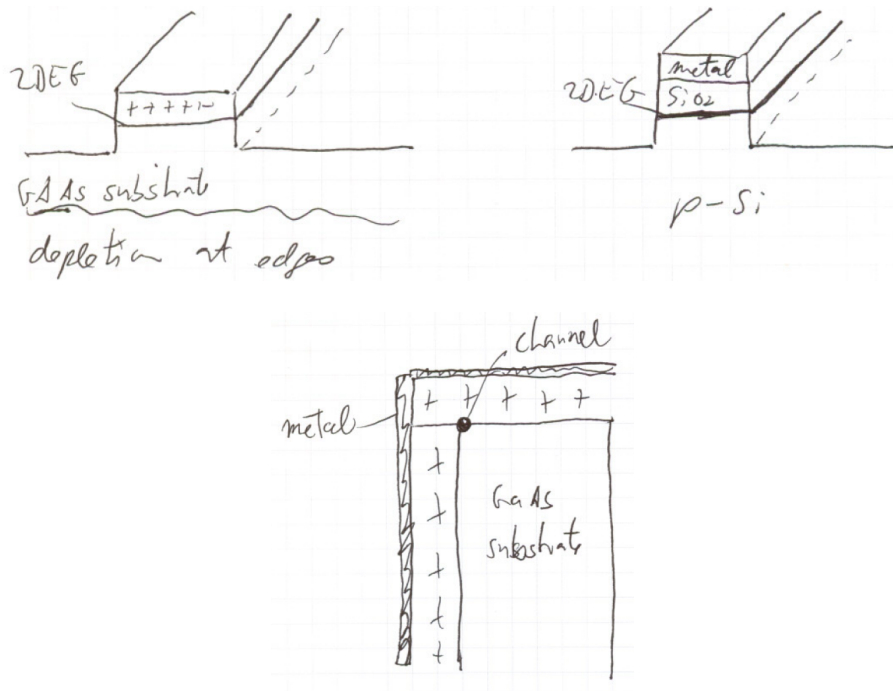
- without V_g no electrons in quantum well
→ gates are necessary for creating the 2DEG

b) Gates at hetero structures (GaAs AlGaAs):

- define conductive and non-conductive areas in the 2DEG
- without V_g the 2DEG is filled with electrons
- negative V_g depletes electrons in 2DEG underneath $\rightarrow$ insulating area $\rightarrow$ definition of channel



Other technical realizations: etched channels



4.4 Cleaved edge overgrowth (1D wires)

4.5 Carbon nanotubes

- graphene sheet rolled up to a tube
- single walled nanotubes (SWNT): 1 tube, diameter 0.5-3nm
- multiwalled nanotubes (MWNT): several tubes inside each other, number of tubes 1-20, diameter 5-30nm
- length up to mm
- here: SWNT
- electronic properties depend on roll direction (chirality) can vary from metal via narrow-band to wide band gap semiconductor
- subband splitting of 1dim subbands 50meV-1eV

→ fabrication of CNTs: talk 3

→ electronic properties of CNTs: talk 4

In addition to their own interesting properties SWNT are in use in molecular electronics as electrodes for contacting single molecules.

4.6 0-dimensional structures

(Quantum dots)

- defined by gates onto 2DEGs, various techniques
- semiconductor nanoparticles e.g. CdSe
- clusters from gas phase
- weakly coupled molecules → more details later

other 0-dim structures not relevant for molecular electronics

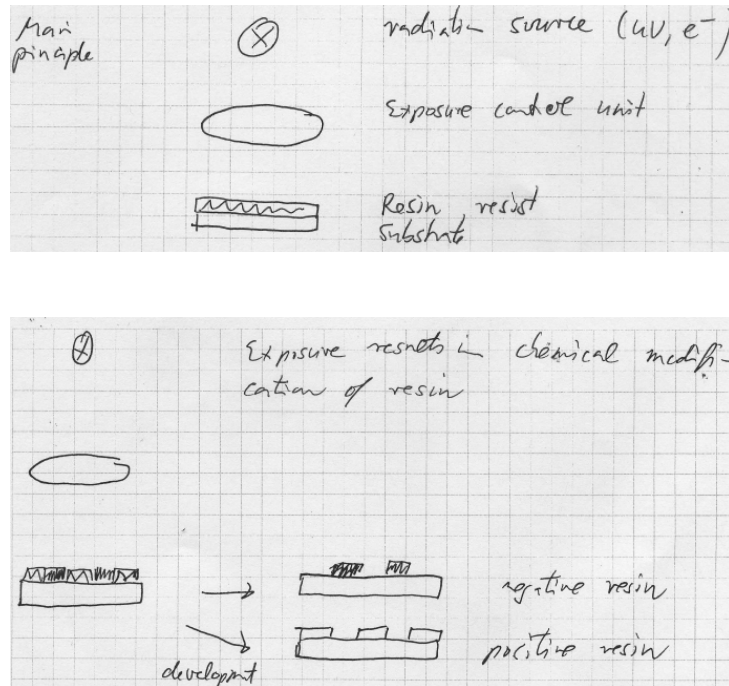
4.7 Fabrication of gates, lithography

Lithography methods:

- optical lithography
- electron beam lithography

Technical aspects are topic of the lab course. Here: restriction to principles

Goal: Laterally confined structures



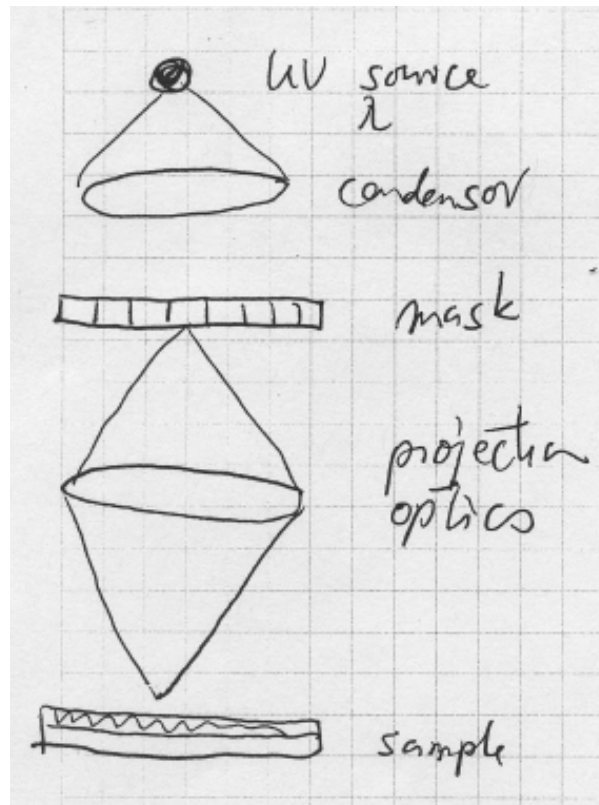
4.7.1 Optical lithography

Optical lithography is the standard patterning process in microelectronics and has been refined steadily to achieve now lateral resolutions well below the optical wavelength of the used light. The wavelength ranges from 345 nm (UV) via 193 nm (deep UV(DUV)) to 13 nm (extreme UV (EUV)). In nanoelectronics optical lithography is mainly used for patterning the course structures. Therefore we restrict ourselves here to describe the most frequently used variation in microelectronics: projection lithography

- resolution is diffraction limited to roughly $\lambda/2$
- improvement by diffraction-correction of mask + stepping
- half-pitch in product 2013: 22 nm (with 193 nm Ar excimer)

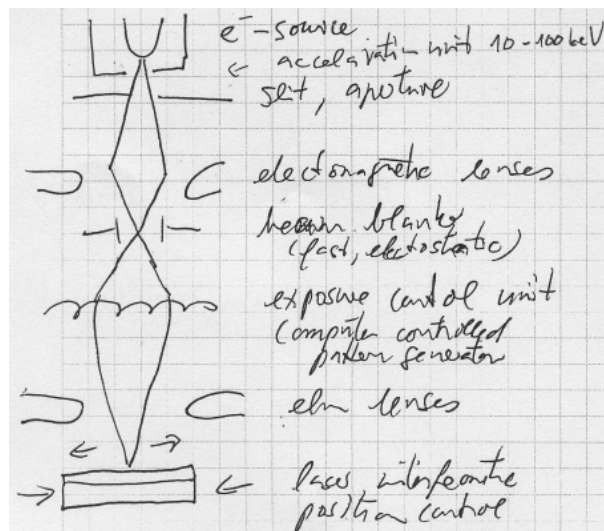
4.7.2 Electron-beam lithography

- most frequently used method in nanoelectronics
- scanning e-beam without mask $\rightarrow$ serial, slow
- resolution limited by resist, back scattering of electrons and coulomb repulsion of electrons "proximity effect"
- resolution ≈ 10 nm



4.7.3 Further processing

- a) additive: metal deposition, lift-off process
- b) subtractive: etching
- c) material modification (ion deposition, doping)



Chapter 5

Molecules for Molecular Electronics

Part of the fascination of molecular electronics lies in the fact that the molecular toolbox is almost infinite, which makes us believe that it is possible to find an appropriate molecule for any imaginable application. So far, however, only a few classes of molecules have been explored in molecular electronics. In this section we shall introduce some of these molecules and discuss their basic properties. But before doing that, it is convenient to recall the most common functional elements in digital electronic circuits that molecules are supposed to mimic. The main elements and their requirements are the following:

- Conducting wires: low resistance, high ampacity.
- Insulators: high resistivity, high breakdown voltage.
- Switches: high on/off resistance ratio, reliable switching, small leak current in off position.
- Storage elements: long storage time, low loss.

When extending the scope to cover also logic circuits one additionally has to consider:

- Diodes: high forward/backward current ratio.
- Amplifiers: high gain.

Finally, since most of the existing devices containing molecules are composite devices in which the molecules are connected to either metal or semiconductor electrodes yet another function has to be realized:

- Anchoring groups: reliable contact between functional molecular unit and electrode.

In order to be able to compete with standard semiconductor technology, the time constants of all devices have to be small, i.e. capacitances and/or resistances have to be small. Since dissipation is already one of the most severe problems in nowadays semiconductor devices, signal sizes, i.e. the level of the current should be considerably smaller than in those devices. Since our main interest lies in exploring the fundamental properties of molecular electronic devices, we shall not pay attention to those requirements for the rest of this course.

From the very beginning of molecular electronics, it has become clear that carbon-based molecules offer the required versatility to realize most of these desired functionalities. Carbon is the basis of a great variety of solid structures including graphite, diamond, graphene, and molecules like the cage-shaped fullerenes and - last but not least - the quasi one-dimensional nanotubes.

5.1 Hydrocarbons

Another very rich class of carbon-based molecules is the hydrocarbons with the possibility to tune their degree of conjugation. The electronic richness of both classes stems from the fact that the degree of hybridization of the molecular orbitals depends on the conformation and the environment. The carbon atom has four valence electrons which in the case of diamond are sp^3 hybridized corresponding to a tetrahedral arrangement of the bonds in space. This conformation is realized in the saturated hydrocarbons

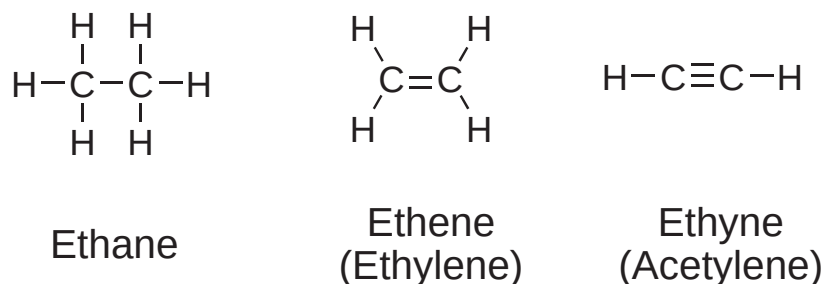


Figure 5.1: Examples of hydrocarbons. *Left:* Ethane with C-C single bond. *Middle:* Ethene with one C-C double bond. *Right:* Ethyne with one C-C triple bond.

with the sum formula C_nH_{2n+2} which are called *alkanes*.¹ Each carbon atom has four direct neighbors, either C or H atoms and all bonds are σ -bonds, see Fig. 5.1. Bigger alkanes with $n \geq 4$ exist in several isomers, some of which are ring-shaped (*cycloalkanes*). Since all electrons are used for forming chemical bonds they are basically localized and the alkanes are insulating.

In graphite the valence electrons are sp^2 hybridized in the graphite plane with an angle of 120° between the bonds. The fourth electronic orbital has p character with its lobes pointing perpendicular to the graphite plane. The wave functions of neighboring carbon atoms overlap and form the electronic π -system, which in case of graphite is responsible for the in plane and the finite plane-to-plane conductance. The same situation takes place in the *alkene* hydrocarbons containing one carbon-carbon double bond, see Fig. 5.1. Interesting for molecular electronics are *polyenes* with the sum formula C_nH_{n+2} , which contain more than one double bond. When these double bonds are alternating with single bonds, the wave function of π -system is extended over the whole molecule. These molecules are called conjugated or aromatic molecules. The criterion of aromaticity is $4n + 2$ π -electrons.

The carbons in hydrocarbons may furthermore be triply bond in sp -hybrids forming *alkynes*. When alternated with single-bonds these linear bonds are very stable and give also rise to delocalized wave functions as in the conjugated species with double bonds.

The delocalization of the wave function is broken when the double or triple bonds do not alternate with single bonds. Furthermore, the conjugation can be tuned by introducing an angle between the planes of the individual cyclic parts. The consequences of breaking the conjugation for the conductance of a molecular junction will be discussed in section 11.5.

In a very common representation only the bonds are shown: single bonds as single lines, double bonds as double lines, triple bonds as triple lines. The carbon atoms themselves are not displayed. The positions of the carbon atoms are at the kinks between these lines. Neither the hydrogen atoms nor the bonds to them are drawn. The number and positions of them can be deduced by fulfilling the valence four at each carbon. As an example we show in Fig. 5.2(a) the polyene hexatriene (consisting of six carbons and with three double bonds) in various representations.

As for the alkanes larger species of alkenes and alkynes arrive in several isomers. When two doubly-bond carbon atoms are surrounded by different groups one has to distinguish between the *cis* conformation, in which the neighboring groups are on the same side of the double bond, and the *trans* conformation with the neighbor groups being located on opposite sides of the double bond. A *cis-trans* conformation change sets the basis for a class of molecules with in-built switching functionality.

The typical conformations of polyenes are zigzag-shaped lines reflecting the preferred 120° orientation of the sp^2 hybrid. When building the angle to the same side cyclic molecules are formed. The ideal cyclic polyene geometry is the benzene molecule consisting of six carbons forming planar ring with perfect conjugation, see Fig. 5.2(b). Since the π -electrons are delocalized over the whole ring, it is not obvious between which carbons the double bonds and where the single bonds have to be drawn. Therefore, one often uses a notation in which the π -electrons are symbolized by an inner ring.

Molecules consisting of several benzene rings merged along one bond are called *polycyclic aromates*. The most prominent examples are naphthalene, consisting of two benzene rings, anthracene consisting of three rings in a linear arrangement, tetracene with four and pentacene with five rings in series. Also angular arrangements of the rings or combinations with rings containing five carbon are used. Examples are shown in Fig. 5.3. Also five-rings (cyclopentadiene) and less often seven-rings (cycloheptatriene) are

¹The transport through alkane-based molecular junctions will be discussed later.

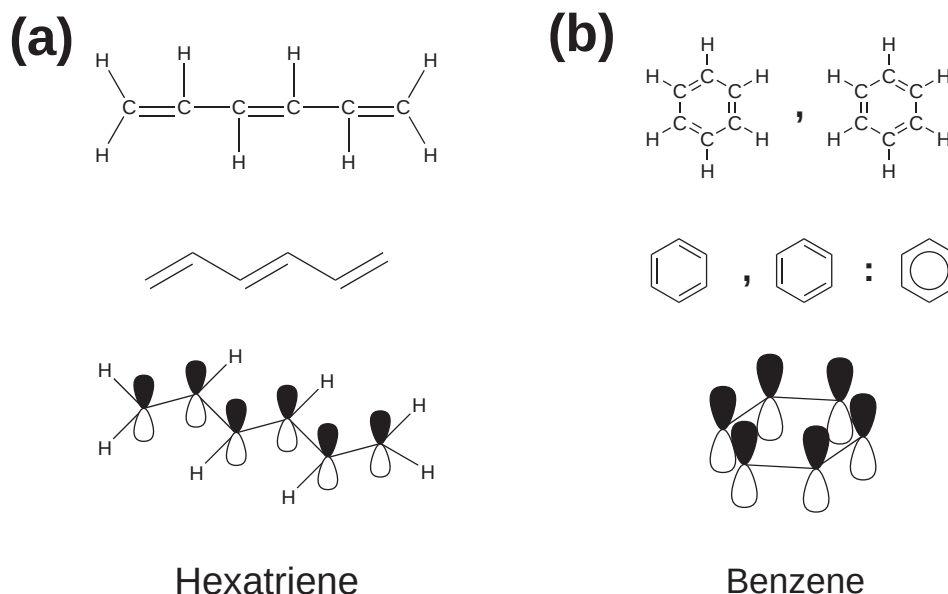


Figure 5.2: Various representations of the hexatriene and the benzene molecule. (a) The polyene hexatriene is chosen as an example for a conjugated linear hydrocarbon molecule. (b) The benzene molecule. Top and center panel: Because of the delocalization of the π -electrons the positions of the double bonds are not defined. Therefore, they are often symbolized by an inner ring.

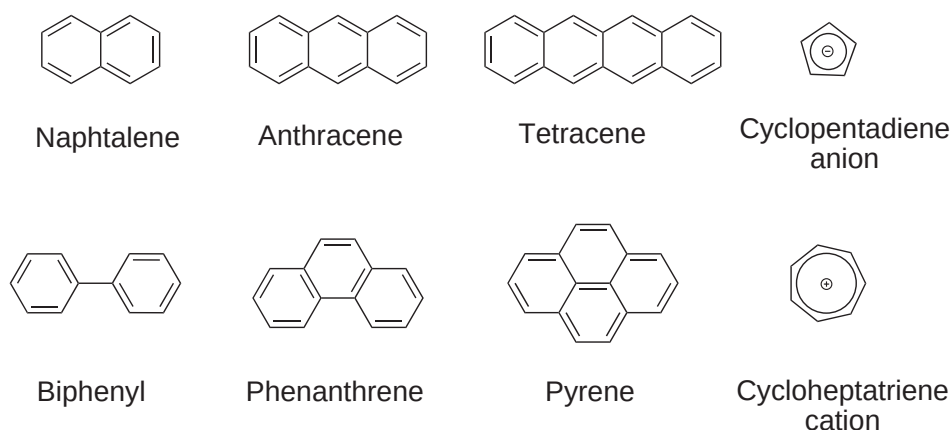


Figure 5.3: Examples of polycyclic molecules.

possible. They are aromatic if six π -electrons per ring exist. In the case of cyclopentadiene this means that an extra electron has to be added to the ring to provide a stable π -electron sextet (anion), while in cycloheptatriene one electron charge has to be withdrawn (cation), see Fig. 5.3.

In *heterocyclic molecules* one or more carbon atoms are replaced by an atom of another species. Some heterocycles in use in molecular electronics are depicted in Fig. 5.4. The most common substituents are sulfur, nitrogen and oxygen. Because of their chemical valence they possess more electrons than the carbons. In hexagonal rings the additional electrons do not contribute to the π -system, but may be used for forming bonds to other atoms, e.g. to the metal electrodes. In five-rings they help stabilizing the conjugation.

5.2 All carbon materials

As mentioned in the beginning, also pure carbon molecules are promising for molecular electronics. Carbon nanotubes are sheets of graphite which are rolled together. They have diameters ranging from 1 nm to several tens of nanometers and length of up to millimeters. Depending on the orientation of the

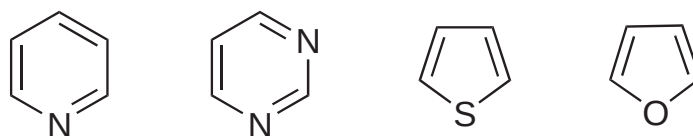
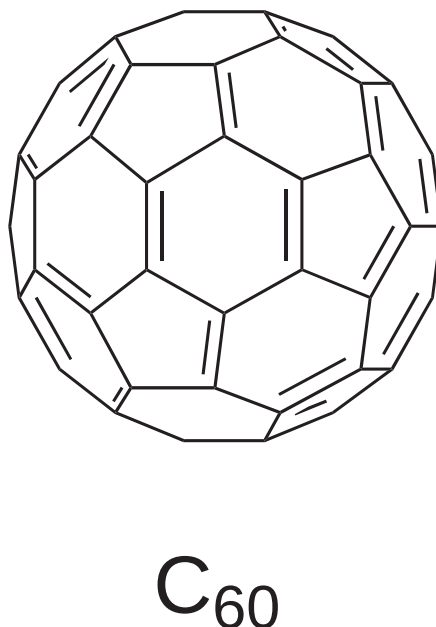


Figure 5.4: Examples of the most common heterocyclic aromates.

Figure 5.5: Line representation of the bonds of the fullerene molecule C₆₀.

long axis with respect to the hexagons various nanotubes with varying electronic properties are possible.² Since defect-free carbon nanotubes are ballistic conductors they may serve as interconnects for bridging long distances.

Finally, the combination of pure carbon hexagons with pentagons, but without hydrogen sets the basis for the fullerenes. Since the bond length in pentagons is smaller than in hexagons, these molecules are not planar but have a curvature. The most famous fullerene is C₆₀ (see Fig. 5.5) consisting of 20 hexagons and 12 pentagons in the same conformation as in a soccer ball. It has a completely delocalized π system, making it also a good candidate for molecular electronics applications.

5.3 Metal-molecule contacts: anchoring groups

A common problem in molecular electronics is the difficulty to form stable and electronically transparent chemical bonds of the molecules to the metal electrodes. Among the manifold possibilities one particular solution has been chosen as standard system. This is the combination of a sulfur atom to gold electrodes. The reason to choose gold lies in the fact that it is inert to chemical reactions, which allows to prepare clean surfaces and tips. The drawback of this inertia is the fact that it hardly undergoes chemical reactions with other species. One of the rare exceptions is sulfur in its thiol (sulfur-hydrogen) form. This bond is mechanically stable with a force in the order of 1.5 nN [51]. The thiol-gold binding scheme has successfully been tested in self-assembled monolayers (SAM) (see below) on flat surfaces as well as in single-molecule contacts on tips. It provides sufficient electronic transparency for most applications. This is the reason why alkanedithiols (i.e. alkanes with thiol endgroups at both ends) and benzenedithiols (a benzene ring with thiols usually at opposite ends) represent the testbeds for molecular electronic circuits. The alkanedithiols are the archetypical insulators, while benzenedithiol is the most simple aromatic

²An excellent review about the conformation and resulting electronic properties of nanotubes is given in Ref. [50].

molecule which can be coupled to metal electrodes. However, alternatives to the thiol bonding scheme are also under study.

5.4 Conclusions: molecular functionalities

We want to close this section by pointing out which molecules can be considered as possible candidates for various electronic components in molecular circuits:

- Conducting wires: polyenes and alkynes.
- Insulators: alkanes.
- Switches: cis/trans conformation changes of manifold molecules, the prototype being azobenzene, consisting of two benzene rings connected via a C=C double bond. In many examples the conjugation is reduced in the trans isomer because the π -systems of both parts are not coplanar. The second prototype of switches are ring-opening-ring-closure transformations which can be triggered optically. In these switches one of the hydrocarbon rings or heterocycles is opened thereby affecting the conjugation of the π -system.
- Storage elements: all kinds of molecules with at least two states may serve as storage elements, including among others conformations, redox states, spin states, and vibrational states.
- Diodes: molecules which consist of two different, and electronically decoupled parts. An example is the famous suggestion by Aviram and Ratner [85] mentioned in the first chapter.
- Amplifiers: in principle all molecules the electronic levels of which can be tuned by a gate electrode might act as amplifiers. Although electronic three-terminal devices following this principle of bipolar transistors have been demonstrated, they do not provide current amplification yet.
- Anchoring groups: thiols, amines, nitros, cyanos or heterocycles with the substituent atoms serving as linkers to the metal electrodes

Chapter 6

Fabrication of molecular contacts

6.1 Fabrication of metallic atomic-size contacts

6.1.1 Introduction

In this chapter we shall present the most common methods which have been developed during the last years for the fabrication of metallic atomic-size contacts. Both the contacting methods and the physical properties of atomic contacts found the basis for contacting single molecules. On the other hand, these techniques have been further refined for contacting molecules. These refinements are now also used for studying atomic contacts. Therefore, the decision in which chapter one or the other method is described is somewhat arbitrary. Manifold variations of the techniques exist and are permanently improved further. The aim of this chapter is to introduce into the most important principles and to compare the techniques regarding their advantages and drawbacks.

As important as the sample preparation is the quality of the electronic transport measurements. When dealing with tiny contacts, care has to be taken to reduce the influence of the measurement onto the contact itself. We will therefore end this chapter with a few brief remarks about the most common measurement setups and possible artifacts. This aspect as well as the technical implementation of the fabrication methods will be the subject of the lab course.

6.1.2 Techniques involving the scanning tunneling microscope (STM)

One of the most versatile tools for the fabrication of atomic-size contacts and atomic chains is the scanning tunneling microscope (STM) (for a review, see Ref. [1]). It has been used for that purpose from the very beginning of its invention [2]. While in the standard application of an STM a fine metallic tip is held at distance from a counter electrode (in general a metallic surface) by making use of the exponential distance dependence of the tunneling current, the tip can also be indented into the surface and carefully withdrawn until an atomic size contact or short atomic wire forms. An artist's view of the STM geometry and the atomic configuration of a contact is shown in Fig. 6.1. For many metals it has been shown that the tip will be covered by several atomic layers of the metal of the counter electrode upon repeated indentation such that clean contacts may be formed consisting of the same metal for both electrodes.

The main advantages of the STM in this application are its speed and versatility. When the electrodes forming the contacts are prepared in ultra high vacuum conditions, the STM furthermore allows to gather information about the topography of the two electrodes on a somewhat larger than the atomic scale before or after the formation of the contact. Since however, the tip is usually pressed into the substrate and the atomic-size contact is formed when withdrawing, the exact atomic configuration of the atomic-contact cannot be measured directly.

This problem is partially solved when the contact is formed upon approaching [3]. For good metals the distance dependence of the conductance follows an exponential increase until a sudden "jump to contact" occurs which is marked by a step-like increase of the conductance. The jump indicates the formation of a chemical bond between the tip and the electrode and thus the formation of a single-atom contact. The geometry of the substrate side of the contact can be well controlled by first preparing and characterizing a clean terrace of a single crystalline substrate and subsequently evaporating a sub-monolayer small amount of metal atoms onto it. The surface can then be scanned and the tip can be approached right on top of one of the extra atoms. This technique enables to form hetero junctions, i.e. contacts between two

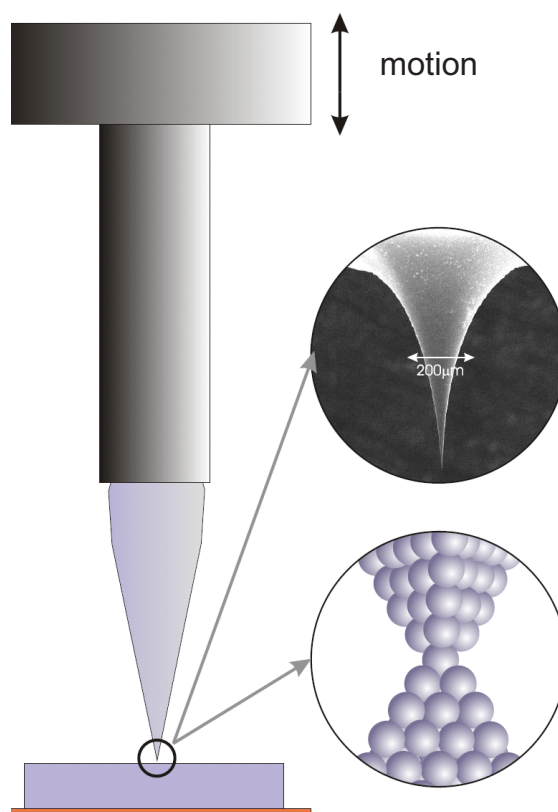


Figure 6.1: Working principle of the fabrication of atomic contacts with an scanning tunneling microscope (STM). The electron micrograph shows a STM tip. The width at half length is in the order of 100 to 200 μm . The lower inset gives an artist's view of the atomic arrangement of an atomic contact. Courtesy of C. Bacca.

different metals. The determination of the atomic configuration on the tip-side of the contact remains unsolved, though.

Spectroscopic measurements on the scale of electron volts allow one to deduce information about the cleanliness and the electronic structure of the metal [4].

The main drawbacks are its limited stability with respect to the change of external parameters such as the temperature or magnetic fields and the short lifetime of the contacts in general because of the sensitivity of the STM to vibrations. In the early years of STM-based atomic-contact studies they were furthermore limited to rather high temperatures in the range of 10 K or higher. This drawback has been overcome in the last years. Nowadays ultra high vacuum (UHV) STMs, which work with sufficient stability at temperatures below 1 K and in strong magnetic fields are even commercially available.

6.1.3 Methods using atomic force microscopes (AFM)

Another scanning probe technique which complements STM in many aspects is the atomic force microscope (AFM). Instead of the tunnel current an AFM uses the distance dependence of the force between a fine tip and a surface. Depending on the chemical nature of both the tip and the surface this force consists of several contributions and its distance dependence may be complex and even nonmonotonic. The working principle of the AFM is based on measuring the force by recording the deflection of a cantilever that carries the tip. The deflection can be detected by optical means or by the detuning of an oscillator circuit due to the deflection. The AFM has become a very versatile tool in surface science which works in various environments and temperature ranges. In surface science the main advantage of AFM as compared to STM is its possibility to work on insulating substrates. For the fabrication and characterization of atomic contacts the AFM is in use in two different variations. The first one is the combination with an STM which records the current while the AFM measures the force that is necessary to form or break the contacts [5]. The second one is the so-called conductive AFM which uses a metal-covered tip on a

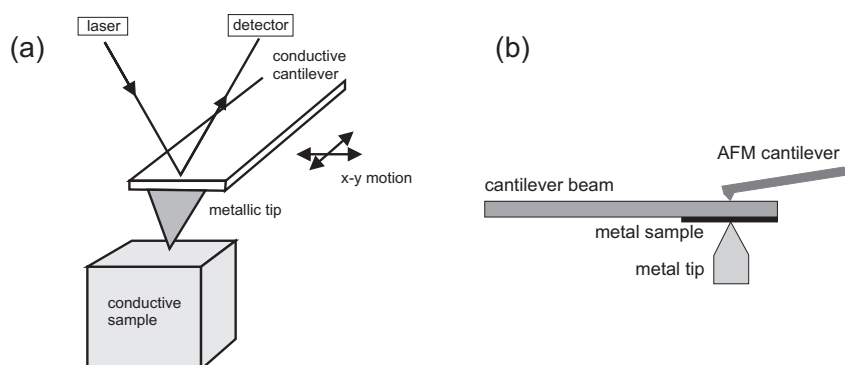


Figure 6.2: Fabrication and characterization of atomic contacts with an atomic force microscope (AFM). (a) The conductive AFM uses a conductive cantilever and metallic tip for recording the electrical signal. The deflection of the cantilever beam is detected optically and used for recording the topographic information of sample. After Ref. [6]. (b) In the combined AFM-STM the sample is clamped to a cantilever. The metallic contact is formed between the sample and the metal tip. The metal tip is part of an STM and records the electrical signal. The deflection of the cantilever is recorded with a separate AFM. This signal is used for measuring the force acting on the cantilever when the atomic contact rearranges. After Ref. [5].

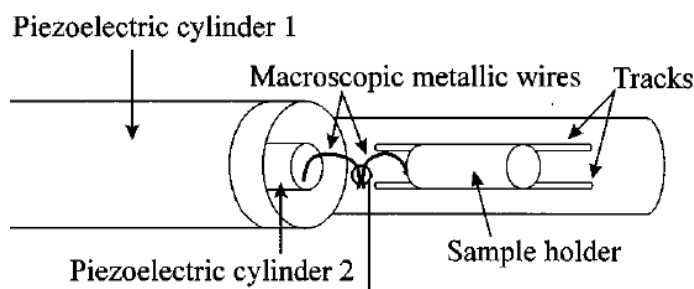


Figure 6.3: Experimental setup used to visualize contacts between macroscopic metallic electrodes inside a scanning electron microscope (SEM). Adapted with permission from [8]. Copyright 1997 by the American Physical Society.

metallic surface and both quantities, the current and the force, are available simultaneously, Fig. 6.2 [1]. The force signal can be used to determine the topography.

6.1.4 Contacts between macroscopic wires

Transient atomic chains and contacts with lifetimes in the millisecond range can also be fabricated in a table-top experiment first demonstrated by N. Garcia and coworkers [7], which we call here “dangling-wire contacts”. Two metal wires in loose contact to each other are excited to mechanical vibrations, such that the contact opens and closes repeatedly. One end of each wire is connected to the poles of a voltage source and the current is recorded with a fast oscilloscope. This method is in principle particularly versatile because it enables the formation of hetero junctions between various metals. However, in order to provide clean metallic contacts a thorough cleaning of the wires would be required, similar to the tip and surface preparation in a STM. Another drawback is the lack of control of the distance of the electrodes. It is thus mostly used as demonstration experiment in schools with Au-Au contacts. The method has later been improved by attaching the wires to piezo tubes. This realization thus resembles contacts fabricated in the STM and have also been used within the chamber of an scanning electron microscope for simultaneous imaging and conductance measurements, see Fig. 6.3.

6.1.5 Transmission electron microscope

Another interesting method for preparing and imaging atomic contacts are transient structures forming in a transmission electron microscope (TEM) when irradiating thin metal films onto dewetting substrates [9, 10]. The high energy impact caused by the intensive electron beam locally melts the metal film

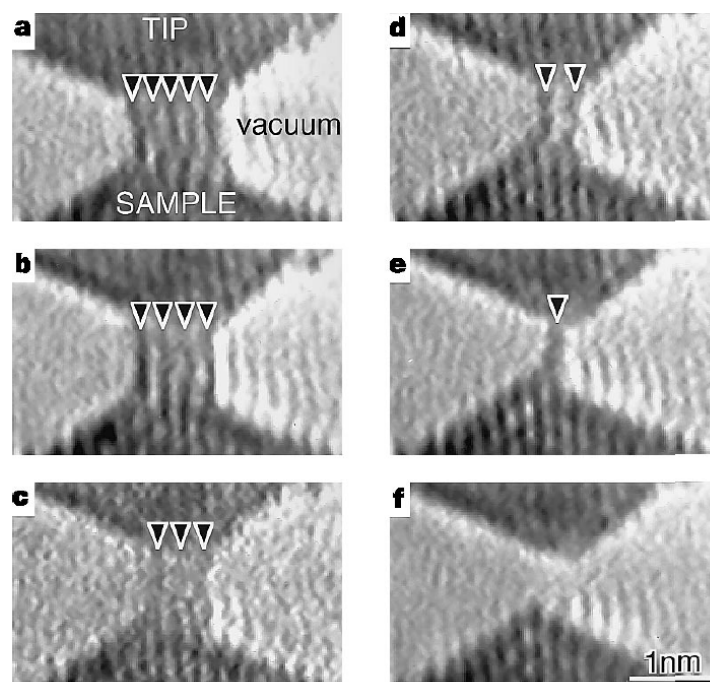


Figure 6.4: High resolution TEM images of short atomic wires fabricated with an STM inside the vacuum chamber of the TEM. The arrows indicate the number of atomic rows. In panel f the contact is broken and forms a tunnel contact. Reprinted by permission from Macmillan Publishers Ltd: Nature [10], copyright 1998.

causing the formation of constrictions which eventually shrink down to the atomic size and finally pinch-off building a vacuum tunnel gap. A typical system for these studies is Au on glassy carbon substrates. Several variations of this principle have been developed that allows one to contact both electrodes forming the contact, see Fig. 6.4. The high electron current density necessary for imaging causes also high local temperatures resulting in short lifetimes of these contacts. However, they offer the unique possibility to simultaneously perform conductance measurements and imaging with atomic precision. Similar results have been obtained with variations of the STM inside a TEM [11]. This method enabled to directly prove the existence of single-atom contacts, single-atom wide and several atom long chains as well as to establish a correlation between contact size and conductance [10, 9, 12]. For Au and Ag contacts it has been shown that preferably well ordered contacts with growing directions corresponding to the symmetry axes of the crystal structure are formed.

6.1.6 Mechanically controllable break junctions (MCBJ)

Already before the development of the first STM another technique enabling the fabrication of atomic-size contacts and tunable tunnel contacts has been put forward. The first realizations include the needle-anvil or wedge-wedge point contact technique pioneered by Yanson and co-workers (for a review see [13]) and the squeezable tunnel junction method described by Moreland and Hansma [14] and Moreland and Ekin [15] who used metal electrodes on two separate substrates which are then carefully adjusted with respect to each other. The needle-anvil technique was mainly used to form contacts with diameters of typically several nanometers and thus having hundreds or thousands of atoms in the narrowest cross section. These two techniques formed the starting point for the development of the mechanically controllable break junctions (MCBJ) by C. Muller and coworkers [16], which nowadays is applied for the fabrication of atomic contacts in various subforms, the most common of which are the so-called notched-wire [17] and thin-film MCBJs [18]. The working principle which is depicted in Fig. 6.5 is the same for both variations: A suspended metallic bridge is fixed on a flexible substrate, which itself is mounted in a three-point bending mechanism consisting of a pushing rod and two counter-supports. The position of the pushing rod relative to the counter supports is controlled by a motor or piezo drive or combinations of both. The electrodes on top of the substrate are elongated by increasing the bending of the substrate. The elongation can be reduced again by pulling back the pushing rod and thus reducing the curvature

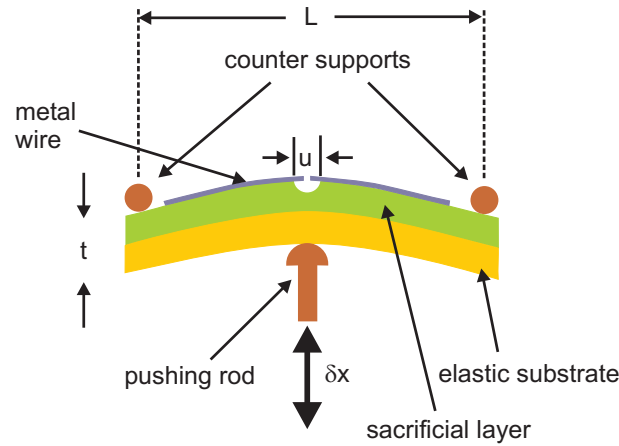


Figure 6.5: Working principle of the MCBJ (not to scale) with the metal wire, the elastic substrate, the insulating sacrificial layer, the pushing rod, the counter supports and the dimensions used for calculating the reduction ratio (see text).

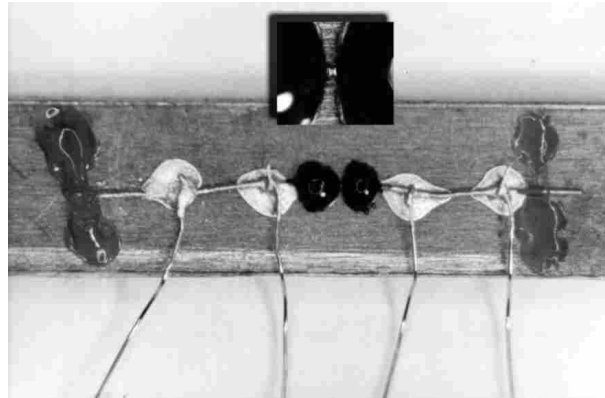


Figure 6.6: The 100 nm wide gold wire is glued with epoxy resin (black) onto the substrate. The electrical contact is made by thin copper wires glued with silver paint. The inset shows a zoom into the notch region between the two black drops of epoxy resin. Reprinted from [83]. Copyright 2003, with permission from Elsevier.

of the substrate. In order to break a junction to the tunneling regime, considerable displacements of the pushing rod and thus important bending of the substrate is required. Therefore the most common substrates are metals with a relatively high elastic limit like spring steel or bronze. The substrates are covered by an electrically isolating material such as polyimide before the junction can be fixed on it.

The notched-wire MCBJ, an example of which is shown in Fig. 6.6, uses a thin metallic wire (diameter 50 μm to 200 μm) with a short, knife-cut constriction to a diameter of 20 μm to 50 μm . The wire is glued at both sides of the notch to the substrate and connected electrically to the measurement circuit at both ends. The distance between the glue drops is of the order of 50 μm to 200 μm .

Variations of this method have been put forward which enable contacting of reactive or brittle materials out of which no wires can be formed [19]. For this purpose the sample preparation is performed in protective environment. A beam-shaped piece of the material is cut in a non-reactive liquid such as dodecanol or other slowly evaporating alcohols, or glycerine. Four holes are drilled into the metal and a wedge is cut in the middle between the holes. An example is shown in Fig. 6.7. The beam is screwed with the help of two electrically isolating bolts to the substrate, one on each side of the wedge. The remaining two holes serve for screwing metallic wires to the beam for the conductance measurements.

For a version which enables scanning the two electrodes with respect to each other, at first two piezo tubes are glued to the substrate. The metal wire is then glued on top of the piezos. After mechanically breaking the wire, the piezos are polarized such that they are bent and the two parts of the wire are sliding along each other [20]. This realization corresponds to a high-stability STM, but with very restricted scan possibility. It is therefore used only sparsely. Finally, simultaneous force and conductance measurements are possible when adding a tuning fork like in AFMs. Details of this very sophisticated method are given

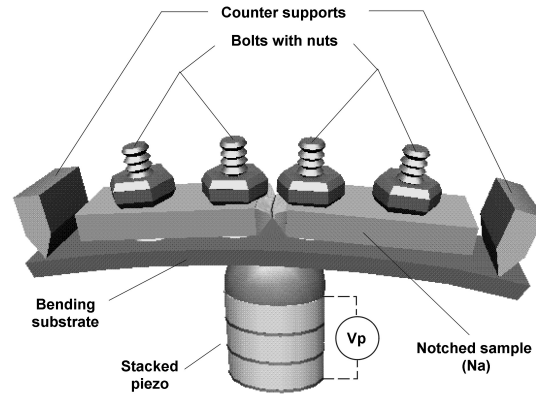


Figure 6.7: Principle of the MCBJ technique adapted for reactive metals. Reprinted from [83]. Copyright 2003, with permission from Elsevier.

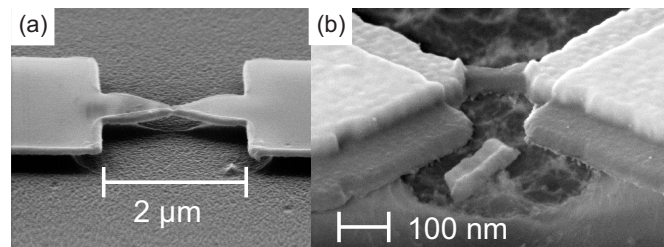


Figure 6.8: Lithographic MCBJ. (a) Electron micrograph of a thin-film MCBJ made of cobalt on polyimide taken under an inclination angle of 60° with respect to the normal. The distance between the rectangular shaped electrodes is $2\ \mu\text{m}$, the thickness of the thin film is $100\ \text{nm}$ and the width of the constriction at its narrowest part is approximately $100\ \text{nm}$. (b) Electron micrograph of a thin-film MCBJ made of cobalt (medium grey) with leads made of gold (light grey) taken under an inclination angle of 50° with respect to the normal. The distance between the rectangular shaped electrodes is $2\ \mu\text{m}$, the thickness of the Co film is $80\ \text{nm}$, of the Au film is $100\ \text{nm}$ and the width of the constriction at its narrowest part is approximately $100\ \text{nm}$. The sample has been fabricated using shadow evaporation through a suspended mask such that two images of the mask exist. The Au shadow of the bridge is broken off.

in Ref. [22].

Fig. 6.8 shows two examples of thin-film MCBJs, which were fabricated using the usual techniques of nanofabrication, i.e. electron beam lithography and metal deposition by evaporation. There are mainly two differences to standard nanostructuring. The first one is the substrate, which in case of MCBJs has to provide sufficient elastic flexibility without breaking or irreversible bending. The second difference is the final etching step which is needed to suspend the nanobridge (with typical dimensions of $2\ \mu\text{m}$ in length and $100\ \text{nm} \times 100\ \text{nm}$ at the narrowest part of the constriction) above the substrate by partial removal of a sacrificial layer underneath the metal film. Fig. 6.9 summarizes the fabrication procedure. A piece of metal with a typical thickness of a few hundred micrometers serves as substrate. The metal should have a high elastic deformation limit. Typical metals are bronze or spring steel. For particular purposes, in particular when capacitive effects have to be minimized, the metal is replaced by a plastic substrate. Both metal or plastic are thoroughly polished to reduce the roughness to less than a micrometer. The remaining corrugations are then filled with a thin layer of polyimide (thickness $1\text{--}2\ \mu\text{m}$), which is spin-coated and hardbaked in vacuum. The polyimide also serves as electrical insulator between the nanostructure and the substrate. Subsequently the electron resist is spin-coated and thermally treated as required for electron beam structuring. Fig. 6.9(c) shows an example in which a double-layer resist is used. The double-layer is necessary for, e.g. evaporation of the metal under arbitrary angle. The next step is electron-beam writing in a scanning electron microscope equipped with a pattern generator or in a commercial electron-beam writer. After development of the resist in a selective solvent the resist mask remains on top of the polyimide layer. The mask itself may be partially suspended when using a double-layer resist. Subsequently the metal will be deposited either by evaporation, sputtering, chemical vapor deposition or other means. Shadow evaporation, i.e. evaporation of several materials under different

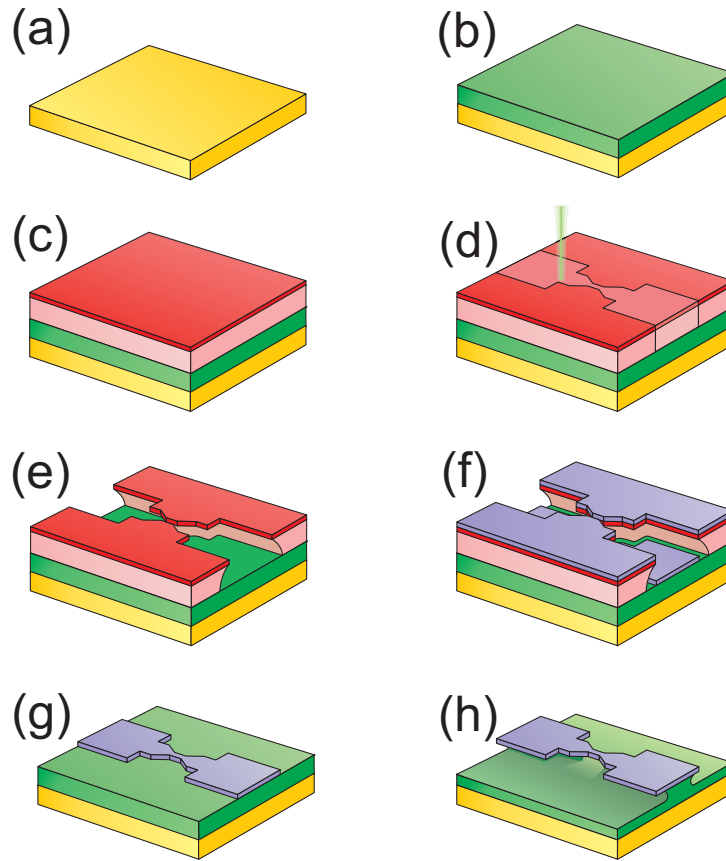


Figure 6.9: Fabrication scheme of thin-film (lithographic) MCBJ. (a) The substrate (metal, plastic) is polished mechanically. (b) the sacrificial wafer (polyimide) is spin-coated and baked. (c) The resin (typically a bi-layer electron sensitive organic material) is spin-coated and baked. (d) The resin is exposed in an electron beam writer or a scanning electron microscope equipped with a pattern generator in the desired pattern. (e) The chip is developed in a solvent which selectively removes the exposed parts of the resin. The result is a mask, which resides on the sacrificial layer, in the shape of the exposed pattern. (f) The metal is deposited by evaporation or sputtering. (g) The mask with the metal on top of it is lifted-off in a more aggressive solvent which attacks the unexposed parts of the resin. The result is a metal layer in the shape of exposed pattern. (h) Finally the thickness of the sacrificial layer is reduced in an isotropic plasma. The narrow parts of the metal pattern are suspended and form the bridge which will be broken in the MCBJ mechanism.

angles can be used for forming contacts between different metals or for supplying nanobridges of one metal with electrodes made of another metal. The advantage of the shadow-evaporation technique lies at first in its self-alignment property because the same mask is used for all metal depositions. The second advantage is given by the fact that all depositions can be made in a single vacuum step, which enables one to fabricate clean interfaces between the metals. After the metal deposition the mask is stripped in a more aggressive solvent. Finally the structure is exposed to an isotropic oxygen plasma which attacks the polyimide layer. Consequently its thickness is reduced and all narrow metal parts, like the nanobridge become suspended like a bridge.

Both versions of the technique - the notched-wire MCBJs and the lithographic MCBJs - share the idea of enhanced stability due to the formation of the contact by breaking the very same piece of metal on a single substrate and by transformation of the motion of the actuator into a much reduced motion of the electrodes perpendicular to it. The small dimensions of the freestanding bridge-arms give rise to high mechanical eigenfrequencies, much higher than the ones of the setup. As a result the system is less sensitive to mechanical perturbations by vibrations.

Assuming homogeneous beam-bending of the substrate we can calculate the reduction ratio r between the length change of the bridge u and the motion of the pushing rod x (see Fig. 6.5).

$$r = \frac{6tu}{L^2}, \quad (6.1)$$

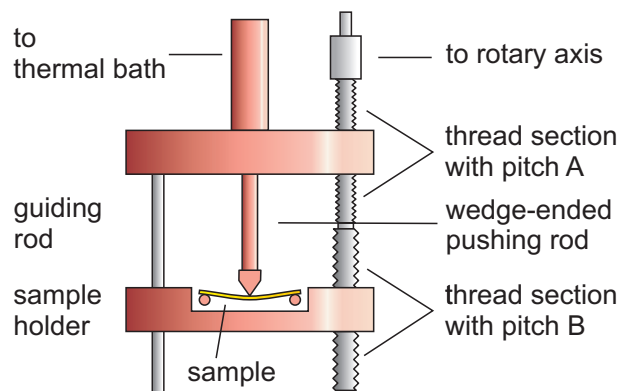


Figure 6.10: Sample holder with differential screw for thin-film MCBJ. A motor drives a rotary axis which ends in a thread with two different pitches. Rotating the axis results in varying distance between ground plate and sample holder. The sample resides on two counter supports connected to the sample holder. It is bent by the pushing rod which is attached to the ground plate. Three guiding rods (only one of which is shown) ensure smooth and linear motion.

where t is the thickness of the substrate, u the length of the free-standing bridge arms and L the distance of the counter supports. This quantity denotes the factor with which any motion of the pushing rod is reduced when it is transferred to the point contact. In a real MCBJ setup, however, the beam-bending is in general non-uniform. Furthermore, also the sacrificial layer has a finite elasticity and is deformed when bending the MCBJ. These effects can be accounted for by a correction factor, which enhances r by a factor of roughly 4 [23]. The effective reduction ratio has a typical value of 10^{-3} to 10^{-2} for the notched-wire MCBJs and 10^{-6} to 10^{-4} for the thin-film MCBJs. The relatively weak reduction ratio of the notched-wire MCBJs usually requires the use of a piezo drive for controlling and stabilizing single-atom contacts, while the lithographic MCBJs can be controlled with purely mechanical drives, i.e. a dc-motor with a combination of gear boxes, and a differential screw.

A common realization of a bending mechanism suitable for thin-film MCBJs and use at low temperatures $T < 1$ K is shown in Fig. 6.10. A rotary axis is connected to a differential screw which consists of a thread, the two sections of which have a slightly different pitch. The typical values for the pitches A and B are 0.7 to 0.8 mm and pitch differences 50 μm to 150 μm . Each full turn of the axis changes the distance between the sample holder and the ground plate by the difference of the pitches. The shape of the end of the pushing rod can be semi-cylindrical or wedge shaped, depending on the desired deformation of the substrate. Because of the off-line axis arrangement of rotary axis and pushing rod several guiding rods are needed to reduce torque and ensure linear motion of the sample holder with respect to the ground plate. The pushing rod can be designed such that it hosts a piezo tube. The MCBJ is electrically contacted via spring contacts or by gluing the wiring to it via silver paint. The thermal contact of the sample to the thermal bath can additionally be provided by thick wires and copper braid. Care has to be taken when choosing the materials combination of the thread and its counterpart to avoid friction because lubrication at low temperature and in vacuum is difficult.

Typical motion speeds of the piezo drive lie between 10 nm/s and 10 $\mu\text{m/s}$ corresponding to results in 10 pm/s to 100 nm/s for the electrodes forming the atomic contacts. For purely mechanical drive these values are 10 nm/s to 1 $\mu\text{m/s}$ for the pushing rod and 10 fm/s to 10 nm/s for the contact. Due to the in-built reduction also the piezo-driven setups are in general slower than STM systems. The high stability enables comprehensive studies on the very same atomic contact at various values of control parameters such as fields and temperature.

On the other hand the small r values require considerable absolute motion of the pushing rod and deformation of the substrate in order to achieve sufficient displacements of the electrodes. This reduces the possible choices of the substrate material considerably.

MCBJ mechanisms have been developed for various environments including ambient conditions, vacuum, very low temperatures [24] or liquid solutions [25]. The latter one is of particular interest for the study of single-molecule junctions and will be explained in detail in the following Chapter. The disadvantages of MCBJs as compared to STM techniques are the small speed and the fact that the surrounding area of the contact cannot easily be scanned. As for STM setups clean contacts can only be guaranteed when working in good vacuum conditions. The sample preparation itself, however, does not require clean

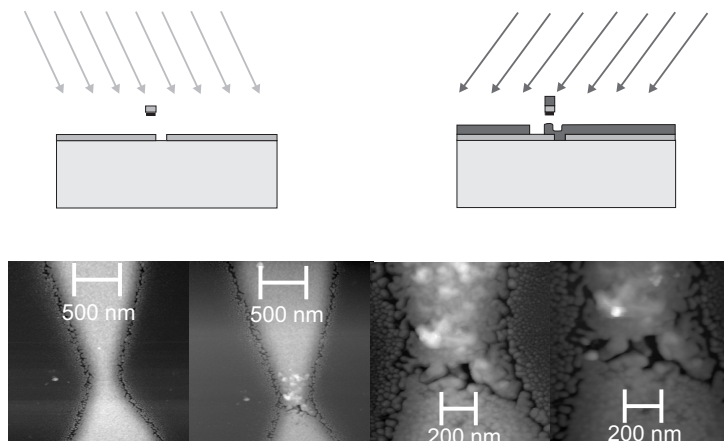


Figure 6.11: Electromigration technique. *Top*: Fabrication via shadow evaporation through a suspended mask of an electrode structure to be used for producing atomic contacts by electromigration. The arrows indicate the directions from which the metal is deposited. The electromigration will nucleate at the thinnest part of the electrode structure. *Bottom*: Series of atomic force microscope images taken in the tapping mode of an electromigrated contact made of Au on Si in different phases of the electromigration process. From left to right: before electromigration ($R = 40 \Omega$), $R = 105 \Omega$, $R = 630 \Omega$, $R = 30.000 \Omega$. Courtesy of D. Stöfler and R. Hoffmann.

conditions because the atomic contacts are only formed during the measurement by breaking the bulk of the electrodes.

6.1.7 Electromigration technique

A third method for the formation of atomic-size contacts is controlled burning of a wire by electromigration (see Fig. 6.11). This technique has been optimized for the formation of nanometer sized gaps for trapping individual molecules or other nanoobjects [26, 27]. Before the wire finally fails and the current drops drastically, atomic size contacts are formed for a rather short time span [28, 29, 30]. During the electromigration process the transport changes from ohmic behavior, i.e. limited by scattering events of the electrons to wave-like electronic transport, which can be described by the Landauer picture (see Chapter 4).

The term electromigration denotes a process in which ions are moved due to high electrical current densities. We concentrate here on the electromigration behavior of metals. It has been understood that several effects contribute to the total force acting on a metal atom which forms the conductor, the two most important being the so-called direct force due to the electric field. It causes the electrical current and thus points into the direction of the field. The second one is caused by momentum transfer of the conduction electrons onto the ions. It has opposite sign and is called the wind force. When the total force overcomes the binding force of the ions, they start to diffuse but can be pinned again at defects or positions where the current density and driving force falls below this threshold value. Depending on the material, the temperature, the crystallinity, the surface roughness, and many other parameters either the direct force may exceed the wind force or vice versa [31]. Therefore the exact direction of the material transport depends on the microscopic structure of the wires. In many cases the motion of the material is such that the cross section of the conductor is locally reduced and its electrical resistance increases. The higher resistance causes higher losses, enhanced dissipation, increasing temperature in the wire which further enhances the dissipation of ions. An important role plays the temperature of the lattice because the diffusion and the threshold current strongly depend on temperature. Electromigration has become one of the most important origins of failures in integrated circuits, due to the miniaturization of the metallic interconnects without reducing the current by the same factor. Consequently, electromigration has widely been studied in electrical engineering with the aim to achieve the highest possible threshold current density for it to set in and the smallest diffusion speed [32].

For the formation of atomic contacts a high threshold current is not important but the possibility for controlling speed, shape and size of the final structure. One of the most important preconditions is to define the position at which the electromigration starts, and the contact forms. For this purpose a

short and thin metallic wire is fabricated by lithographic methods as described in the previous section. Typical dimensions are a length and width of 50 to 100 nm and a thickness of 10 to 20 nm. The thin wire is connected to wider and thicker electrodes which consequently have smaller resistivity. A convenient method to fabricate these structures is shadow evaporation through a suspended mask as shown in Fig. 6.11. First, thin layers of the metal (typical thickness 10 nm) are evaporated under the angles Θ and $-\Theta$. The angle is chosen such that both layers slightly overlap underneath the suspended part of the mask. Afterwards a thick layer of the electrode metal is deposited perpendicular to the substrate plane. The ideal structure would consist of a single-crystalline wire in the thin part of the wire, the boundaries of which are covered by the thick electrodes in order to avoid electromigration of possible contaminants from the grain boundaries. It is advantageous to work on a substrate with high thermal conductivity in order to control the temperature.

The electromigration process itself is performed such that an electrical current is continuously ramped up while the resistivity is monitored. As soon as the resistance starts to increase a computer-controlled feedback loop controls the current such that the rate of the resistance increase is kept constant or slowed down. The resistance increase is partially due to the temperature increase caused by the Joule heating of the driving current. Although it has been shown that in the ohmic regime the current density is the quantity which determines the diffusion of the ions, it is advantageous to control the voltage in order to produce atomic size contacts. When the resistance increases the current becomes smaller, which helps to limit the migration speed. The low-resistive electrodes ensure that the voltage drops locally making the driving force acting only locally as well. Consequently, the dissipation and Joule heat generation are local as well. The procedure should be stopped when the desired resistance is achieved. For the study of atomic contacts the interesting regime is reached when the resistance exceeds roughly one kilohm. For usual metals this corresponds to contacts with a narrowest cross section of roughly 10 atoms. An important finding is that the behavior changes markedly when the size of the smallest cross section corresponds to a few atoms. However, the exact position of the position at which the wire finally breaks is difficult to predict. As will be explained later the electrical transport of contacts of this size is determined by the wave properties of the electrons rather than by collisions with defects. If this happens the resistance may start to decrease again before the wire finally is burned through. This non-monotonous behavior complicates the control scheme further. Several control schemes have been put forward which are optimized for various sample geometries, metals and working conditions such as vacuum or low temperature [84, 28, 29, 30, 33]. So far only a few studies exist in which the electromigration process has been imaged in detail, although these kind of studies are very insightful. One example is shown in Fig. 6.11, where AFM images have been taken after discrete electromigration steps. A particularly nice series of TEM images showing that the most dramatic shape changes occur during the final phase can be found in Ref. [29].

An important difference to STM techniques and MCBJs is the fact that the wire forming the contact is in solid contact with a substrate. The advantages are at first ultimate stability which will become important when studying atomic or molecular junctions as a function of external fields. The second advantage lies in the fact that no particular requirements exist for the properties of the substrate, besides the fact that it should be sufficiently insulating. Often silicon - the standard substrate in microelectronics - is used. With suitable doping it can be used as back-gate for inducing an electric potential and building a three-terminal device. This technique is important for studying effects like Coulomb blockade, which will be explained later.

The main drawback of the electromigration technique is the fact that it is a single-shot experiment: Once an atomic contact has been established there is only limited possibility to fine tune its atomic configuration, in particular coming back to a larger contact is almost impossible. After burning through the wire it cannot be closed again. As described before, the control of the final part of the electromigration process is tricky because the character of the transport changes from ohmic to wave-like. A combination of electromigration with the lithographic MCBJ technique overcomes this problem: a thin-film MCBJ is thinned-out by electromigration to a narrow constriction with a cross section of less than 10 nm (see Fig. 6.12). The substrate is then bent carefully for completely breaking the wire or arranging single-atom contacts. This last step is reversible and repeatable for studying small contacts [34] or trapped nanoobjects [33]. Because only the very last part of the breaking requires mechanical deformation of the substrate it is rather fast and enables the use of more brittle substrates such as silicon.

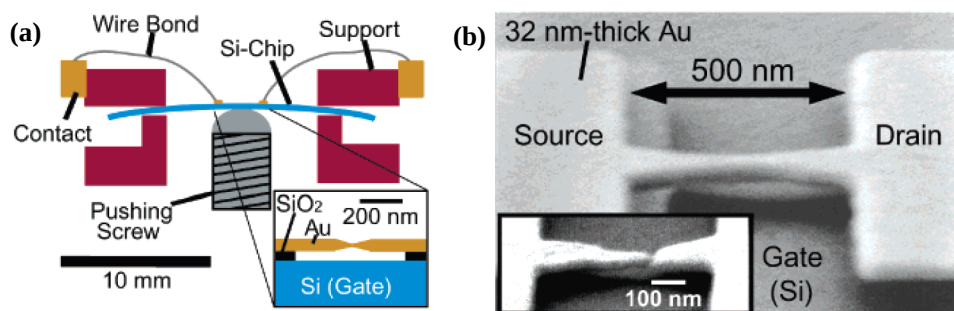


Figure 6.12: Electromigrated MCBJ with gate on silicon substrate. (a) Working principle and (b) electron micrograph of an electromigrated MCBJ. The substrate is doped silicon and can be used as back-gate. Reprinted with permission from [33]. Copyright 2005 American Chemical Society.

6.1.8 Electrochemical methods

A completely distinct method for the formation of atomic-size contacts uses electrochemical deposition and removal of metal atoms. Electrochemical deposition of metals is a standard technique for surface treatment and in micromachining. For the purpose of forming atomic contacts basically the same principles are used. The main difference to the macroscopic techniques is the shape of the starting electrodes and the feedback which controls the deposition speed. Nanocontact formation by electrochemical methods starts from metal electrodes with a gap or with a continuous wire that is first broken either mechanically or by electromigration. The working principle is depicted in Fig. 6.13. The electrode structure is then immersed into an electrolyte containing metal ions. The electrochemical setup is adapted from the three-electrode cyclic voltammetry principle [35]. The deposition and dissolution of metal is controlled by applying an electrical potential difference between a so-called counter electrode and the electrodes forming the nanocontact, which serve as “working electrodes”. A fourth electrode defines the reference potential. The conductance is monitored and used as control signal for the potentiostat which controls the deposition rate. The typical control voltages are in the range of 20 mV to 1 V and can be adjusted to optimize the electrochemical process. It should exceed the bias voltage if one aims at symmetric deposition on both electrodes forming the contact. Obviously the place at which the fastest deposition and dissolution takes place can further be controlled by the size and the polarity of the bias voltage. A typical metal combination is gold as electrode material because of its weak chemical reactivity and silver for the formation of the atomic contacts [36, 37]. Silver is easily dissolved in acids, like e.g. in nitric acid, and simultaneously silver atomic contacts have well understood transport properties, as will be further detailed later. One main advantage of this technique is its versatility, since electrochemical deposition methods on the macroscale have been developed for almost all metals. A further advantage is the simplicity of the working principle, in particular the simplicity with which the starting electrodes can be produced: macroscopic wires as well as deposited thin films [38, 39] or STM setups [40] are possible. Furthermore the contacts are mechanically stable because no suspended parts are required.

Electrochemical contacts are often regarded to be three-terminal devices: The two electrodes forming the contact correspond to source and drain, the control electrode to the gate electrode in the language of semiconductor transistors. Since the electrochemical control involves diffusion of ions, it is slower than the usual electrostatic gating in semiconductor technology. It is however much faster than the purely mechanical control used in the lithographic MCBJ technique. One obvious drawback is the fact that the control mechanism requires liquid environment. It is not obvious how one can bring the contacts into dry environment, vacuum or low temperatures. Anyhow, after removal of the electrochemical environment the contacts cannot be varied anymore (or one of the other techniques, e.g. MCBJ or electromigration, have to be applied for this purpose).

6.1.9 Recent developments: Membrane MCBJ and three-terminal MCBJ

As mentioned in the introduction of this chapter, many variations of the standard methods described above have been developed. In particular, combinations of the archetypical methods have been described. As an example we present here two new versions of the MCBJ technique. The first one has been introduced by Waitz *et al.* [41]. It uses thin-film-wires on silicon membranes with a thickness of a few hundred nanometers. The membrane is deformed by a fine tip on the rear side. At variance to the MCBJ

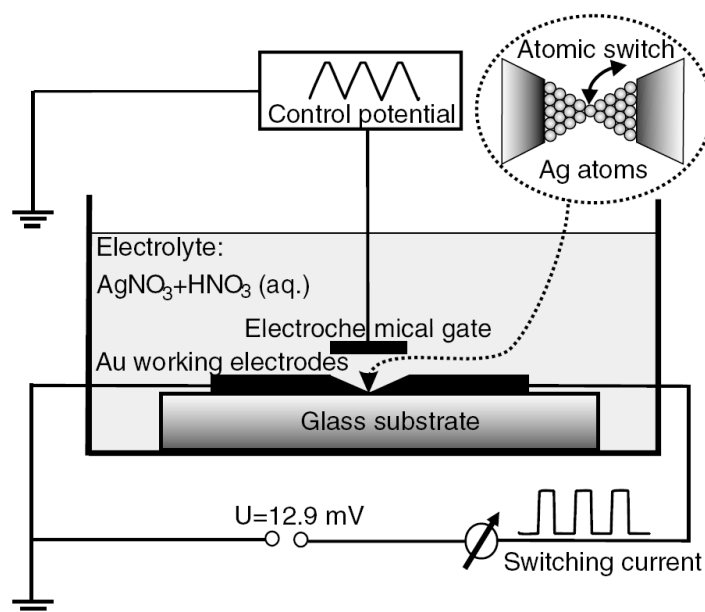


Figure 6.13: Setup for the electrochemical fabrication and control of atomic contacts. For particular choices of the control potential the atomic contact can be switched between defined conductance values and thus a "switching current" is recorded. Reprinted with permission from [36]. Copyright 2003 by the American Physical Society.

techniques on bulk substrates the elasticity of the membrane rather than the bending determines the stretching of the metal wire, see Fig. 6.14. The deformation of the substrate is applied locally and it is thus possible to address particular positions while the rest of the circuit on the substrate remains mainly unaffected. This is important when the MCBJ is embedded in a more complex electronic circuit close to the atomic contact, which should not be affected when changing the atomic contact. Such complex circuits are required e.g. for studying Coulomb blockade. Another advantage of this method as compared to bulk substrates is that the membranes are electrically insulating or only poorly conducting. This reduces the capacitance of the circuit to ground and is advantageous when fast measurements are required. A further difference to standard MCBJ techniques is that smaller suspended length of the metal wire can be used. This enhances stability and reduces often undesired effects such as magnetostriction when investigating magnetotransport. Finally, by combining this membrane MCBJs with electromigration it is possible to control atomic-size contacts at room temperature without suspension at all [42].

The second recent improvement, which we want to describe here, is the successful incorporation of a gate electrode into the lithographic MCBJ techniques without combination with electromigration [43]. It is based on the lithographic MCBJ technique on metallic substrates using two lithography steps. In the first step a thin and rather narrow metallic gate strip is patterned. The gate is then covered by an approximately 50 nm thick insulating sacrificial layer and the resist system for the second lithography step in which the nanobridge is patterned. After evaporation of the nanobridge metal the sacrificial layer removed by dry etching as in the conventional process for lithographic MCBJs. The result is shown in Fig. 6.15: a nanobridge that is suspended approximately 50 nm above the gate electrode. With this technique three-terminal devices with controllable source-drain coupling are now possible.

6.1.10 Electronic transport measurements

This topic will extensively be discussed in the labcourse. The interested participants may have a look at this section already by now.

Usually the first electrical characterization of nanoscale contacts is the measurement of the linear conductance as a function of an outer parameter such as temperature, magnetic field or size of the junction. The next more complex quantity is the nonlinear conductance, i.e. measurements of the current-voltage (I-V) characteristics or the differential conductance. Since these quantities belong to the most common properties of any material characterization their correct measurement is supposed to be trivial, and manifold sophisticated equipment is on the market. In fact, several suppliers of electronic measurement units

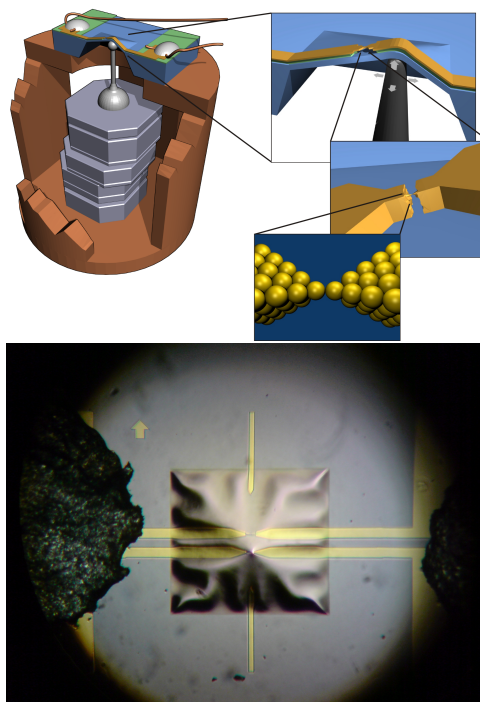


Figure 6.14: MCBJ on silicon membranes. *Top*: Working principle of the membrane MCBJ (not to scale). One or several lithographic MCBJs are defined on the front side of the membrane. A glass or graphite tip is scanned along the rear side of the membrane with the help of micromechanically controlled scan tables. The vertical motion of the tip controls the deformation of the membrane. The close ups at the right side illustrate the deformation of the membrane with a graphite tip, the rupture of the nanobridge, and give an artist's view of the atomic arrangement of a single-atom contact. The thickness of the membrane is in the order of 300 nm, the lateral dimension of the membrane is typically $1\text{ mm} \times 1\text{ mm}$. The length of the suspended bridge is smaller than the one for lithographic MCBJs on massive substrates. The thickness of the sacrificial layer is in the order of 100 nm only. When reducing the lateral size of the constriction first by electromigration, non-suspended metal bridges can be used. *Bottom*: optical micrograph of a membrane carrying two MCBJs made of gold. The tip is positioned underneath the lower bridge where the membrane is deformed. The size of the membrane is $0.6\text{ mm} \times 0.6\text{ mm}$.

offer information material or seminars about low-level, high-resolution electronic measurements, and we encourage our readers to access this literature. Therefore textbooks about nanoscience only rarely address this issue. However, when dealing with nanoobjects it is not easy how to perform a good conductance measurement. In this section we will not give a complete overview over the various techniques. But since the scope of this course is to serve as introduction for beginners in the field of molecular electronics, we want to sensitize the participants to this issue. The particular facts which have to be taken into account in molecular conductance measurements are the following:

- Wide range of conductances from nanosiemens (corresponding to $10^{-5} G_0$ ($G_0 = 2e^2/h$ is the conductance quantum with e the elementary charge and h Planck's constant) to siemens.¹
- Correct choice of bias voltage to assure working in the linear regime is difficult because the effects giving rise to nonlinearities happen on varying voltage scales ranging from microvolt to volt.
- Self-heating of the contacts due to Joule dissipation is not always easy to detect and to discriminate from the intrinsic properties of the sample.
- Sudden voltage spikes and jumps may destroy the sample. Therefore abrupt switching actions in the electrical measurement circuit have to be minimized, often hampering optimum range adjustment.
- Extreme variation of the differential conductance within small changes of the bias.

¹1 Siemens is the inverse of $1\ \Omega = 1\text{ Volt/Ampere}$ and thus the unit of the conductance in the international system of units (SI).

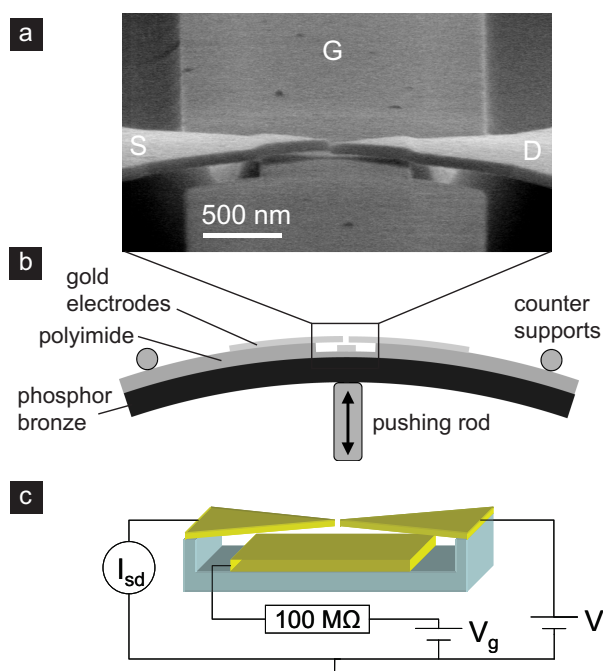


Figure 6.15: MCBJ with gate electrode on bulk substrate. (a) Scanning electron micrograph of a lithographic MCBJ with gate electrode, (b) working principle of the MCBJ, (c) and electronic circuit for the gated MCBJ. Reprinted with permission from [43]. Copyright 2009 American Chemical Society.

- Limited lifetime of the junctions to study.

The typical signal sizes which have to be resolved are of the order of a few nanovolts for the voltage and picoamperes for the current. For particular experiments the requirements might even be stronger. The relative measurement accuracy which is required for most investigations is 10^{-4} or better corresponding to a resolution of typically 14 bits when expressed in digital units. These requirements mean that one often works at the resolution limit of commercial electronic equipment. When enhancing the size of the excitation signal to obtain response signals well above the noise floor one risks to at least smear out the electronic characteristics of the sample by warming it up. In the worst case the sample is destroyed by the heat dissipation.

When designing a measurement circuit the first choice that one has to take is whether one feeds the current and measures the voltage or vice versa. For measurements of the linear conductance, or when the I-Vs are mainly linear, the most important criterion is to optimize the signal-to-noise-ratio. The general rule is that measuring voltage is the better solution for small conductances whereas measuring current is good for high conductance values. When, however, a well-defined energy difference between source and drain is required, e.g. for investigating Coulomb blockade², a voltage bias is obviously the best choice. For other purposes the transport current is the decisive quantity and has to be defined. When dealing with hysteretic I-Vs or junctions revealing negative differential resistance (NDR) the measurement strategy is crucial for reaching all interesting parts of the I-Vs. Similar choices have to be made concerning the position of the electric ground level of the circuit and whether one pole of the sample will be directly connected to it.

Small nonlinearities in the I-Vs may easily disappear in the noise floor of the electronic circuit. They are much easier to detect with a low-noise lock-in amplifier working at a small but finite frequency. When the electric circuit under study is biased with a harmonic voltage signal, the lock-in detector measures directly the first derivative of the I-V when locking it on the bias frequency. The second derivative (which is an important quantity for detecting vibrational excitations) can then be determined by numerical differentiation of the dI/dV . Alternatively it can be directly measured when recording the response at twice the excitation frequency.³

In any case the energy scale given by the excitation voltage has to be kept smaller than the width of the vibrational resonances under study. Furthermore the excitation energy has to be smaller than the

²Coulomb blockade and related effects shall be explained later

³Practically all companies producing lock-in amplifiers offer tutorial material available online.

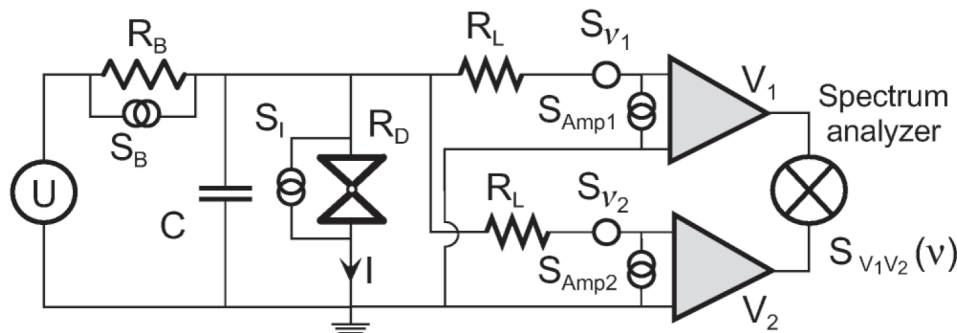


Figure 6.16: Schematic experimental setup for measuring the voltage dependence of the shot noise of an atomic contact. An atomic contact (double triangle symbol), of dynamic resistance R_D , is current biased through a resistance R_B . The voltage V across the contact is measured by two low noise preamplifiers through two nominally identical lossy lines with total resistance R_L in each line and the total capacitance C introduced by the setup across the contact. The spectrum analyzer measures the cross-correlation spectrum of the two voltage lines. The S_i ($i = B, \text{Amp}_1, \text{Amp}_2$) are the known current noise sources associated with the bias resistor and the two amplifiers. S_I represents the signal of interest, i.e. the shot noise associated with the current through the contact. S_{v_1} and S_{v_2} represent the voltage noise sources of each line (amplifier 1 connecting leads). Reprinted with permission from [45]. Copyright 2001 by the American Physical Society.

temperature, otherwise the spectra will be smeared out.

Abrupt changes of the conductance as a function of the bias or another parameter, e.g. the conformation of the junction, result in abrupt changes of the dissipated power as well. On the one hand this is a difficult task for the measurement electronics to cope with. On the other hand this forces one to take precautions, i.e. introduce measures for current limitation, which themselves hamper a perfect voltage bias.

The limited lifetime of the junctions forces one to perform fast measurements, a fact resulting in limited signal to noise ratios and limited statistical information. Atomic and molecular junctions at room temperature reveal intrinsic noise caused by atomic motion. Therefore low-temperature experiments are very appealing. In standard cryostats the wires are rather long and thermalization requires higher cable resistances. Additional measures for high-frequency filtering are required. All these facts reduce the bandwidth of the measurement circuit. As a result it is not trivial to perform fast measurements at low temperatures.

As will be explained in later, many important properties of quantum transport cannot be revealed from conductance measurements alone, but more complex transport properties such as shot noise or thermoelectric voltage have to be studied.

Obviously, for a meaningful noise measurement one has to discriminate the shot noise signal from the undesired but unavoidable noise of the measurement circuit. A fruitful method to do so is a correlation measurement using two identical sets of cables [44, 45]. All noise signals which originate from the wiring are uncorrelated to each other. Signals from the sample are fed into both wires. They are correlated and are recorded in a spectrum analyzer. Only those parts are processed further. An example of such a wiring is shown in Fig. 6.16. It is particularly demanding to measure shot noise at high frequency. A successful solution based on coupled quantum dots has been reported in Ref. [46] and a version using superconducting tunnel contacts in Ref. [47].

For measuring the thermopower a small voltage signal has to be detected which is created by a small temperature gradient across the sample. This means that this temperature difference has to be applied and detected with high precision. One example where this has been successfully achieved is given in Fig. 6.17. It is designed for detecting the conductance and the thermopower of molecular junctions at room temperature [48, 49].

With these examples we will finish our short and incomplete list of electronic measurement setups. Our aim was to make clear that although the fabrication of atomic and molecular junctions is not simple, the correct measurement of their electronic transport properties might be even more demanding.

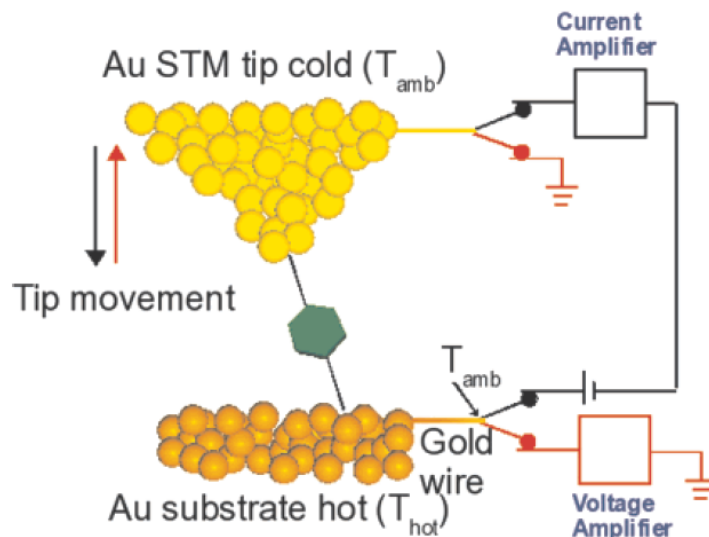


Figure 6.17: Schematic description of the experimental setup for measuring thermoelectric voltage based on an STM break junction. Individual molecules (symbolized by a hexagon) are trapped between the Au STM tip kept at ambient temperature and a heated Au substrate kept at temperature ΔT above the ambient. When the tip approaches the substrate, a voltage bias is applied and the current is monitored to estimate the conductance. When the conductance reaches a threshold of $0.1 G_0$, the voltage bias and the current amplifier are disconnected. A voltage amplifier is then used to measure the induced thermoelectric voltage, while the tip is gradually pulled away from the substrate. Reprinted with permission from [49]. Copyright 2008 American Chemical Society.

6.2 Fabrication of single-molecule contacts

6.2.1 Introduction

In this chapter we shall present the most common methods for contacting molecules. Although we are mainly interested in single molecule devices, we shall also introduce the most basic methods which are in use for contacting molecular ensembles, since many interesting effects in molecular electronics have first been observed in devices containing these assemblies. Of course, this list can never be complete because new methods and variations of existing ones are constantly being developed. Let us remark that we shall focus here on methods to contact molecules with metal electrodes. Devices including at least one semiconductor electrode have also been realized and examples will be briefly described when discussing the phenomenon of negative differential resistance (NDR).

In the fabrication of molecular junctions not only the kind of the electrodes used is crucial, but also the deposition method of the molecules. Thus, any report about electric current through molecular junctions has to address the "protocol", i.e. the precise contacting scheme including the way how, the moment when, and the conditions under which the molecules are brought into electric contact with the electrodes. For this reason, we shall introduce in this chapter the most common deposition methods, then we shall turn to single-molecule contacting schemes and we shall end by addressing the ensemble techniques.

Particularly interesting are techniques which enable the fabrication of three-terminal devices. In these systems, two of the terminals serve to inject the current and measure the voltage, while the third one acts as a gate that controls the electrostatic potential in the molecule. The incorporation of this third electrode is crucial for revealing the transport mechanism and it allows us to tune the current through a molecular junction, very much like in the transistors fabricated with the standard semiconductor technology.

6.2.2 Deposition of molecules

Molecular deposition methods are manifold because of the rich variety of molecules in use. In most experiments the molecules are deposited from solution onto the metal films forming the electrodes. Various solvents and a wide range of concentrations are used. The molecules are allowed to chemisorb to the metal electrodes. After an incubation time the molecular solution is rinsed away with pure solvent. For low-temperature measurements the devices are then dried in a gas (nitrogen) flow. In some cases the

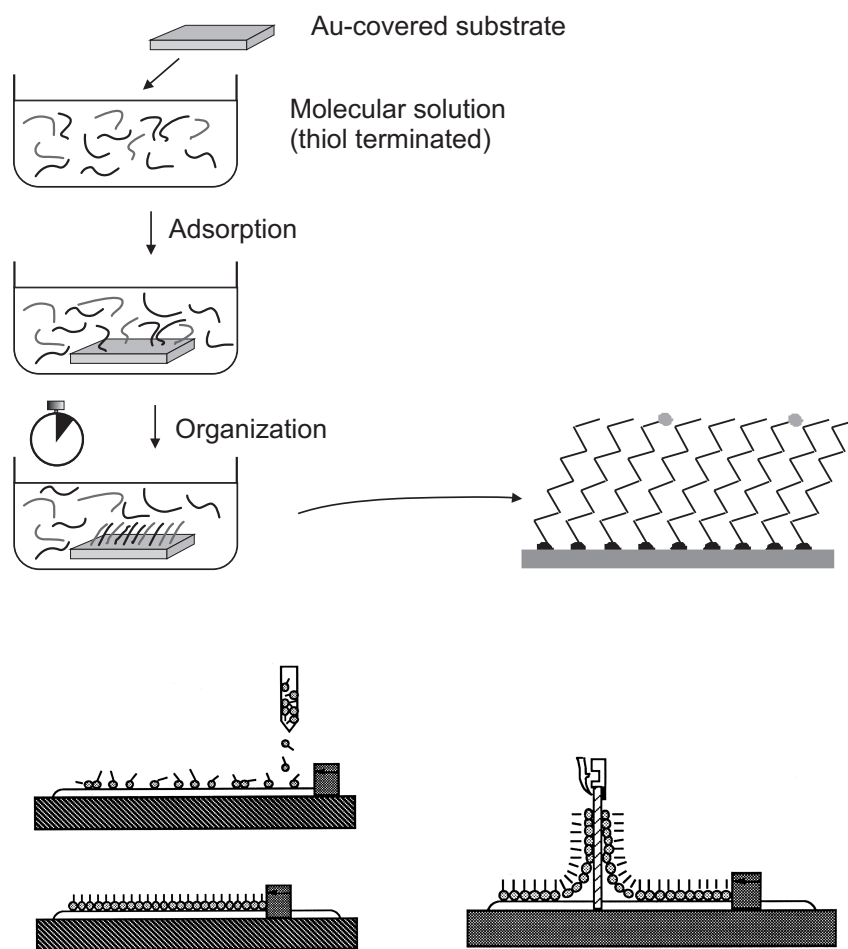


Figure 6.18: *Top*: Formation of a self-assembled monolayer (SAM) shown for two species of alkanethiols on a gold-covered substrate. The substrate is immersed into the molecular solution. The molecules adsorb and assemble with the thiol-terminated end on the substrate. After an incubation time a self-assembled monolayer is formed. *Bottom*: Fabrication of a Langmuir-Blodgett (LB) film. The left panel shows a droplet of an amphiphilic molecule dissolved in a volatile solvent. It is spread on the water-air interface of the trough. The solvent evaporates and leaves a diluted and disordered monolayer behind which is then compressed with the help of a moving barrier. The right panel shows how the monolayer is transferred onto the substrate. Reprinted with permission from Ref. [53].

electronic measurements are performed without drying, in solution - either in presence of the pure solvent or with the molecular solution. A variation of this deposition from solution is spin-coating. A drop of the molecular solution is given on the substrate which is mounted on the chuck of spin-coater. Upon rotation of the substrate the solution is wide-spread over the wafer such that a very small concentration of molecules on the substrate is achieved. As an example we mention individual carbon nanotubes, which after spin-coating can be localized by atomic force microscopy or other techniques. A particular nanotube can subsequently be contacted via lithographically defined metal electrodes.

Many molecules, in particular rod-like molecules form self-assembled monolayers (SAM) on metal surfaces. For that purpose the substrate covered with the metal layer is dipped into the molecular solution. The mostly amphiphilic molecules are equipped with one anchoring group that facilitates the chemical adsorption on the surface. The most common combination for molecular electronics devices is thiol-terminated molecules for adsorption on gold surfaces. The molecules organize such that they form ordered monolayers (see Fig. 6.18). This procedure sounds simple, but in practice many parameters have to be well controlled for obtaining reproducible SAM quality. A recent review of this technique is given in Ref. [52].

Another highly developed technique is monolayer formation via the Langmuir-Blodgett (LB) technique [53, 54]. A LB film consists of one or more monolayers of an organic material, deposited from the surface of a liquid onto a metal surface by immersing the solid substrate into the liquid. The molecules form a

monolayer on the surface of the solution. The monolayer is transferred to the substrate when dipping it into the solution. Upon repetition of the immersion a multilayer consisting of several monolayers and, thus films with very accurate thickness can be formed (see Fig. 6.18). The film formation relies on the fact that amphiphilic molecules with a hydrophilic head and a hydrophobic tail are used. These molecules assemble vertically onto the substrate. For other molecules a horizontal adsorption may be favored, yielding low-density films. The density and ordering can be enhanced by concentrating the molecular layer on the surface of the solution with a spatula before the substrate is dipped into it.

In particular, for the preparation of samples for low-temperature measurements, remainders of the solvent may hamper the formation of clean metal-molecule-metal junctions. Therefore, alternative “dry” deposition methods have been developed. Gaseous molecules (like e.g. hydrogen, oxygen, nitrogen, carbonmonoxide, methane) can be deposited directly from the gas phase by condensation on the cold metal electrodes. Very stable molecules, like the fullerenes or DNA bases may be evaporated thermally from various sources including Knudsen cells or tungsten boats, which are Joule heated by driving a current through them. More sensitive molecules can be deposited using electrospray ionization (ESI). The method starts with a solution in which the molecules to be ionized are dissolved. An electrospray of this solution is created by a strong electric field, which originates from a voltage applied between the spray needle and the end of a capillary. Due to the strong field at the tip apex, charged droplets are created, which are directed towards the capillary, which forms the connection to a vacuum chamber where the already prepared metal electrodes are located [55]. With this method well-controlled submonolayer molecular films may be deposited onto substrates in ultra-high vacuum (UHV).

6.2.3 Contacting single molecules

The fabrication of single molecule electronic devices is a difficult task. The main problem lies in the size of the molecules, which is usually smaller than the resolution of lithographic methods. Thus, sophisticated techniques have to be applied for forming nanometer-size metal gaps. Most of the longer molecules are not conductive enough to be studied in single-molecule devices, but are rather investigated in ensembles. Furthermore, the coupling between the molecule and the electrodes plays an important role. Another consequence of the small size is the difficulty to image the geometry of the junction and to prove that one deals indeed with a single-molecule device. So far, no method exists which allows one to perform systematic measurements of the electronic transport and to characterize the geometry of a given junction with atomic precision. Therefore, several methods are used and are permanently improved. This enables to distinguish between the properties of the metal-molecule combination and the influence of the contacting scheme. The methods may be divided into two main classes. The first one produces rather stable devices, however, the geometry of it cannot be varied and contamination cannot be excluded. Besides the stability, the possibility to add a third electrode is an important advantage. For that purpose, metal electrodes with small volume are desirable for reducing the shielding of the electric field. The second class enables clean contacts and modification of the junction geometry, but offers only limited stability.

The majority of methods in use for contacting individual molecules are based on one of the techniques described in the previous chapter, since contacting single molecules requires at least one atomically fine metal electrode.

Electromigration technique

The electromigration technique described in the previous chapter is successfully used for the fabrication of pairs of metal electrodes for contacting single molecules [84, 56, 57]. For this purpose, the electromigration has to be stopped when the contact is broken and the electrodes form a nanometer-size gap. In vacuum this would be signaled by a sudden increase of the resistance above the typical resistance of a single-atom contact. However, because clean interfaces are needed for achieving well-shaped single-molecule junctions, the molecules are usually deposited - by one of the methods mentioned above - *before* the electromigration process. This complicates the control sequence needed for stopping the electromigration at the right moment, because molecules short-cut the gap resistance. Therefore, many junctions are prepared in parallel and the statistical behavior is determined. Since the metal wire is at ambient conditions before the deposition of the molecules, all kinds of contaminants might be present and have to be carefully removed before deposition of the molecules.

With this technique, all kinds of current-voltage characteristics have been measured ranging from ohmic behavior to Coulomb-blockade behavior. The tunnel contacts may be formed by vacuum gaps (without molecules), single-molecule or multi-molecule contacts. One particular problem of the method is the risk to form small metal grains, the transport properties of which resemble molecular contacts

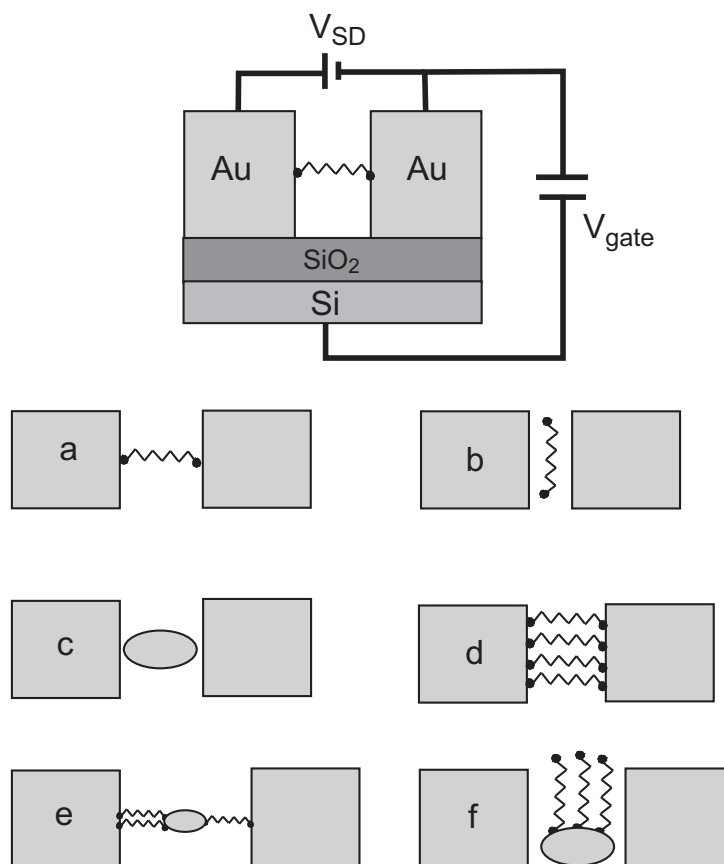


Figure 6.19: Three-terminal devices and possible artifacts in molecular contacts. *Top panel:* Schematic diagram of electromigration gap and measurement configuration. *Bottom panel:* Six models describing possible geometries formed within the electromigration gap by molecule(s) and contaminant metal particles. (a) Single-molecule contact as desired. The molecule is chemisorbed with both ends at the metal electrodes. (b) Single-molecule in the vacuum gap between the electrodes. The molecule is not chemisorbed. (c) Metal-nanoparticle bridging the gap between the electrodes. (d) Multi-molecule contact. (e) The molecules are coupled indirectly via a metal nanoparticle to the electrodes. (f) The molecules are not chemisorbed to the electrodes but to a metal nanoparticle. After Ref. [56].

[56, 57]. Some examples of possible contact geometries are given in Fig. 6.19. Finally, the metal grain may be contacted to both electrodes via one or several molecules. Thus, the yield of this method, i.e. the probability to have a single-molecule contact is in the order of a few percent only. On the other hand, the junctions are extremely stable and well suited for systematic studies of their transport behavior at varying temperature or magnetic field. Because the electrodes are in direct contact to a substrate, it can be used as a back-gate forming a three-terminal device. By applying a gate voltage the transport mechanism can be detected and at least partial information of the contact geometry can be obtained.

Molecular contacts using the transmission electron microscope

In order to obtain very strong coupling between the metal electrodes and the molecule, a particular method has been put forward. It includes furthermore the possibility to image the contact geometry, because the molecules form suspended junctions over slits in thin membranes and can thus be inspected by transmission electron microscopy (TEM). Several variations have been reported, which are optimized for the various molecules. The common point is that the metal electrodes, which have been pre-patterned on a thin membrane or a TEM inspection grid, are rapidly heated up by an intensive electron or laser beam above their melting temperature. Contamination atoms are distilled out of the electrodes and

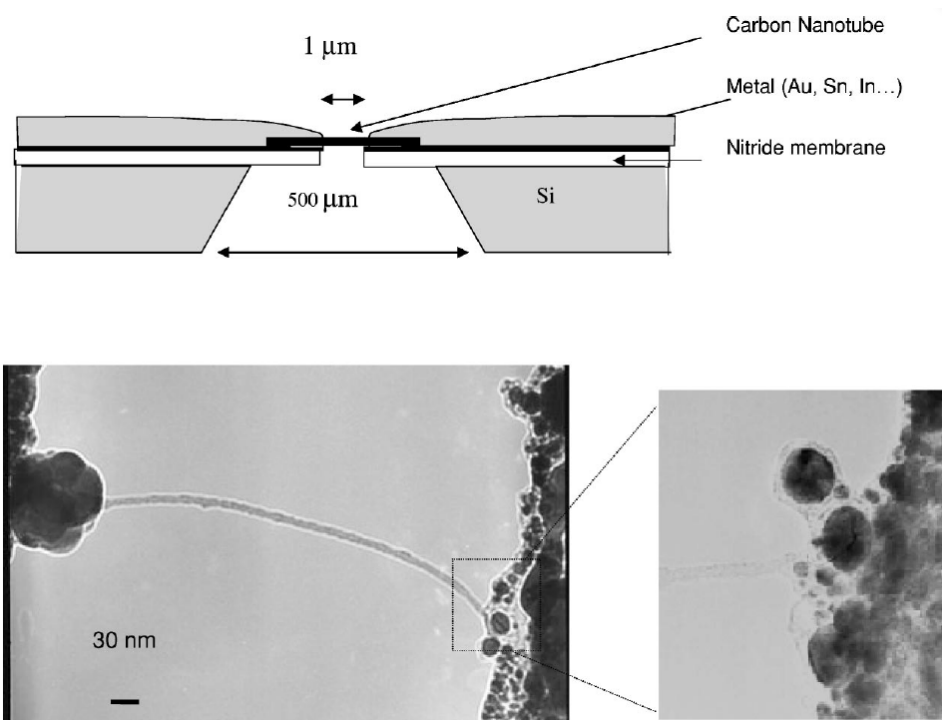


Figure 6.20: Contacting individual molecules in a transmission electron microscope. *Top*: Schematics of the sample geometry. A long molecule is suspended over a slit in a thin membrane and soldered at its ends to two metal electrodes. *Bottom*: Transmission electronic micrograph (TEM) of nanotubes, suspended across a slit between two metallic pads, and detailed view of the contact region showing the metal molten by the laser beam. Reprinted with permission from [59]. Copyright 2003 by the American Physical Society.

defects are driven out as well. The molecules are brought into contact while the metal is liquid. During recrystallization parts of the molecule are soldered into the electrodes resulting in small contact resistances.

This method has been demonstrated to work for long molecules like DNA and carbon nanotubes [59] as well as for chains of clusters [60] (see Fig. 6.20). Possible risks are, of course, destruction of the molecule by the high-energy impact of the laser or electron beam or the hot metal electrodes as well as formation of metal whiskers shorting the molecular junction.

Gold nanoparticle dumbbells

A very elegant method for overcoming the size mismatch between the resolution of lithographic methods in use for the definition of the electrodes and the molecules has been described by T. Dadoosh *et al.* [61]. The authors use gold nanoparticles (GNPs) with a typical diameter of 10 nm. The molecules to be contacted are functionalized at both ends with thiol anchoring groups, which have a high affinity to gold. By these thiol bonds the molecules are attached to the GNPs such that two of them are combined to form a dumbbell. Those dumbbells now have a suitable size for bridging lithographically defined nanogaps and can be deposited onto them straightforwardly. A further advantage of the method is that the statistical behavior of the molecules in contact with the GNPs can be studied by various non-contact methods such as optical spectroscopic measurements before deposition onto the electrodes (see Fig. 6.21).

Scanning probe techniques

Conceptually, the most straightforward method for contacting a single molecule with a fine tip is to deposit the molecule on a metallic substrate and to approach the molecule with the tip until one or several atoms of the molecule are chemisorbed to the tip. However, this is not as simple as it sounds and this method is only suitable for certain molecules. Even if the process is successful, the interpretation of the subsequent conductance measurements is not simple because in STM the electronic signal is

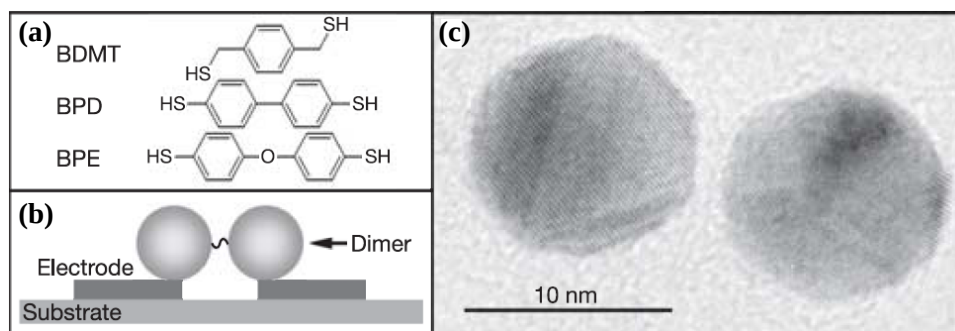


Figure 6.21: (a) The structures of three molecules studied with the dumbbell technique: 1,4-benzenedimethanethiol (BDMT), 4,4'-biphenyldithiol (BPD) and bis-(4-mercaptophenyl)-ether (BPE). (b) The dimer contacting scheme. (c) TEM image of a BDMT dimer made of 10-nm colloidal gold particles. The separation between the two particles corresponds approximately to the BDMT length (0.9 nm). Adapted with permission from MacMillan Publishers Ltd: Nature [61], copyright 2005.

convoluted with the topographic information. Furthermore, the presence of the tip may disturb or even destroy the molecule.⁴ Therefore, various variations of the STM technique have been developed. They all have in common the difficulty to add a third electrode for gating. A certain but nonlocal gate effect can be achieved via electrochemical gates (see below). STM-based techniques are particularly suitable for gathering statistical information because many contacts can be studied in relatively short time. As already explained in the previous chapter, the price for the high flexibility is the low stability and the, in general, short lifetimes of the junctions.

Direct contact

The direct contacting scheme mentioned above requires first a careful preparation and characterization of the surface. Subsequently a sub-monolayer of the molecules is deposited. For stable molecules such as the fullerene C_{60} this can be performed via evaporation [62, 63]. The surface is then scanned and a suitable molecule is selected. Depending on the physical question to study, an isolated molecule or a member of a larger aggregate can be chosen. As described in the previous chapter, for single-atom contacts, the formation of a single-molecule chemical junction is signaled by a sudden increase of the conductance. When this is achieved, the approach can be stopped and spectroscopic investigations can be performed. From the electronic point of view this contacting method usually results in asymmetric contacts, meaning that the molecule is electronically better coupled to the substrate than to the tip. This is important for the interpretation of the transport properties, which will be discussed in Part 4. Often the coupling to the substrate is in the "strong" regime while the electrons have to tunnel from the molecule onto the tip and vice versa, i.e. it is in the "weak coupling" regime. Therefore, this method is most suitable for molecules which are only loosely bound to the substrate, e.g. by a single atom or a few atoms, like for C_{60} , where the binding is given through one pentagon or one hexagon of carbon atoms.

Contacting rod-like molecules

Rod-like or planar molecules have the tendency to lay flat on the surface. In that case the current will not flow along the molecule, but most probably transverse it perpendicularly finding the path of smallest resistance. For those molecules several variations of the scanning probe technique have been put forward. The first method is particularly suitable for imaging and spectroscopy on the molecular orbitals [64]. After preparation of the clean metallic surface, a monomolecular layer of an insulator, e.g. a salt is deposited. The molecules are then evaporated on top of this thin layer which acts as a tunnel barrier between substrate and molecule.

Another possibility is to directly deposit the molecules onto the metal surface, but to design the molecules such that they have edge atoms with high chemical affinity to the tip metal. The tip is then approached to one of these atoms until a chemical bond is formed. Upon carefully withdrawing the tip the molecule is peeled off the substrate, as illustrated in Fig. 6.22. During the peel-off process spectroscopic measurements can be performed which enables to identify the varying charge-transport mechanisms and to quantify the coupling strength [65, 66].

The spatial resolution of the STM imaging can be enhanced by suitable functionalization of the STM tip, e.g. with hydrogen molecules [69]. Recently, it has been demonstrated that molecular orbitals can be even better resolved by atomic force microscopy when the tips are terminated with carbon monoxide

⁴This can be checked by comparing topographic and spectroscopic results, though.

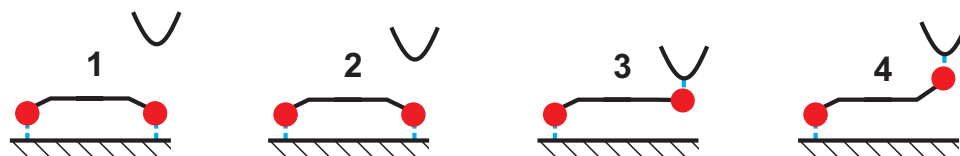


Figure 6.22: Schematics of the contact formation process of a molecular junction with the STM. Four stages of the contact formation during approach (1,2) and retraction (3,4) are shown. At (3) the chemical bond between the contact atom and the substrate is broken and the molecular wire is formed. Reprinted with permission from [6]. Copyright 2008 IOP Publishing Ltd.

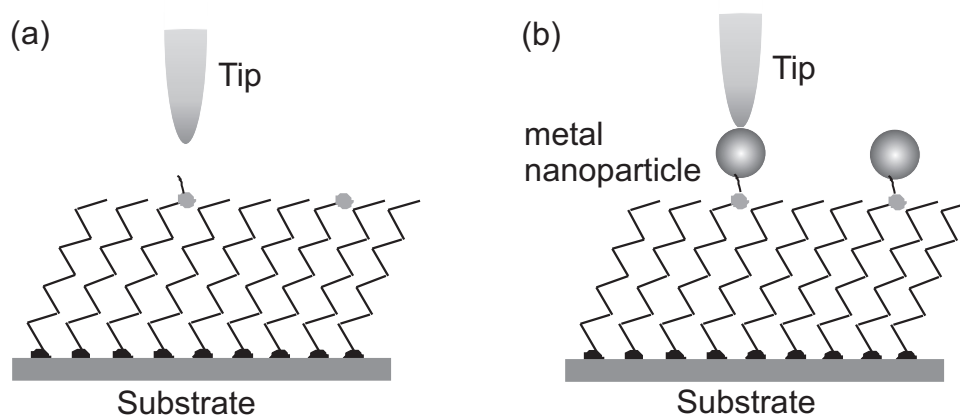


Figure 6.23: (a) Scanning tunneling microscopy (STM) study of electron transport through a target molecule inserted into an ordered array of reference molecules. (b) STM or conducting atomic force microscopy (AFM) measurement of conductance of a molecule with one end attached to a substrate and the other end bound to a metal nanoparticle. After Ref. [86].

(CO) molecules [67, 68].

Finally, an elegant way to contact rod-like molecules is to embed the molecules into a matrix of less conducting molecules, such that the long axis of the molecules is almost perpendicular to the substrate, see Fig. 6.23(a). With the techniques described in section 6.2.2 a self-assembled layer of weakly conducting molecules is prepared. A standard combination would be alkanes with one thiol anchor group on a gold substrate. The thiol binds chemically to the gold releasing the non-thiolated ends to the top of the SAM. The properties of the SAM are chosen such that free places or defects exist at which the study molecule can be incorporated. When scanning the sample with an STM tip the positions of the better conducting molecules can be located and spectroscopic measurements can be performed [70].

In a variation of this technique the study molecules are equipped with two highly reacting anchoring groups, e.g. thiols. One end attaches to the gold surface, the other one pointing to the top of the SAM. These thiols can be used as binding places for gold nanoparticles (GNPs), see Fig. 6.23(b). Depending on the density of the study molecule and the size of the GNPs, one or several molecules are contacted with the same GNP. In this way a very stable molecular junction consisting of substrate, molecule and GNP is fabricated. The prepared sample is then investigated with an STM [71] or a conductive AFM [72]. The tip is either brought into strong contact with the GNP, such that the tip-GNP contact has negligible resistance. Or the transport properties due to the presence of the GNP have to be incorporated in modeling the transport for deducing the properties of the molecular junction. The obvious advantage of this latter method is the high stability of the device. Both variations share the in-built possibility to perform statistical investigations because hundreds of junctions can be prepared on the same chip. The main drawbacks are the complex sample preparation and the limited versatility because successful embedding into the matrix is not obvious.

STM in liquid environment A very powerful tool is the use of an STM in liquid environment. The surface and the tip are prepared as usual for forming atomic contacts, but immersed into a solvent, in which the molecules under study can be dissolved. The tip can be sharpened and covered with substrate atoms by repeated indentation into the substrate. Then molecules are added to the solvent. After an incubation time needed for chemical binding to the substrate, the tip is repeatedly approached to the surface and withdrawn while the conductance is recorded. Upon closing the gap a metal-molecule-metal

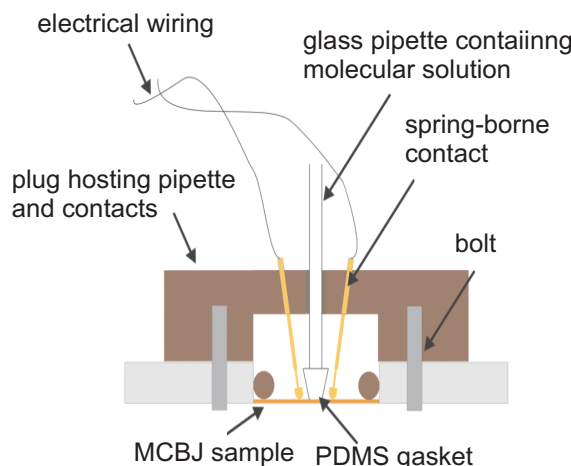


Figure 6.24: A PDMS-sealed glass pipette, in which the molecular solution circulates, is pressed onto the central part of MCBJ chip with the help of a plug screwed to the sample holder. The electrical contacts are realized in this case via spring-borne contacts outside the gasket.

junction consisting of several molecules is formed. When withdrawing the tip, the molecules loose the contact to the electrodes not all at once but in an irregular series. The result is a step-like decrease of the conductance as a function of the distance which varies from repetition to repetition. After breaking the contact to the last molecule, a new junction can be formed. The molecules which get stuck to either the substrate or the tip are replaced by fresh molecules diffusing in from the solution. After a while a new position on the substrate can be chosen. The method is very suitable for gathering statistical information about the preferred conductance values of molecular junctions. However, the stability of the molecular junctions is usually not sufficient for spectroscopic measurements [87, 73].

Mechanically controllable break junctions (MCBJs)

Mechanically controllable break-junctions (MCBJs) (see section 6.1.6) are used for contacting molecules in various environments. For measurements at room temperature under ambient conditions, the molecules are usually deposited from solution. After a reaction period, the remainder of the molecular solution is rinsed in pure solvent and blew dry with nitrogen. At variance to the electromigrated junctions, the molecules are usually deposited *after* forming the electrode gap by breaking the MCBJ. For polarizable molecules it might be helpful to apply a voltage in order to pull one or several molecules into the junction. The junction is then carefully closed until a measurable current flows. Depending on the molecule, the closing traces show plateaus which signal the formation of a molecular junction containing one or several molecules. At room temperature the electrode atoms are rather mobile and the molecular junctions have only limited lifetime of a few minutes. This is, however, a much longer time span than usually achieved with STM setups and is sufficient for measuring I-V characteristics. On the other hand, only limited statistical information can be acquired because of aging effects of the junctions. After several opening or closing cycles no molecular junctions form any more. For recording conductance histograms it is advantageous to perform the measurements in liquid environment, as it was first proposed by Grütter *et al.* [25]. Fig. 6.24 shows a slightly different setup. A pipette is pressed onto the inner part of MCBJ electrodes and sealed with gasket made of a flexible and solvent resistant material (polydimethylsiloxane (PDMS)). The molecular solution is continuously pulled through the pipette, while the MCBJ is opened and closed and the conductance is recorded. Molecules which leave the junctions are replaced by fresh ones from the solution as discussed earlier for STM setups.

Much longer lifetimes of molecular junctions can be achieved at low temperature. Furthermore, the thermal smearing of the electronic properties is considerably reduced. For that purpose several protocols have been developed. When starting with a deposition of the molecules from solution, the solvent and any humidity has to be carefully removed in order to obtain clean molecular junctions without tunnel barriers due to ice formation. For this purpose it is helpful to make use of strong metal molecule binding: A molecular junction is formed at room temperature. When breaking it again it may happen that the breaking does not occur between the molecule and the metal electrode, but that one or several gold atoms

remain attached to the molecule leaving a gap between two metal atoms. The junction is then cooled down and the metal-metal gap is closed again. Of course, water films or other kinds of contamination may form on the metal surfaces as well, but they can be pushed out of the contact such that a good electrical contact can be established.

The problem of ice formation can be solved when forming the electrode gap at low temperatures under cryogenic vacuum conditions. Even though the surface of the native break-junction might be covered with water or other contaminants fresh and clean metal tips are formed. Small molecules, which at ambient conditions are in the gaseous phase (like e.g. hydrogen, oxygen, carbonmonoxide, methane), may be condensed directly onto the cold MCBJ electrodes with a nanometer-size separation [74]. Other small molecules with low evaporation temperature (e.g. water) are first vaporized and then condensed. Similarly, stable molecules like the fullerenes can be evaporated on an opened MCBJ at low temperature [75].

6.3 Contacting molecular ensembles

One main problem in single-molecule studies lies in the fact that the electronic transport depends crucially on the exact coupling between the molecule and the metal electrodes, i.e. on the precise atomic arrangement of the contacts. As a result pronounced sample-to-sample and junction-to-junction variations are observed. Repeated measurements are needed to deduce the typical behavior of a given metal-molecule system. The influence of varying contact geometry averages out in devices containing ensembles of molecules. Furthermore, these ensembles are contacted with rigid and robust electrodes. These devices usually provide better mechanical stability and longer life-times allowing long-time systematic measurements and the variation of outer control parameters like temperature or magnetic field.

However, when interpreting data recorded on ensemble devices one has to bear in mind possible interaction effects between the molecules themselves which might affect their electronic properties. Furthermore, also without interaction effects it is not straightforward to infer the single-molecule junction behavior from the ensemble because the number of molecules which contribute to the transport may be smaller than the total number of molecules in the ensemble, if not all are contacted equally. For instance, some of the molecules forming the ensemble might be in strong coupling to the electrodes while others are only weakly coupled. As a result the transport characteristics may show superpositions of various transport mechanisms. Furthermore, ensemble structures are necessarily larger in space than single-molecule devices giving limits to their maximum integration density. From the point of view of fundamental research the most promising strategy is to compare the results from single-molecule contact schemes with ensemble measurements for revealing the robust properties of the given molecule-metal system. We shall restrict ourselves to methods suitable for small ensembles ranging from roughly a few hundred molecules to several thousand molecules. Very efficient methods have been developed for contacting large area molecular films, which are however, out of scope of this monograph.

6.3.1 Nanopores

One technique which produces rather small ensembles of molecules uses pores in thin freestanding membranes. The method has been used in the 1980's and 1990's for fabricating nanometer-sized metallic contacts for point contact spectroscopy [76]. However, no single-atom contacts can be achieved. A single crystalline silicon wafer is covered from both sides with a thin layer of silicon nitride with a typical thickness of 50 nm to 100 nm. The rear side of the wafer is patterned by optical lithography with squares of typical lateral size of 100 μm . Using first plasma etching for attacking through the nitride, then wet-etching in hydrofluoric acid the squares are etched through the bulk of the silicon wafer. The wet etching process is anisotropic. It attacks particular crystal orientations of the silicon much faster than others. As a result inclined etch walls are formed thereby reducing the size of the squares. The inclined walls become covered with a native silicon oxide layer during the following process steps. Furthermore, the acid attacks silicon much faster than silicon nitride. The process can thus be stopped controllably when a suspended silicon nitride membrane is obtained. Now the membranes are patterned from the front side via electron beam lithography with a small dot in each membrane. Using plasma etching a small pore is drilled into the membrane with a typical diameter of 10 to 50 nm.

The formation of molecular junctions requires three further steps [77]. First, a metal electrode - usually gold - is evaporated from the top side. The device is then immersed into the molecular solution until a SAM has formed. After a suitable reaction time which depends on the molecule-metal combination the sample is rinsed and dried and the second metal electrode is deposited by evaporation onto the rear side,

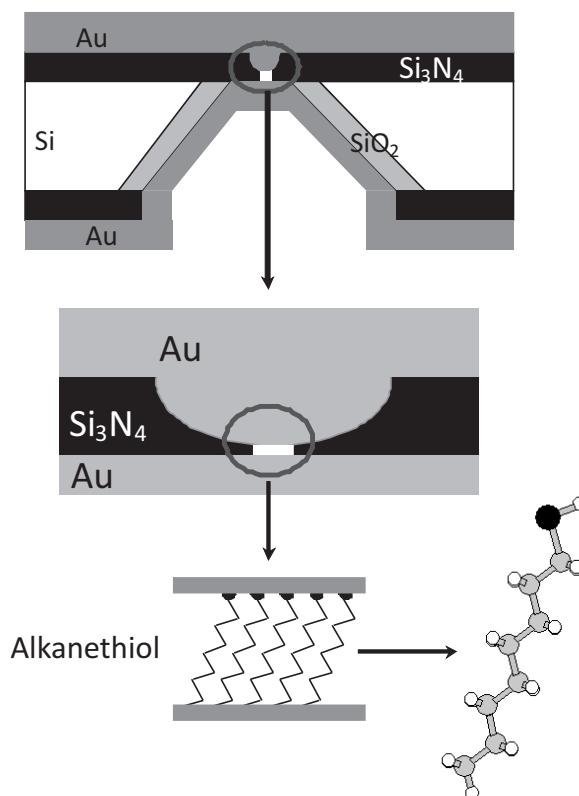


Figure 6.25: Molecular junctions in nanopores. A small molecular ensemble is contacted with metal electrodes in a nanometer-sized pore in a silicon-nitride membrane. Top schematic is the cross section of a silicon wafer with a nanometer-scale pore etched through a suspended silicon nitride membrane. Middle and bottom schematics show a Au-SAM-Au junction formed in the pore area. The structure of octanethiol is shown as an example. Reprinted with permission from [77]. Copyright 2003 by the American Physical Society.

see Fig. 6.25. Care has to be taken that the SAM is not destroyed by thermal impact coming from the metal atoms. With this technique thermally stable molecular ensemble junctions are obtained which are particularly suitable for studies of the temperature dependence of the transport properties. A difficulty of the method lies in the fact that the quality of the first deposited electrode cannot be characterized; it might be covered with water or other contaminants which could hamper the formation of a high-quality SAM. A similar objection was made concerning the second molecule-metal interface: The molecular layer is exposed to ambient conditions before the deposition of the second electrode.

6.3.2 Shadow masks

Another method to fabricate small ensemble devices uses the self-alignment property of shadow masks. The sample fabrication scheme is shown in Fig. 6.26. Via e-beam lithography a suspended mask is produced with a geometry of a wire that is interrupted by a small gap. A first metal layer is evaporated perpendicularly through this mask. The next step is the deposition of a SAM of the molecules. Alternatively molecules can be evaporated on top of the metal under the same angle. Subsequently a second metal layer is evaporated under an inclined angle such that the edge of the metal film covers the molecular layer. The resolution limits of the lithography used for the preparation of the mask restrict the contact size to roughly 50 nm in width. The overlay length is given by the evaporation angle and is usually chosen in the range of 20 to 50 nm. It has been shown that the smoothness of the first metal layer is mandatory for avoiding shortcuts between both electrodes. A second problem of this method is the risk of destroying the SAM by the heat impact during the evaporation of the top electrode or of creating metal grains [56].

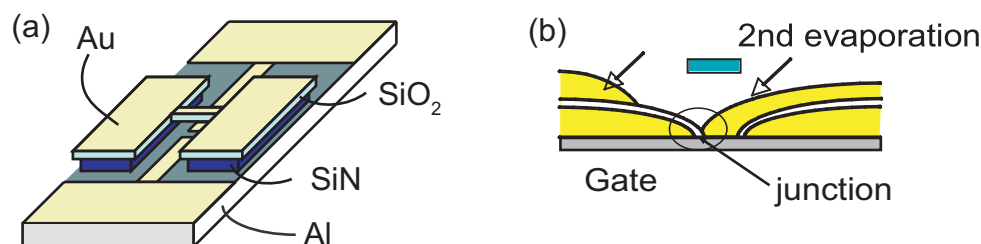


Figure 6.26: Production of shadow mask on silicon substrate. (a) The shadow mask is defined via electron-beam lithography in a $\text{Si}_3\text{N}_4/\text{SiO}_2$ double layer using two dry etching steps. (b) The bridge in the center of the structure is used to separate two metal contacts, which are evaporated vertically onto the substrate. A SAM is deposited on both electrodes. In a second step metal is evaporated under an angle that allows a small overlap between this top electrode and one of the bottom electrodes. If this overlap is small enough, transport through single or a few molecules can be possibly measured. Reprinted with permission from [58]. Copyright 2005, American Institute of Physics.

6.3.3 Conductive polymer electrodes

These problems are partially overcome by a technique described by Akkerman *et al.* [78]. The fabrication method is shown in Fig. 6.27. In a first lithography step metal lines are fabricated and then a second resist is spread over the sample. In the next step this resist is patterned with holes via electron-beam lithography. The molecular ensemble is deposited into these holes. Next, the whole substrate is overcast with a highly conductive polymer which provides the second electrode. The polymer is finally capped by a planar top metal electrode. The result is a very robust molecular junction because the SAM remains embedded into the resist. Furthermore, the deposition of the conductive polymer is less aggressive to the SAM than standard metal deposition techniques. At variance to most of the previously described methods the contact scheme intrinsically gives rise to asymmetric contacts.

6.3.4 Microtransfer printing

A method which combines gentle deposition of the top electrode with the ability to fabricate arrays of molecular junctions with similar contact properties is given by the micro- or nanotransfer printing technique. It produces stable contacts on a substrate and involves also the formation of a SAM (Fig. 6.28). At first an array of bottom electrodes is fabricated using lithographic methods or evaporation through a mechanical mask. Subsequently a SAM of the molecules to study is formed on the substrate. The molecules are functionalized at their top ends with an anchoring group suitable for binding to the metal of the top electrode. In a separate fabrication line a stamp made of a flexible material such as PDMS is fabricated. The stamp is topographically patterned in the geometry of the top electrodes. The metal of the top electrode is evaporated onto it. This stamp is then pressed onto the substrate. During this step the metal is transferred from the stamp to the substrate, thus forming an array of molecular junctions. This technique enables junctions with areas ranging from less than a micrometer squared - and thus named nanotransfer printing (nTP) - up to several hundred square micrometers - microtransfer printing (μ TP) [58, 79]. Besides the in-built statistical information of molecular ensembles the quality of the SAM and the contacts can be investigated by comparing contacts with varying area. Furthermore, the contacts may be gated by applying voltages to the substrate.

6.3.5 Gold nanoparticle arrays

Finally, it is possible to form networks of single-molecule junctions combining the robustness and statistical richness of ensemble studies with the fact that each junction is formed by a single molecule or a very small number of molecules only [80, 81]. The fabrication scheme is shown in Fig. 6.29. At first gold nanoparticles (GNP) with a diameter of roughly 10 nanometers are covered with a spherical ligand shell. The thickness of the ligand shell corresponds to half the length of the molecules which shall be assembled between the GNPs later. A dense-packed, well-ordered, two-dimensional array with an approximate size of $10\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ of these dressed GNPs is deposited onto a substrate which is subsequently patterned with metallic electrodes for performing the contacts to the measurement circuit. The array contains approximately a million nanoparticles. The molecules forming the ligand shell can be replaced with an exchange reaction by the molecules to be studied electrically. By using network analysis methods the

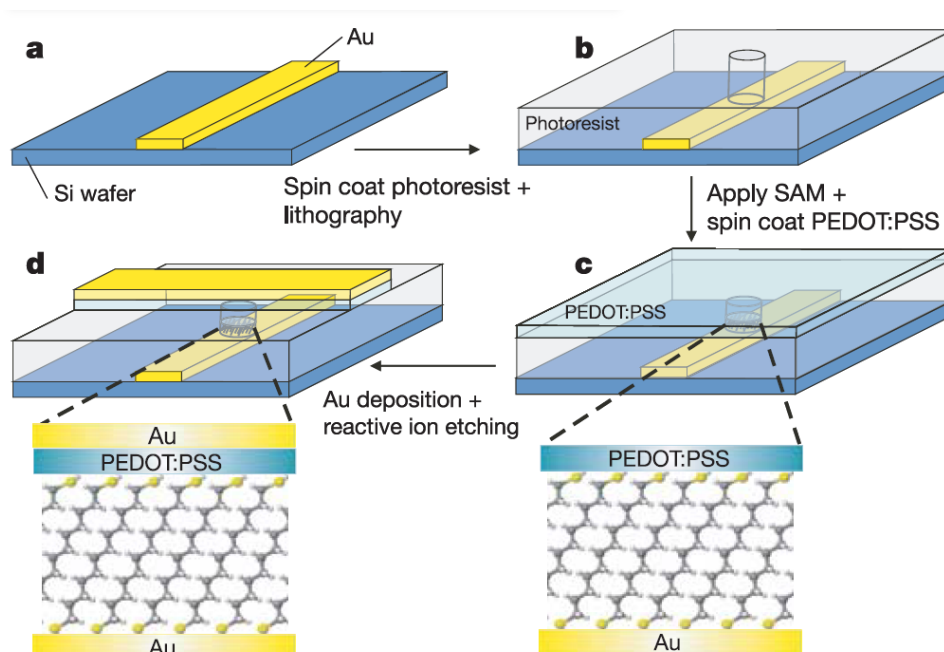


Figure 6.27: Processing steps of a large-area molecular junction. (a) Gold electrodes are vapor-deposited on a silicon wafer and a photoresist is spin-coated. (b) Holes are photolithographically defined in the photoresist. (c) An alkane dithiolSAM is sandwiched between a gold bottom electrode and the highly conductive polymer PEDOT:PSS as a top electrode. (d) The junction is completed by vapor-deposition of gold through a shadow mask, which acts as a self-aligned etching mask during reactive ion etching of the PEDOT:PSS. The dimensions for these large-area molecular diodes range from 10 to 100 mm in diameter. Reprinted with permission from MacMillan Publishers Ltd: Nature [78], copyright 2006.

typical properties of an individual molecular junction can be at least partially deduced from the behavior of the network. Besides the particular stability and in-built ensemble averaging, this method is suitable for the investigation of very small signals, such as electrical response to optical activation of photochromic molecules [82].

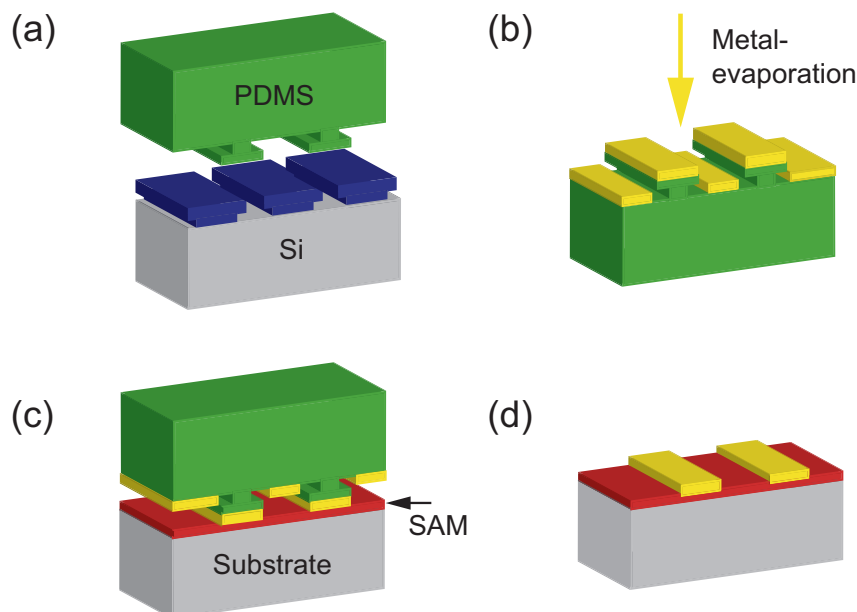


Figure 6.28: Production of nanoscale features by nano transfer printing (nTP). (a) The features are defined by electron beam lithography in a polymethylmethacrylate (PMMA) double layer on a silicon substrate. The elastomeric polydimethylsiloxane (PDMS) is cast into the structures and cured at 60° C. Fluorination of the substrate before this step ensures easy separation of PDMS and substrate after the curing. (b) Layers of 10-30 nm metal gold are evaporated onto the PDMS stamp. (c) Alkanedithiols form a monolayer on a GaAs substrate. The gold on the PDMS stamp binds to this monolayer and is transferred to the substrate. (d) The patterned gold film that forms is transferred on top of the GaAs substrate. Good binding to the monolayer is proved by the scotch tape test. Reprinted with permission from [58]. Copyright 2005, American Institute of Physics.

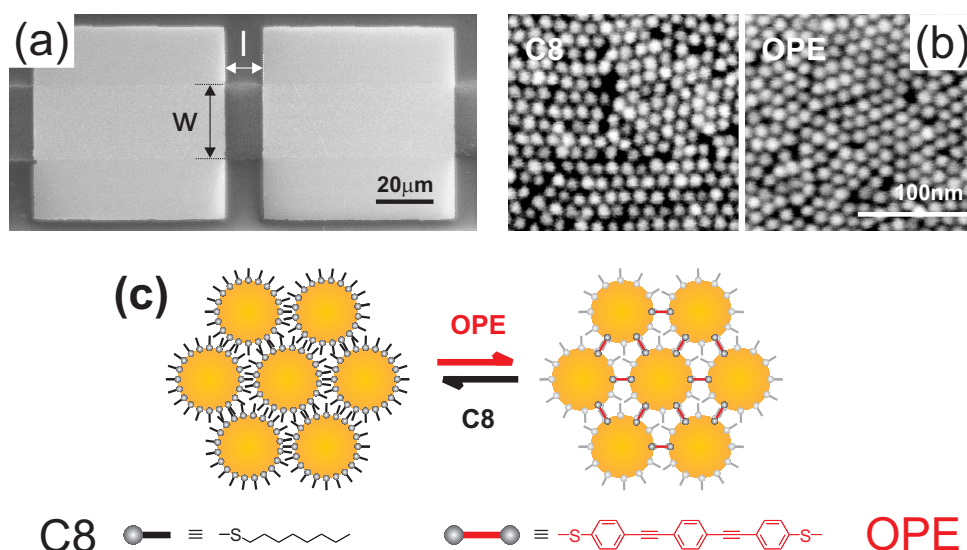


Figure 6.29: Contacting molecular networks with gold nanoparticles. (a) Electron microscopy image of a device: two square-shaped gold contacts were evaporated on top of a nanoparticle array line of width w . (b) Electron micrographs of the array structure before and after OPE (oligo-phenylene-ethynylene) exchange. (c) Schematic of the molecular-exchange process. *Left*: self-assembled alkanethiol-capped nanoparticles before exchange. *Right*: During the exchange process. The OPE molecules displace part of the alkane chains and interlink neighboring nanoparticles to form a network of molecular junctions. Adapted with permission from [80]. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.

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