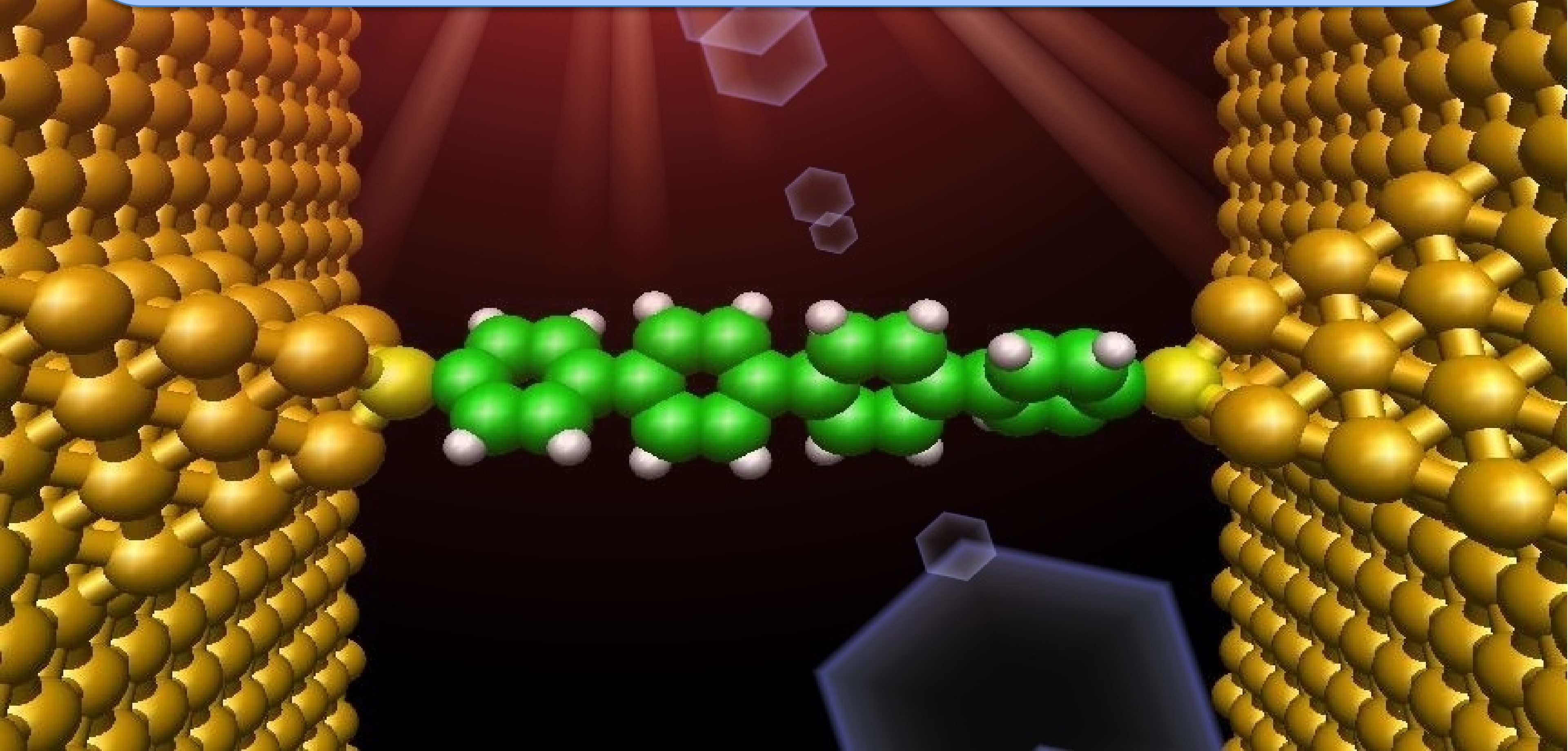
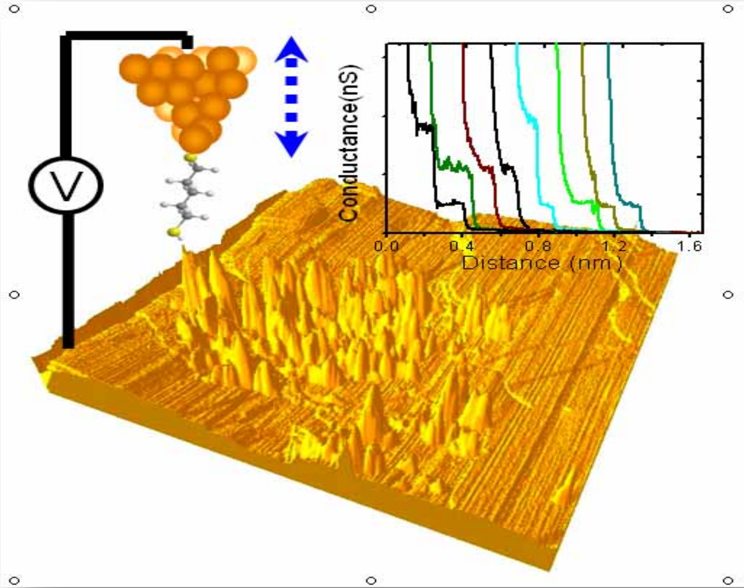
6.2 Contacting techniques for molecular contacts

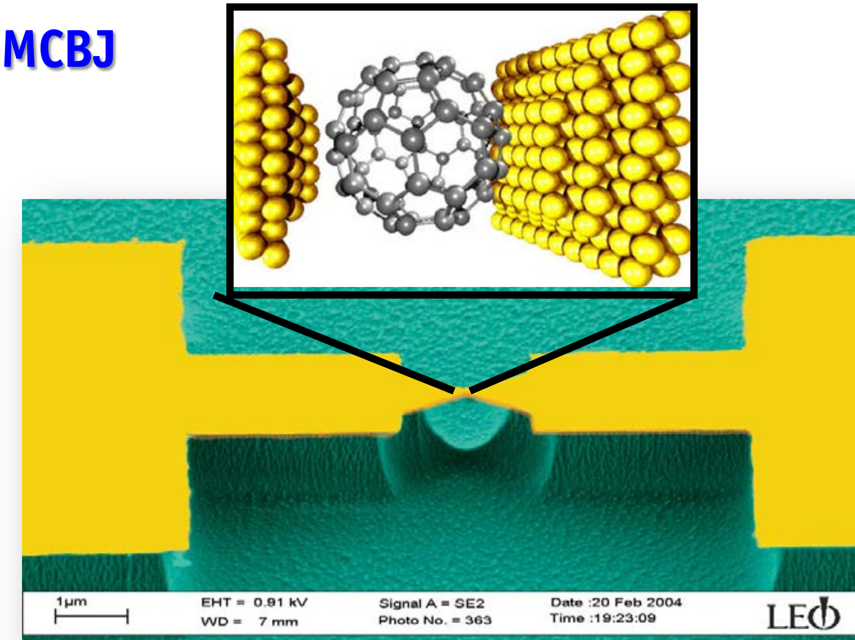


6.2.1 Techniques providing single molecule contacts

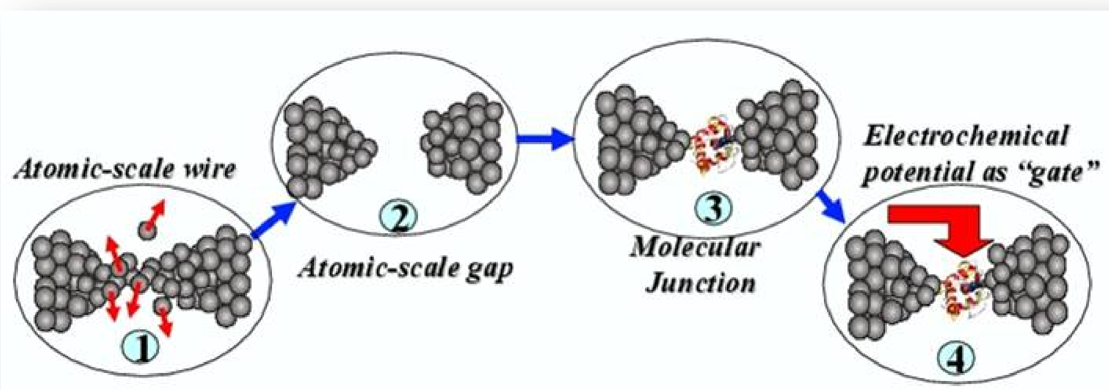
1. STM



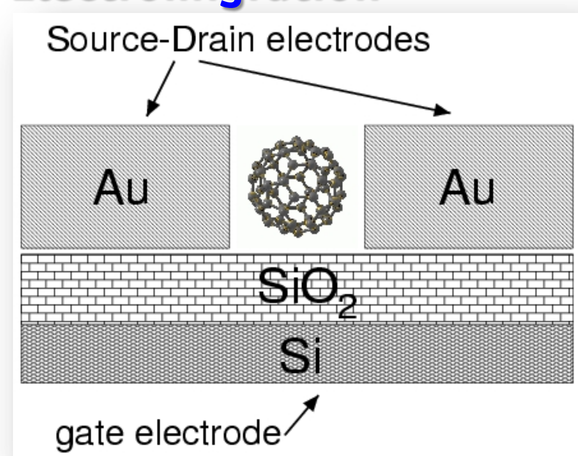
2. MCBJ



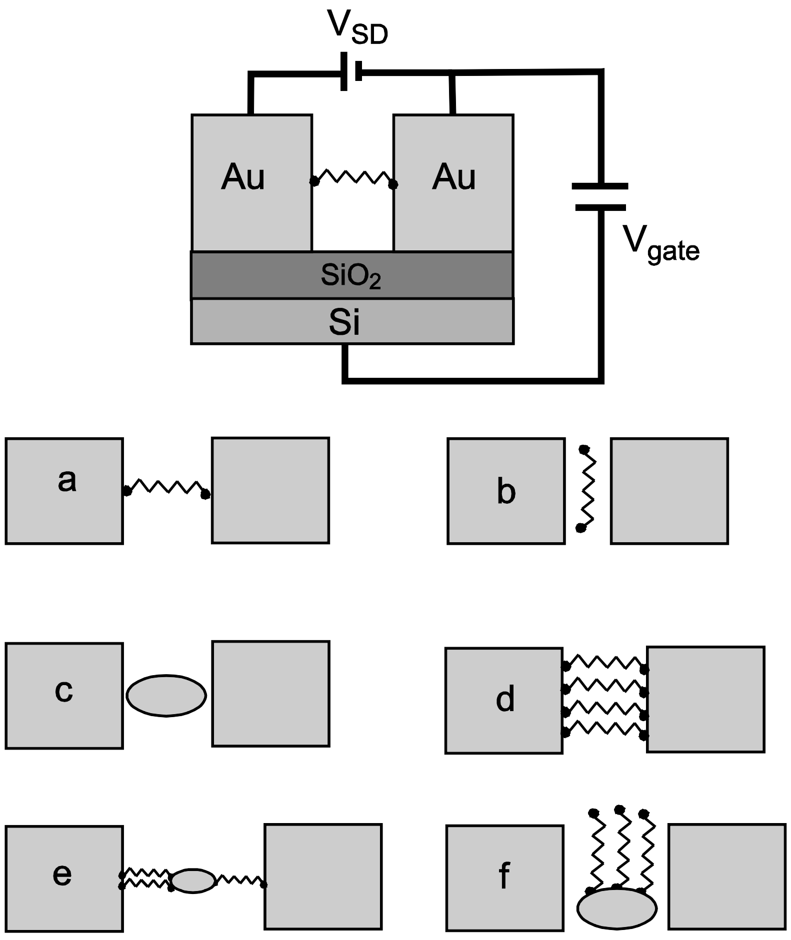
3. Electrochemical methods



4. Electromigration



Artifacts in molecular junctions



6.2.2 Deposition of molecules

Wet deposition:

SAM formation, Langmuir Blodgett Technique, Spincoating

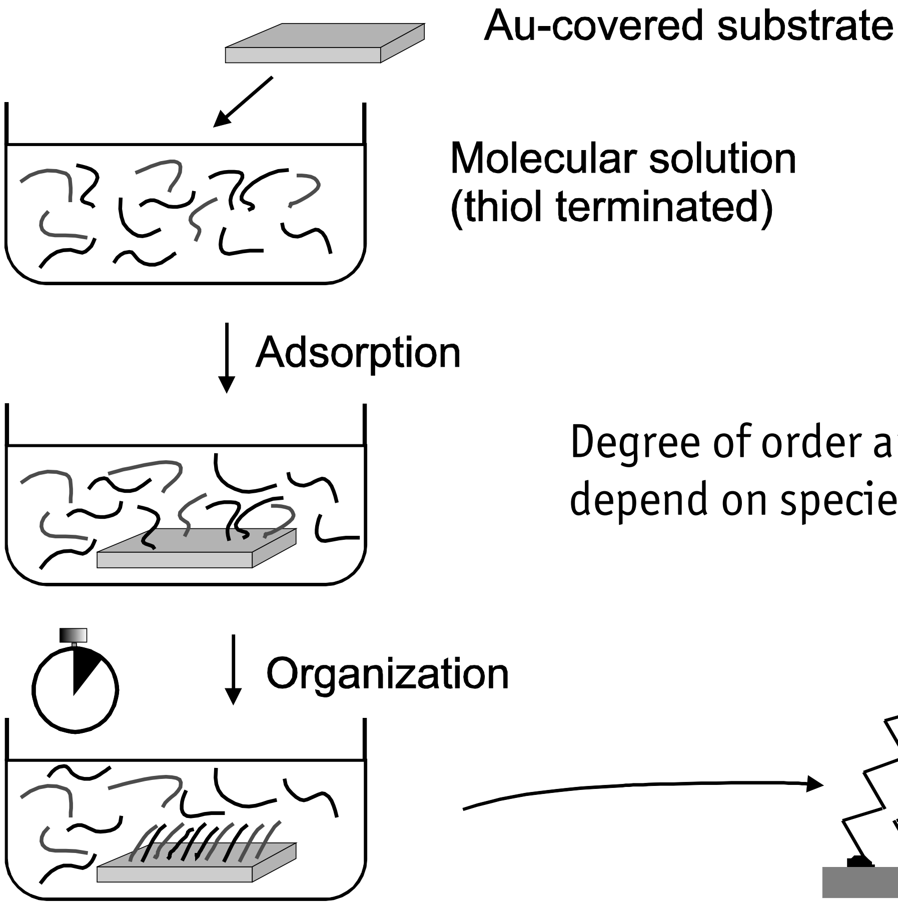
+ easy and versatile
- residues of solvents/water -> bad electrical contacts
- potential chemical reactions with electrode metal
- only possible at ambient conditions (room temperature, no vacuum) -> potential contamination (humidity, oxidation of electrodes)

Dry deposition:

Electro-Spray Ionization, Thermal Evaporation

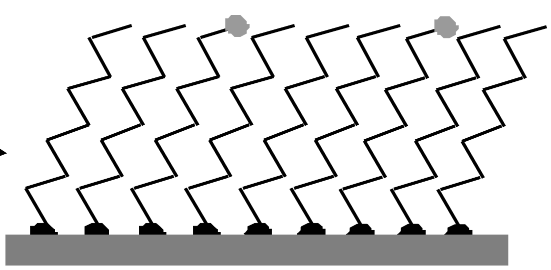
+ good control over amount of molecules
+ deposition onto cold substrate possible
+ clean contacts (no water, no solvents, in situ application possible
+ works for reactive electrode materials
- less versatile,
- potentially detrimental to molecules

Formation of self-assembled monolayers (SAMs)



- for contacting molecular ensembles
- for addressing individual molecules with local probes
- for covering microfabricated electrodes

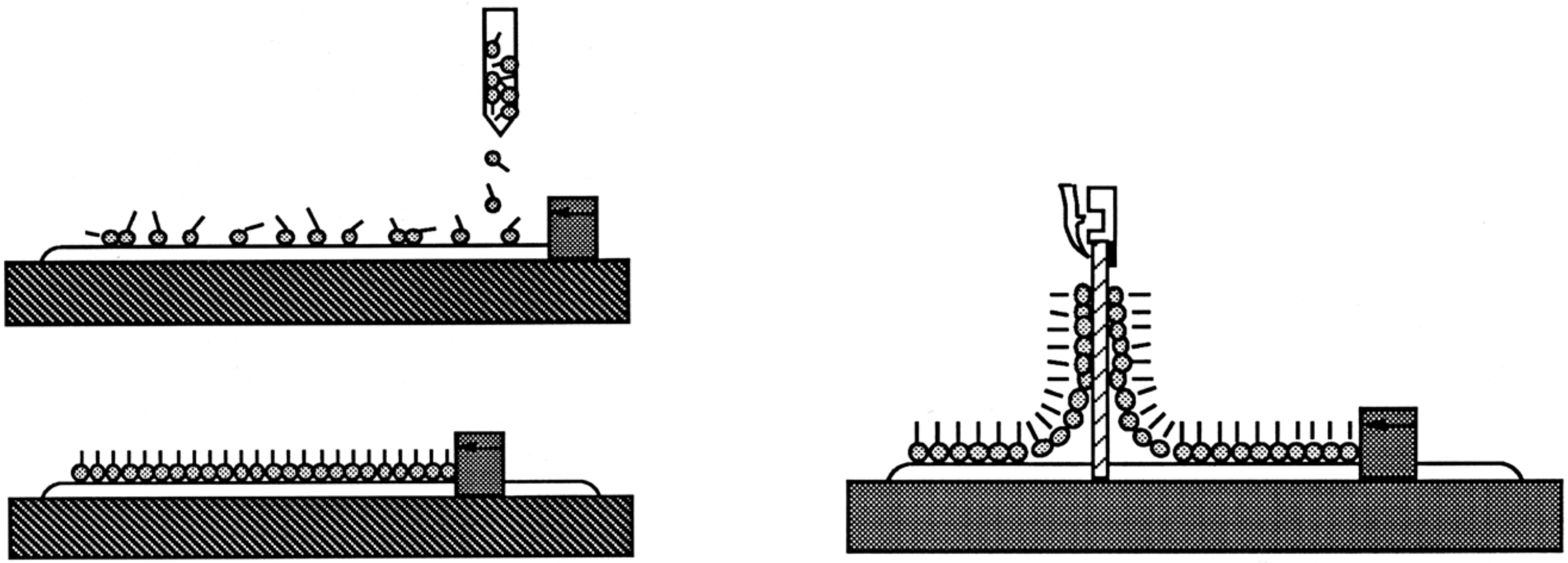
Degree of order and morphology (density, angle) depend on species.



Langmuir-Blodgett technique

Formation of densely-packed monomolecular layers
1. Deposition of amphiphilic molecules onto water surface
2. Pushing molecules together
3. Transfer to substrate (both sides) by immersing and withdrawing into water

Thicker layers possible by repeated indentation

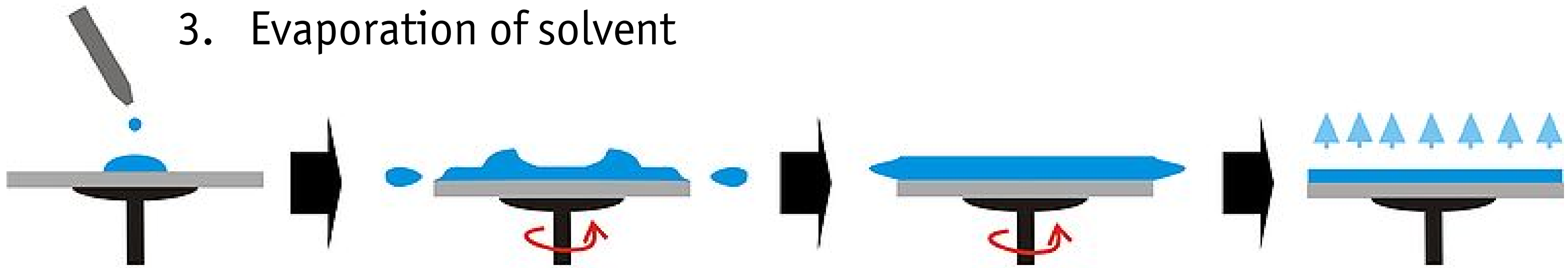


Spincoating

(Lackschleudern oder Rotationsbeschichten)

Standard technique for application of resists in lithography

1. Application of droplet of molecular solution onto rotating substrate
2. Solution spreads to layer with constant thickness thereby spreading the molecules over the substrate
3. Evaporation of solvent



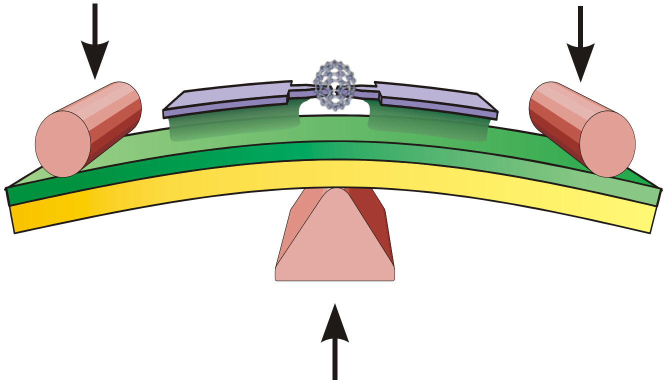
For depositing small amounts of molecules (submonolayer density)
Low densities required for

- addressing and identifying individual molecules with STM/AFM
- avoiding interaction between molecules
- depositing molecules onto prepatterned electrodes
- depositing molecules for subsequent patterning with electrodes

Often used for long molecules (CNTs and DNA)

Image taken from Wikipedia

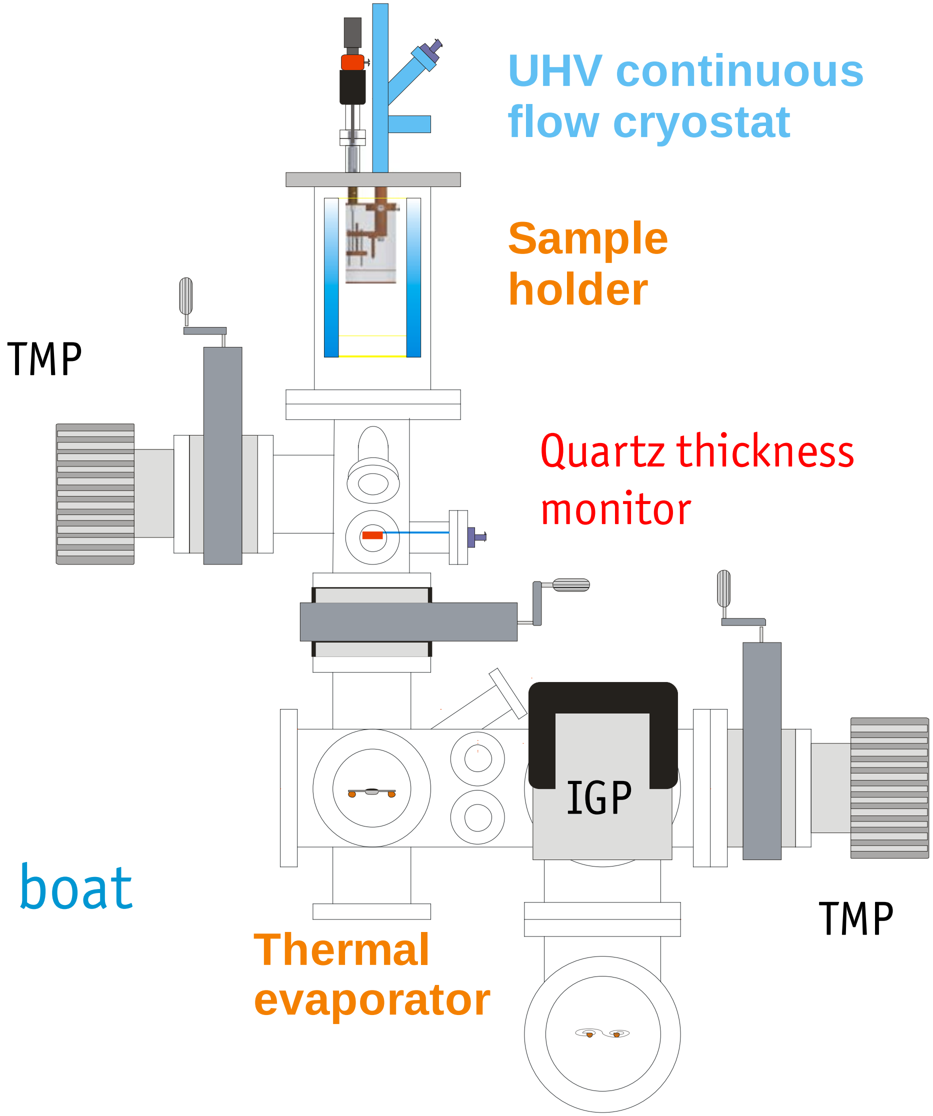
Evaporation onto prepatterned electrodes



TMP = Turbomolecular pump

IGP = Ion Getter Pump

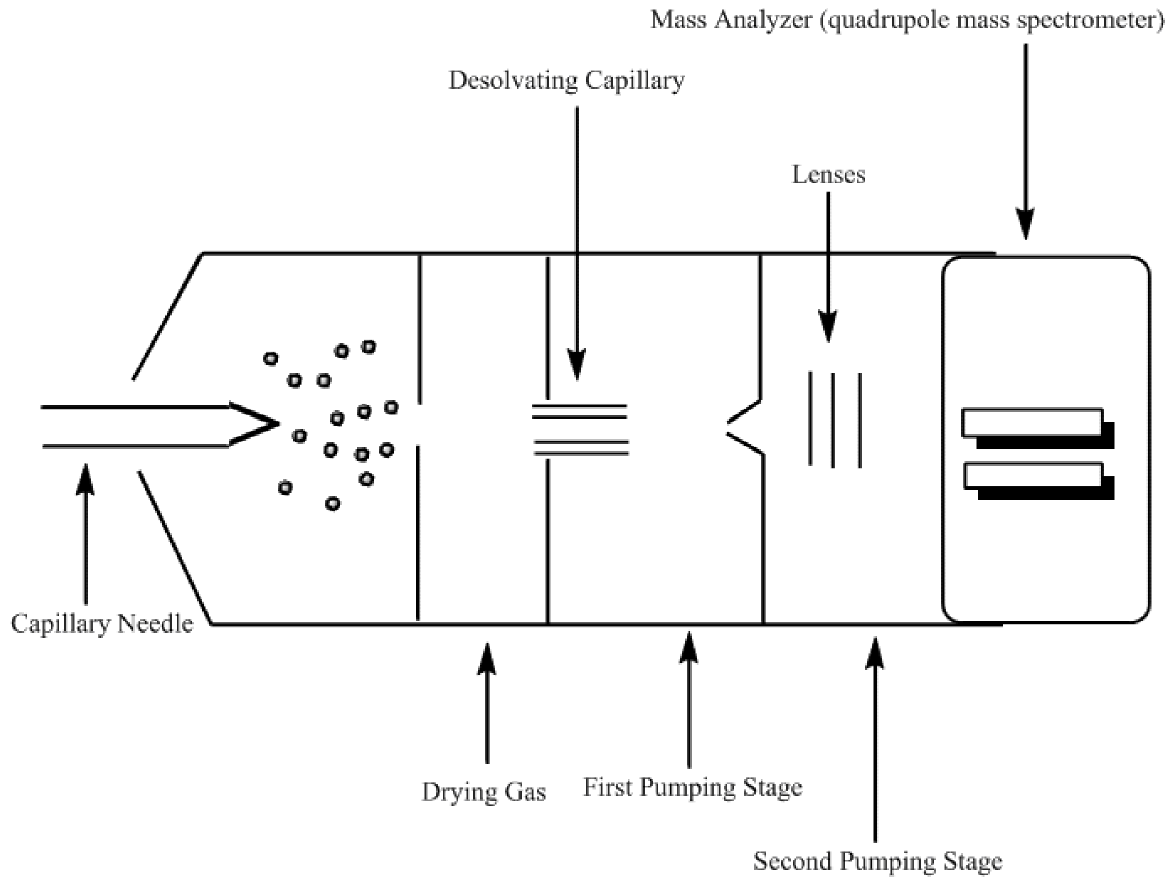
- MCBJ in UHV
- Gold and aluminum electrodes
- Low temperatures ~ 10 K
- Thermal evaporation from tungsten boat
- Thicknesses > 0.005 monolayers



Electro-Spray Ionization (ESI)

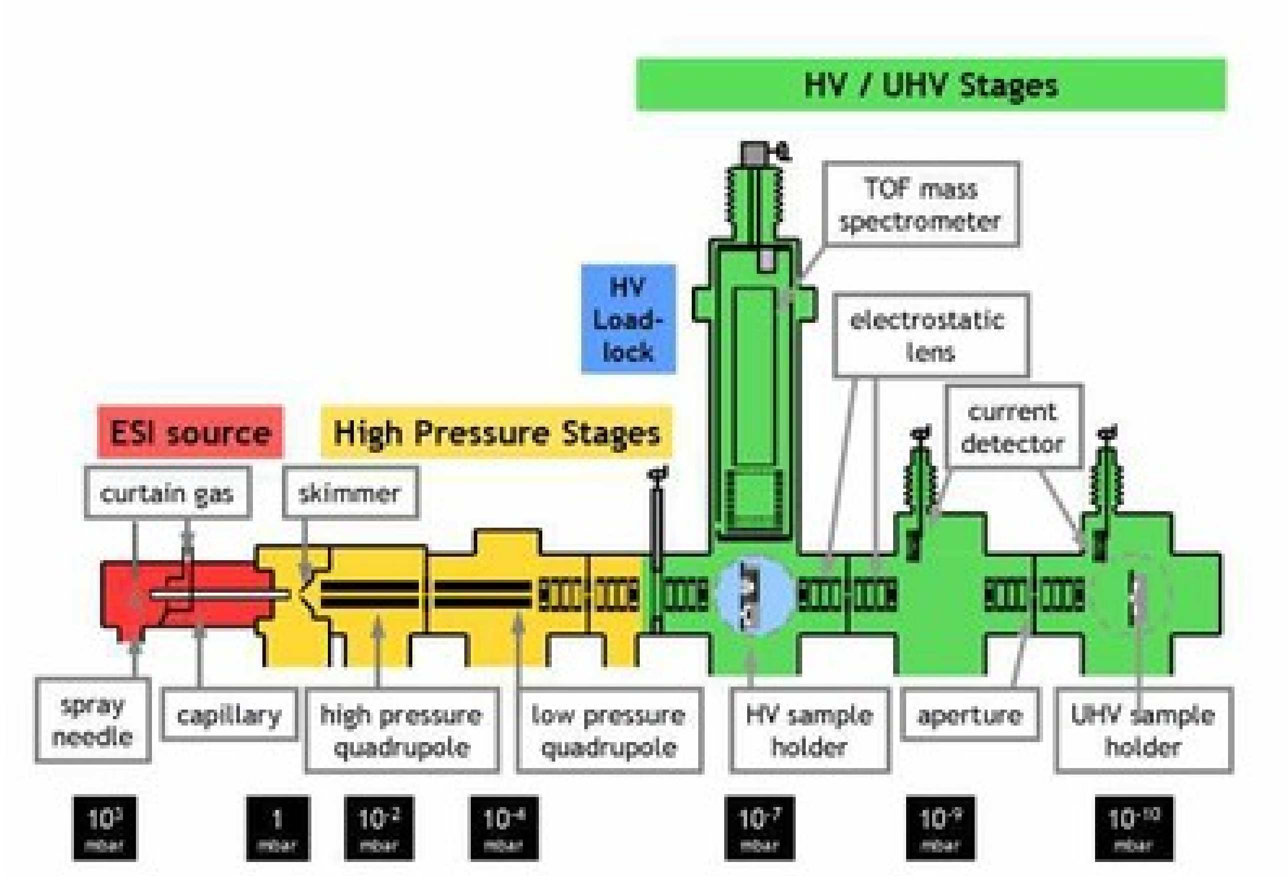
A molecular solution is ionized in electric field and spread into small droplets in vacuum

Nobel Prize in Chemistry in 2002 to John B. Fenn for the Development of ESI for Mass Spectroscopy in Biochemistry



Images taken from UC Davis webpage and Wikipedia

Electrospray Ionization Ion Beam Deposition (ESI-IBD)

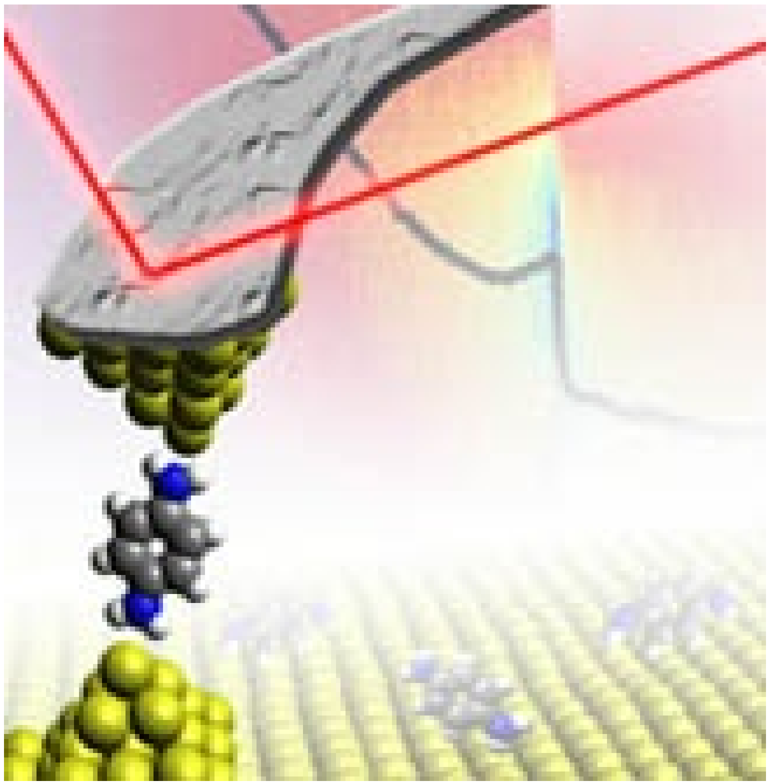


Images taken from webpage of Department Kern at MPI Stuttgart

6.2.3
Contacting single molecules

STM/AFM-based techniques

„STM breakjunctions“



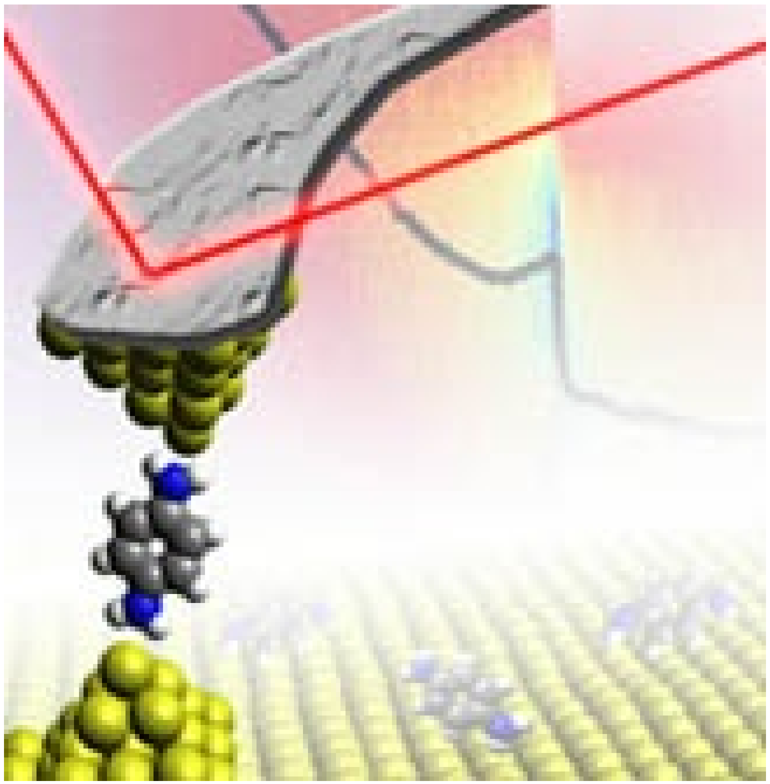
STM/AFM in liquid environment:

1. Application of diluted molecular solution
2. Indentation of tip into metal
3. Withdrawal of tip,
   formation of metal hillock
4. Recording G(z) upon approach and
   withdrawal („closing and opening curves“)
5. Eventually a molecular contact forms,
   signalled by plateaus in the G(z) traces
6. AFM gives distance information

Here: conductive AFM

Image taken from L. Venkataraman‘s web page, Univ. Columbia

„STM breakjunctions“



STM in liquid environment:

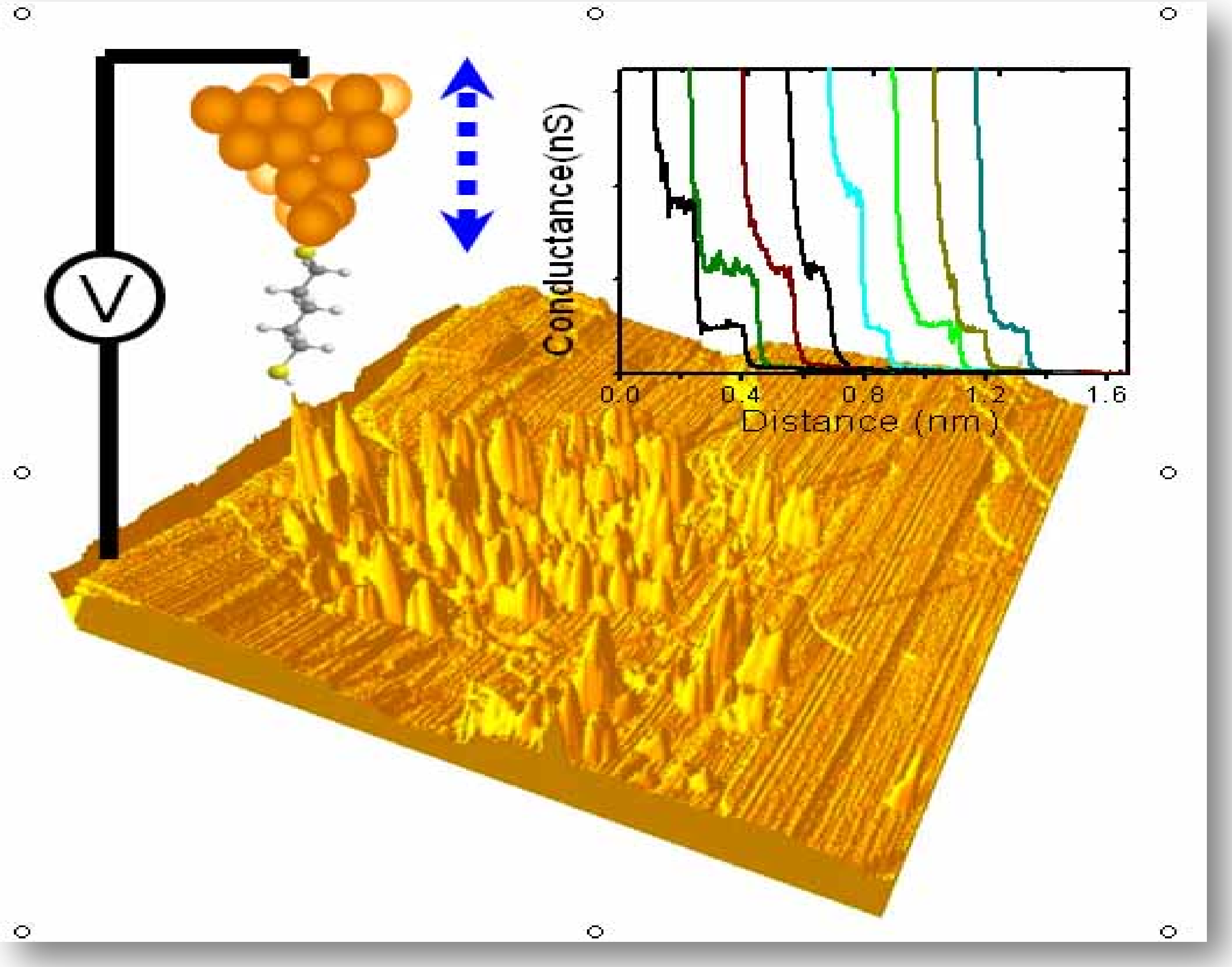
+ very fast, many (> 10^5) repetions possible -> extremely good statistics
- contacts short-lived –> no IVs possible
-> no identification of molecule/contact
- prone to contamination
- influence of solvent, counter ions and spurious potentials
- control of potential by electrochemical means

STM at low temperature in vacuum:

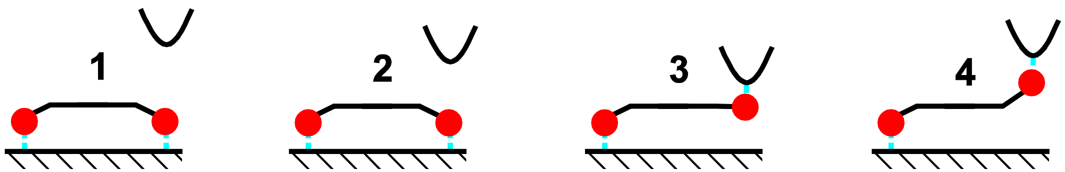
+ fast -> good statistics
+ imaging of environment
+ good contact lifetime

Image taken from L. Venkataraman‘s web page, Univ. Columbia

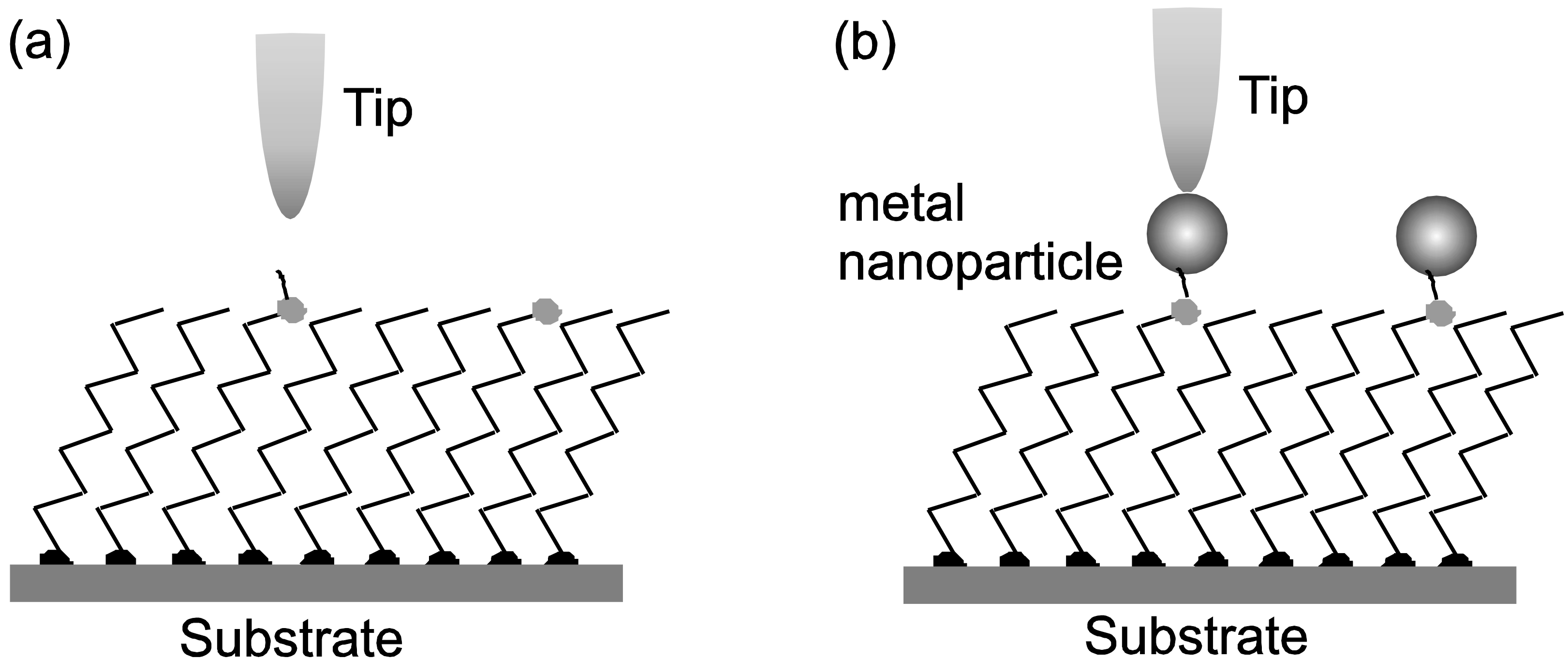
Examples of opening curves



Variations of STM/AFM-based techniques



Contacting a molecule at a functional group with a STM tip, lifting it up and peeling it off to a molecular wire



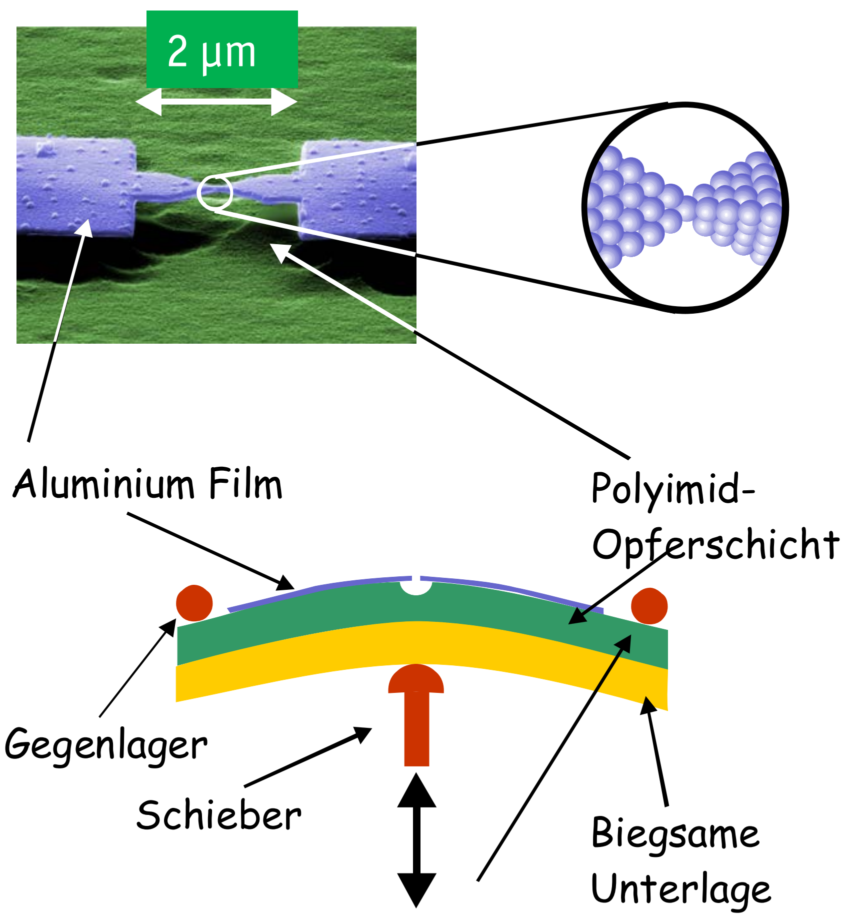
Functionalizing individual molecules in a SAM

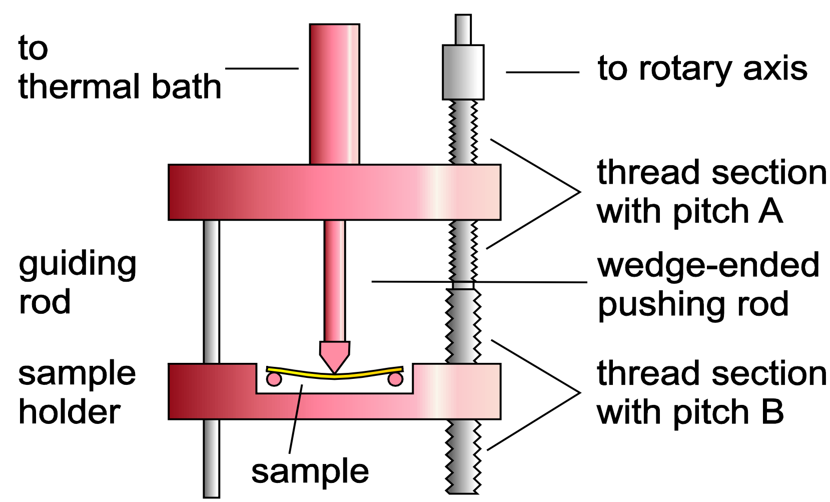
Lithographically fabricated MCBJ

Van Ruitenbeek et al, 1996

$$r \approx 10^{-4} \ldots 10^{-5}$$

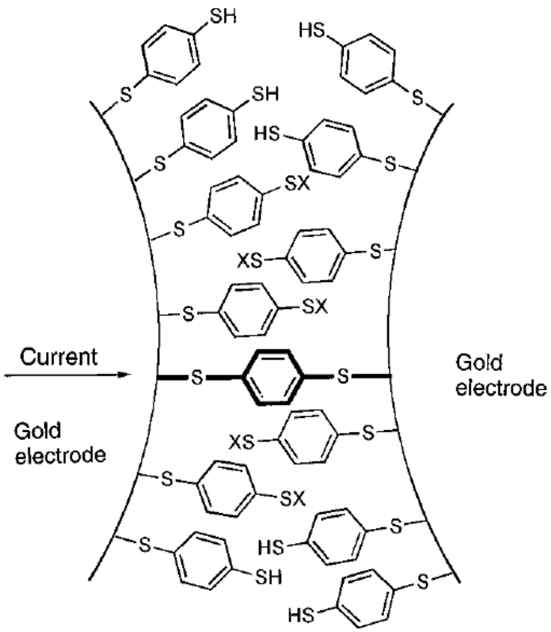
1. Application of molecular solution onto native MCBJ,
2. Evaporation of solvent
3. Repeated opening and closing to form molecular contacts

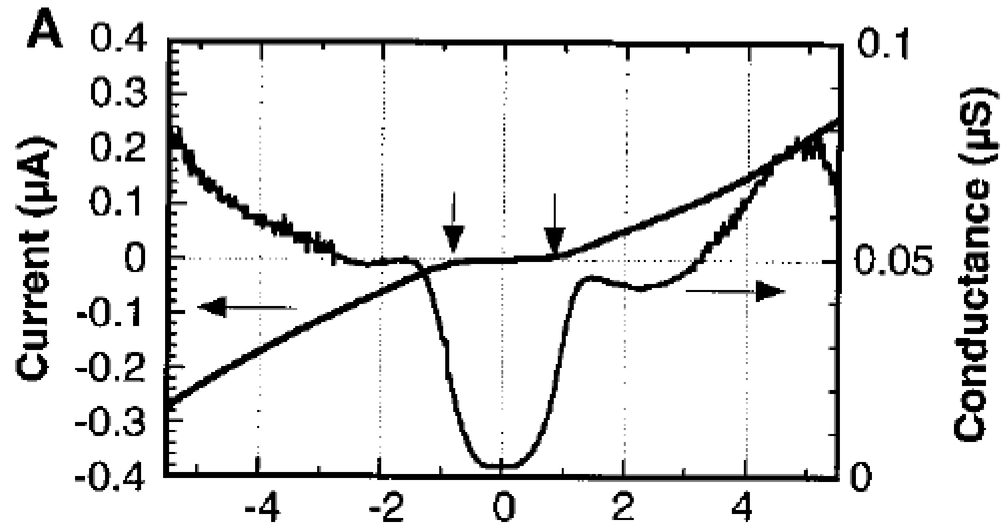


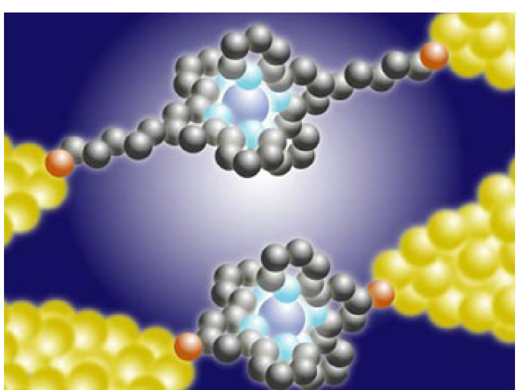


How it began: Au - benzenedithiol - Au

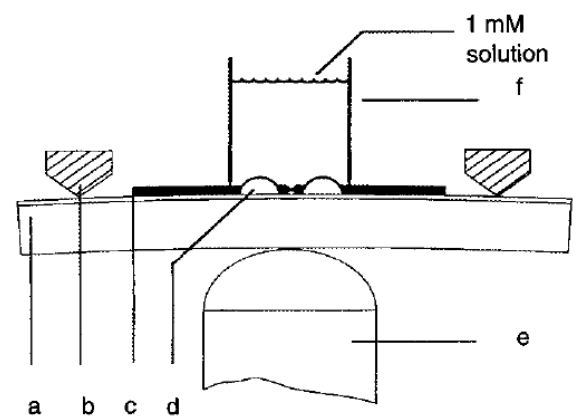
First measurement of single-molecule contacts was realized with MCBJ technique





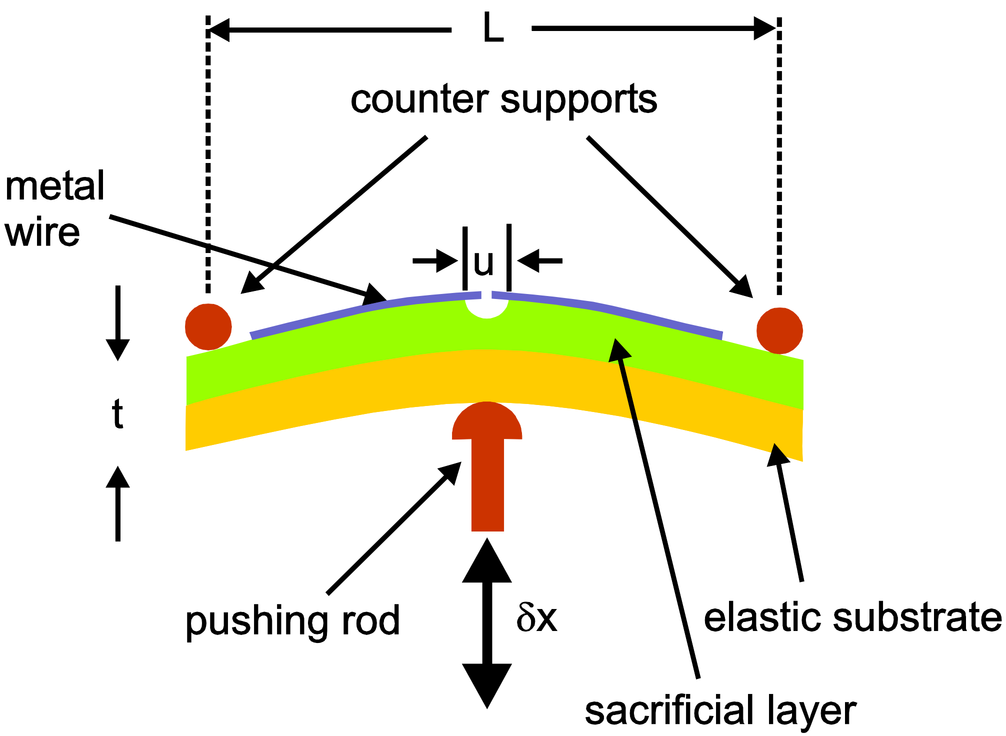


Graphic: P. McEuen, Cornell University



M. Reed et al, Science 282, 252(1997)

Pros & Cons of MCBJ

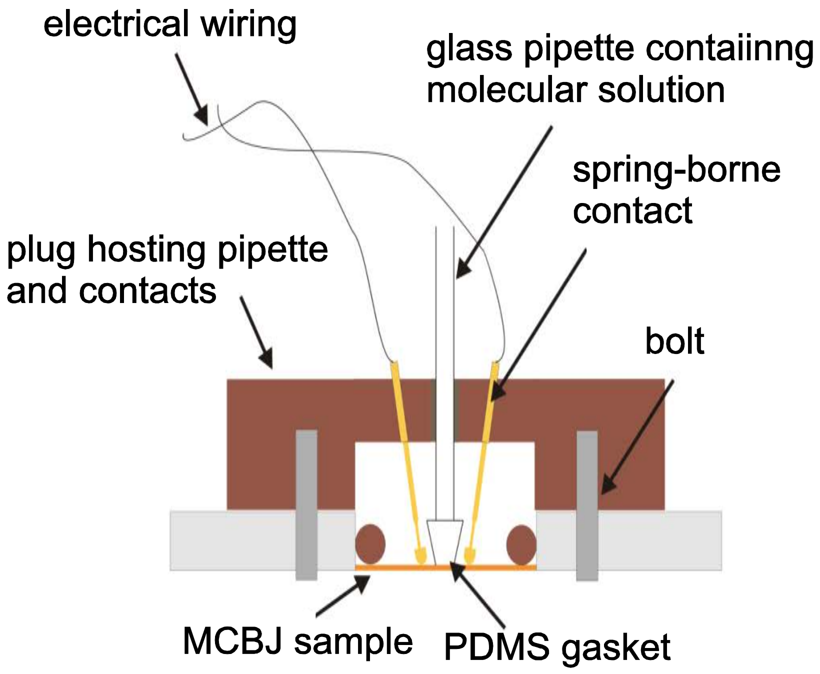


+ high stability
+ integrateble into ICs
- slow -> limited statistics
- sensitive to voltage shocks
- difficult to integrate third electrodes
- no imaging of contact geometry possible

+ „in situ“ mechanical control over conformation of junction (stretching curves)

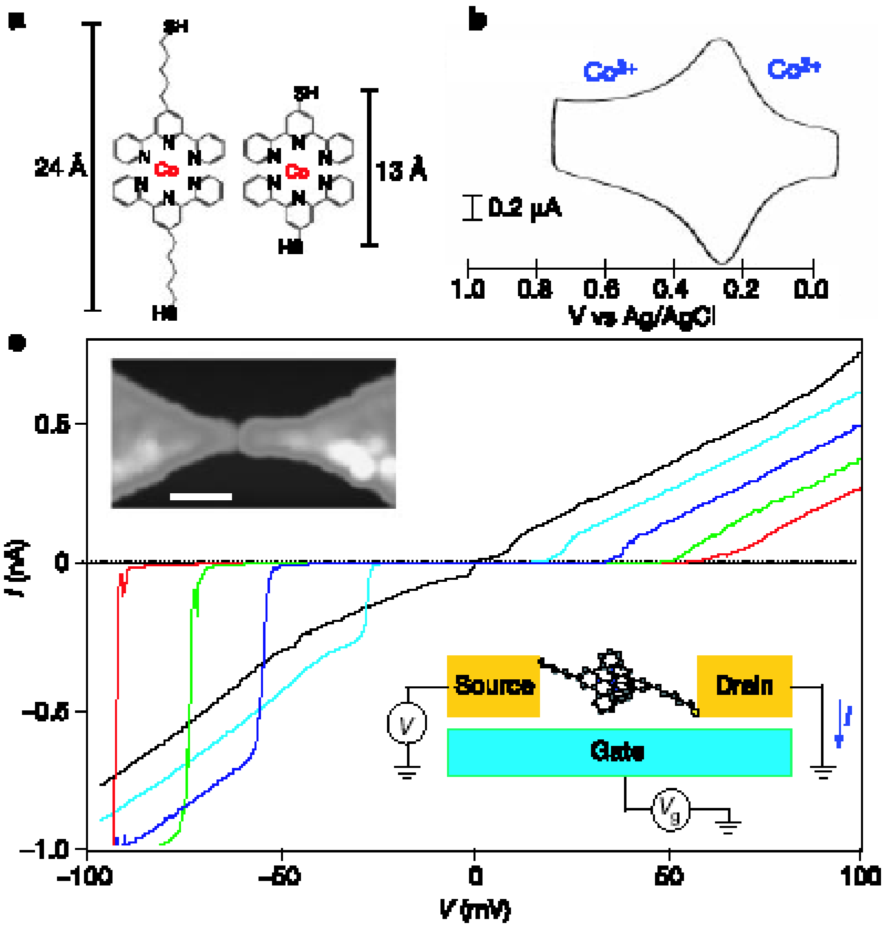
Identification of contact geometry and molecule

MCBJ in liquid environment



- Enables repeated contact formation – statistical information
- Enables natural environment for biomolecules (DNA)

Three-terminal devices using **electromigrated** electrodes



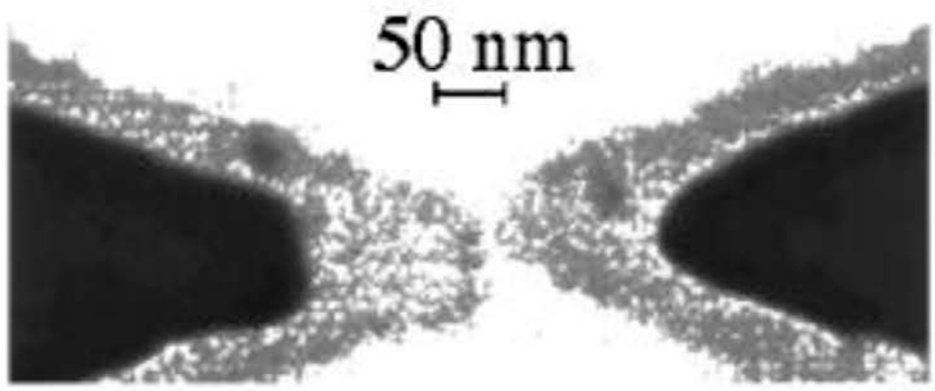
Deposition of molecular solution before or after electromigration

+ very stable contacts
+ possibility to form 3-terminal devices
- low yield
- prone to artifacts due to formation of metal particles
- control over contact geometry
- enhanced probability of multimolecule contacts

Single-molecule transistor?

J. Park et al., Nature 417 (2002) 722

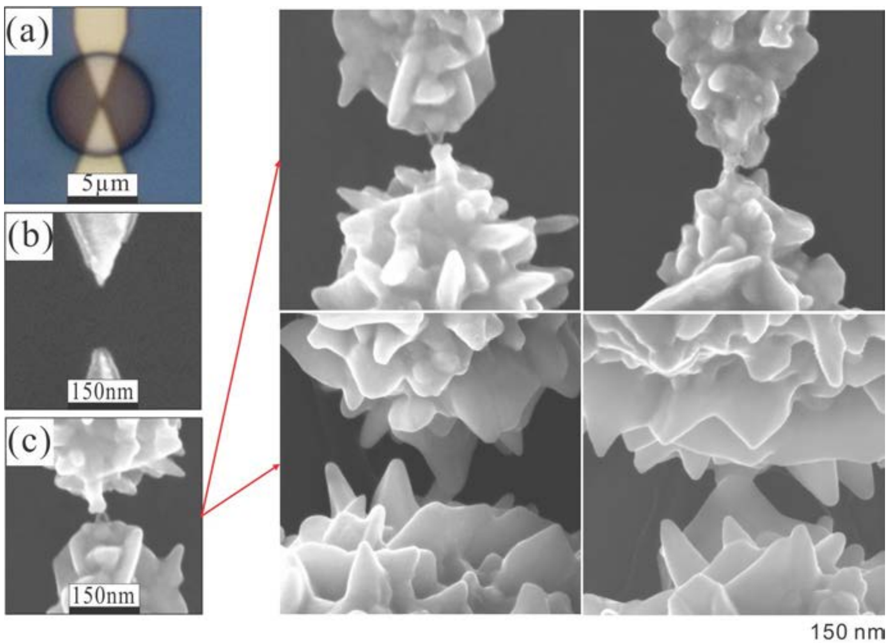
Electrochemical methods

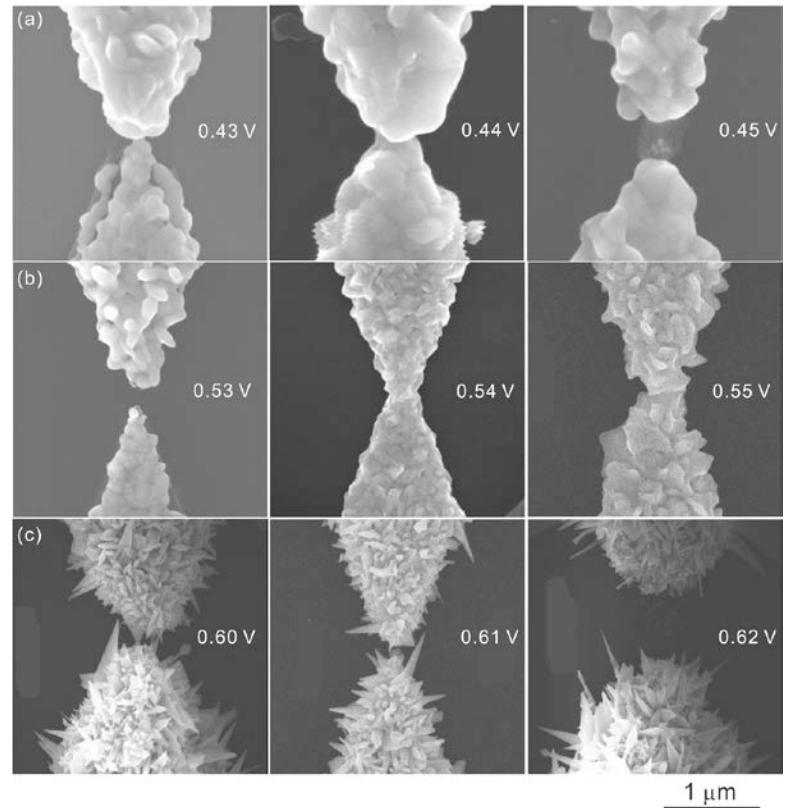


1. Definition of nanogap by e-beam lithography (width 5-20 nm)
2. Reduction of gap size by electroplating metal of choice
3. Application of molecular solution

+ very stable contacts
- low yield
- potentially disordered or dirty contacts
- no control over shapes of electrodes (might by wide and round)
--> high probability of multi-molecule contacts

Electrochemical methods





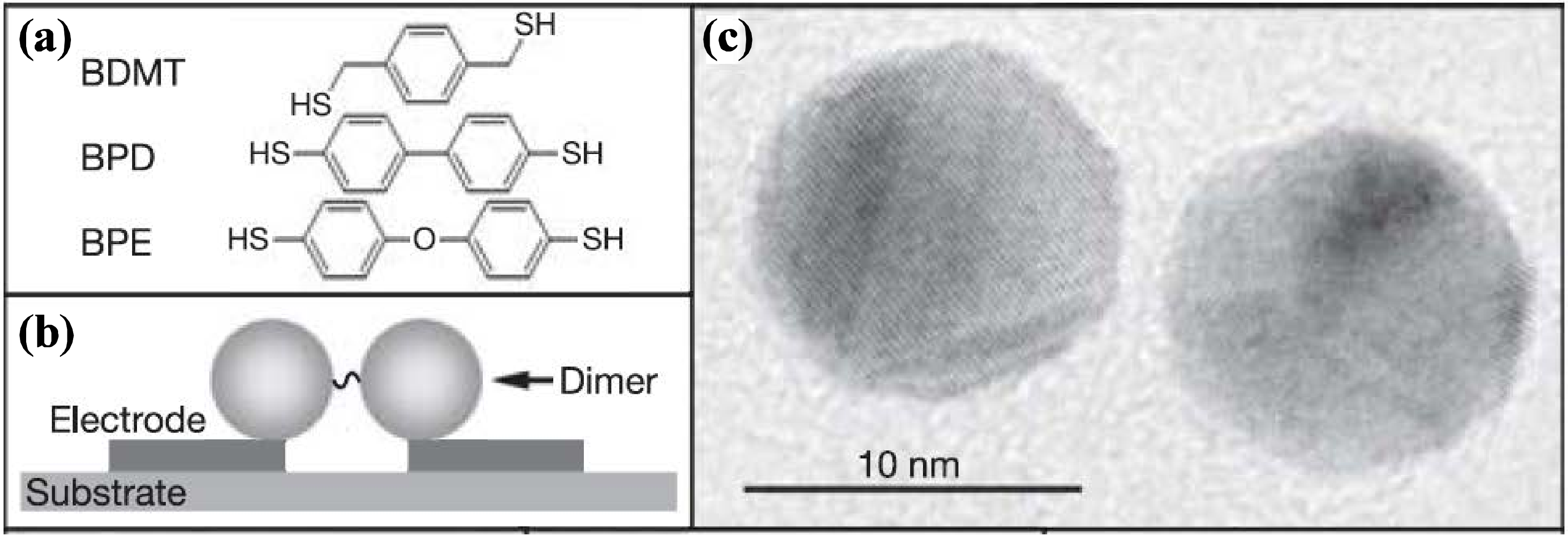
Control of shape of electroplated material by voltage

Courtesy Zhiwei Yi, Research Center Jülich

Special Techniques

Nanoparticle dumbbells

Deposition of dumbbells onto lithograhically faricated metal nanogap electrodes

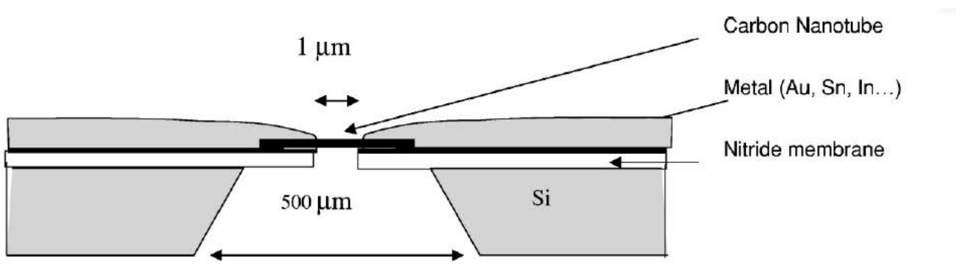


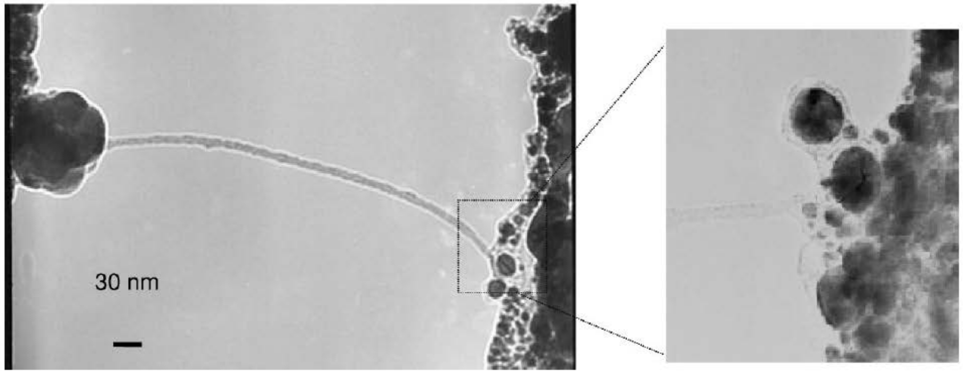
+ stable contacts
+ well-controlled metal-molecule contacts
- low yield
- involved fabrication method
+ TEM characterization possible

Dadosh et al, Nature 2005

Free-standing molecular bridges contacts on patterned membranes

Electron beam melts metal electrodes and burns support of moelcules
Molecules fall down onto prepatterned membrane

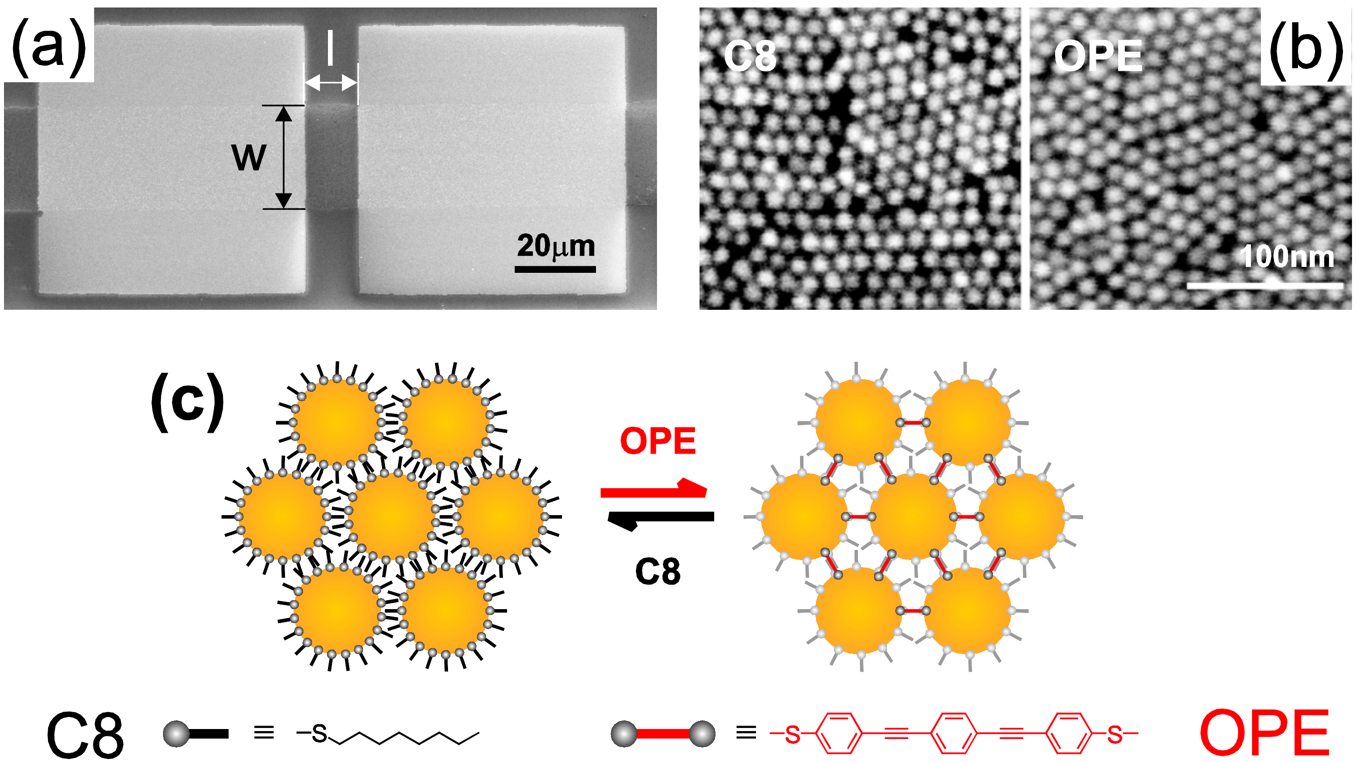




+ Stable & suspended contacts
+ Good contacts provided by soldering molecules to liquid electrodes
- potentially detremental to the molecule
- risk of metal particle fomation
+ suitable for long molecules (CNT, DNA)

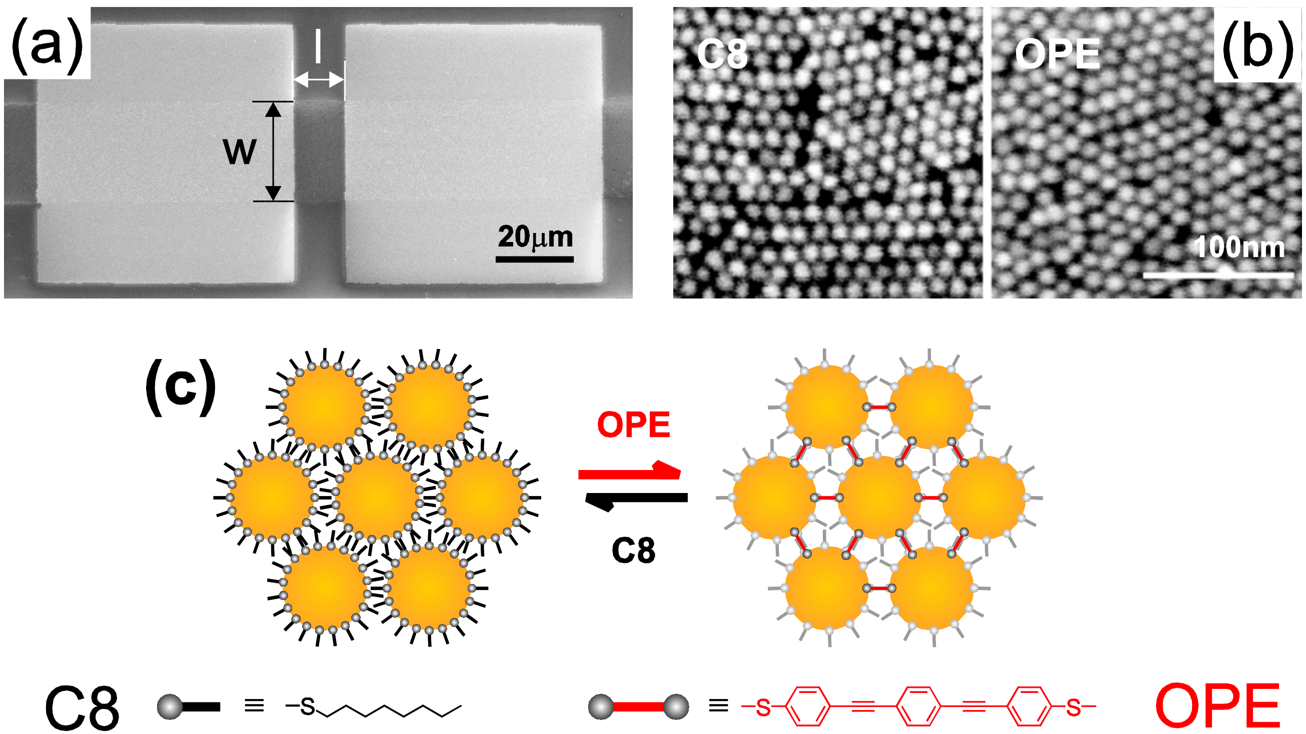
Arrays of single-atom contacts

- Definition of 2d network of Au nanoparticles (GNP) between macroscopic electrodes
- Distance between GNPs defined by alkanedithiol molecules
- Molecules to study incorporated by exchange reaction

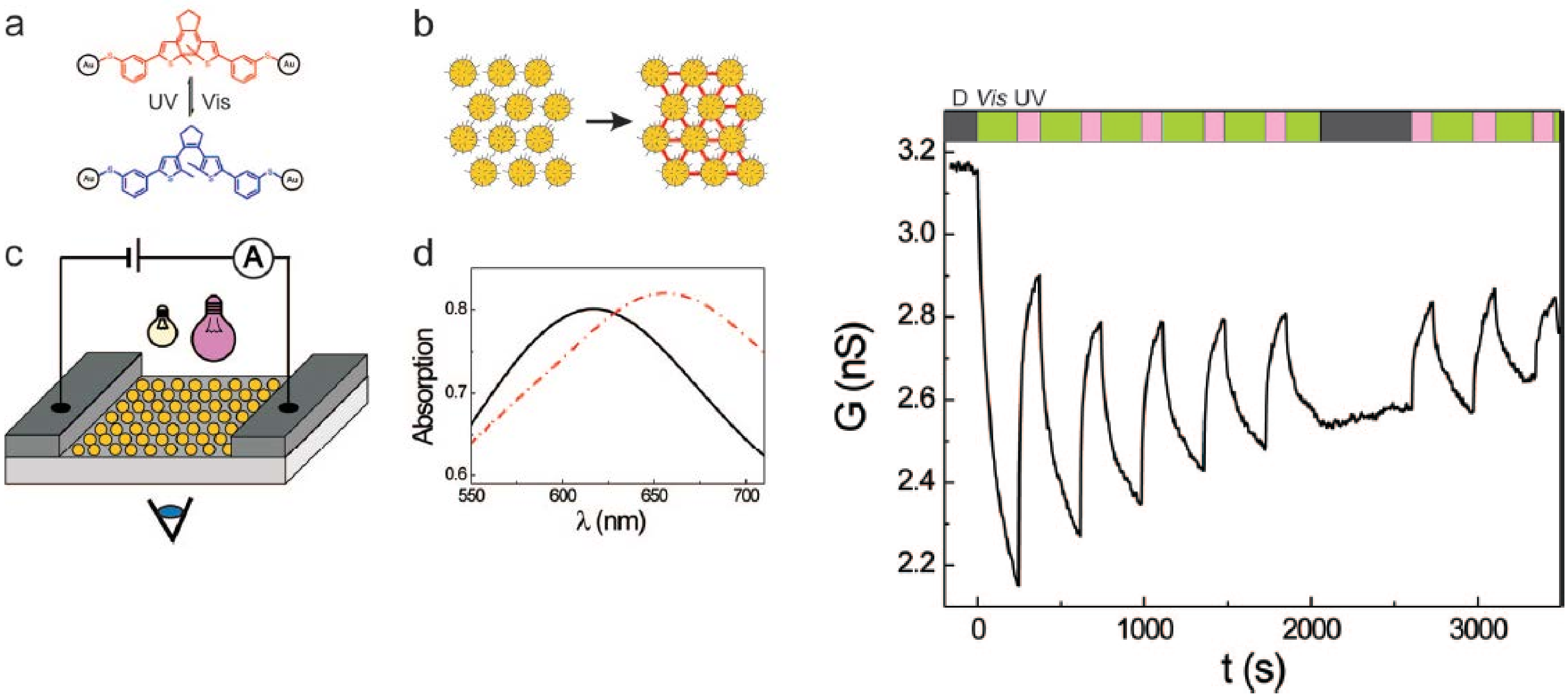


Arrays of single-molecule contacts

+ stable contacts
+ inbuilt statistics (analysis involves network/percolation theory)
+ gateable
+ suitable for analysis in external fields
- yield of exchange reaction has to be determined independently



Light-induced Conductance Switching of Molecules



Ar atmosphere, RT

S.J. van der Molen, Nano Lett. 9, 76 (2009)

6.3 Contacting Molecular Ensembles

Goal: parallel circuit of similar molecular contacts desired to

1. Enhance stability
2. Reduce resistance
3. Enhance lifetime
4. Use standard lithographic techniques
5. Study interaction effects
6. Facilitate access with external fields
7. Open the possibility of structure determination (X-rays, RHEED, LEED,.....)

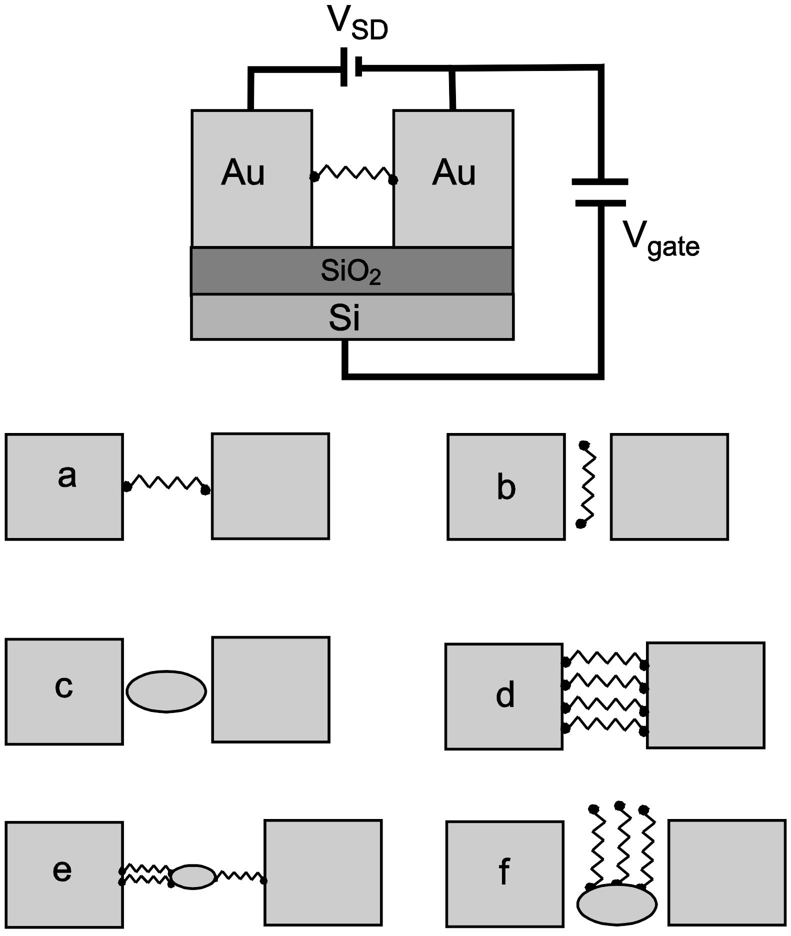
Challenge:

1. Control of contact geometry (all molecules should be in the same conformation)
2. Avoid grain formation
3. Avoid destruction of molecules when depositing second electrode
4. Determination of number of molecules

Benchmarking:

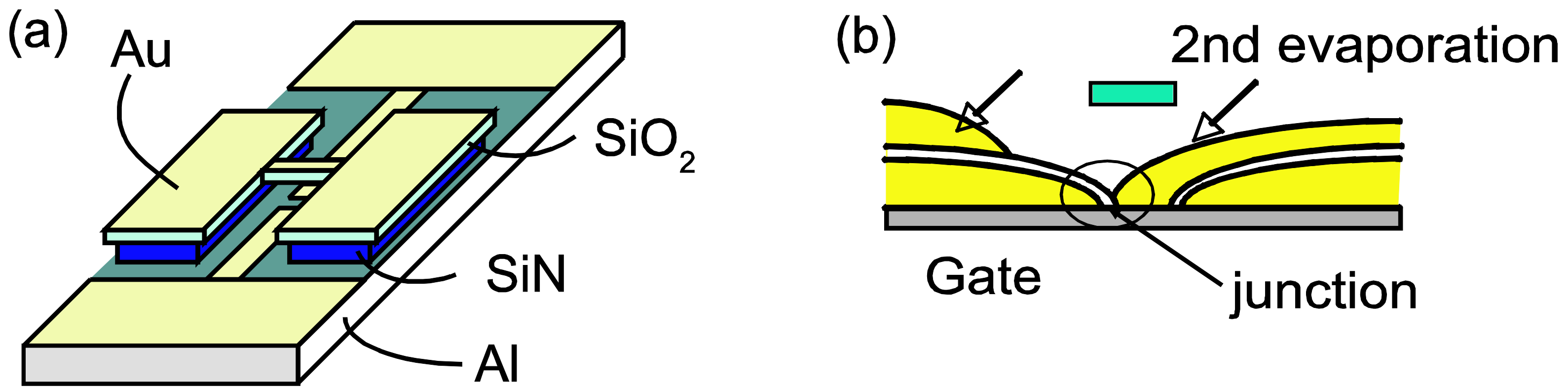
Scaling of conductance with contact size

Artifacts in molecular junctions



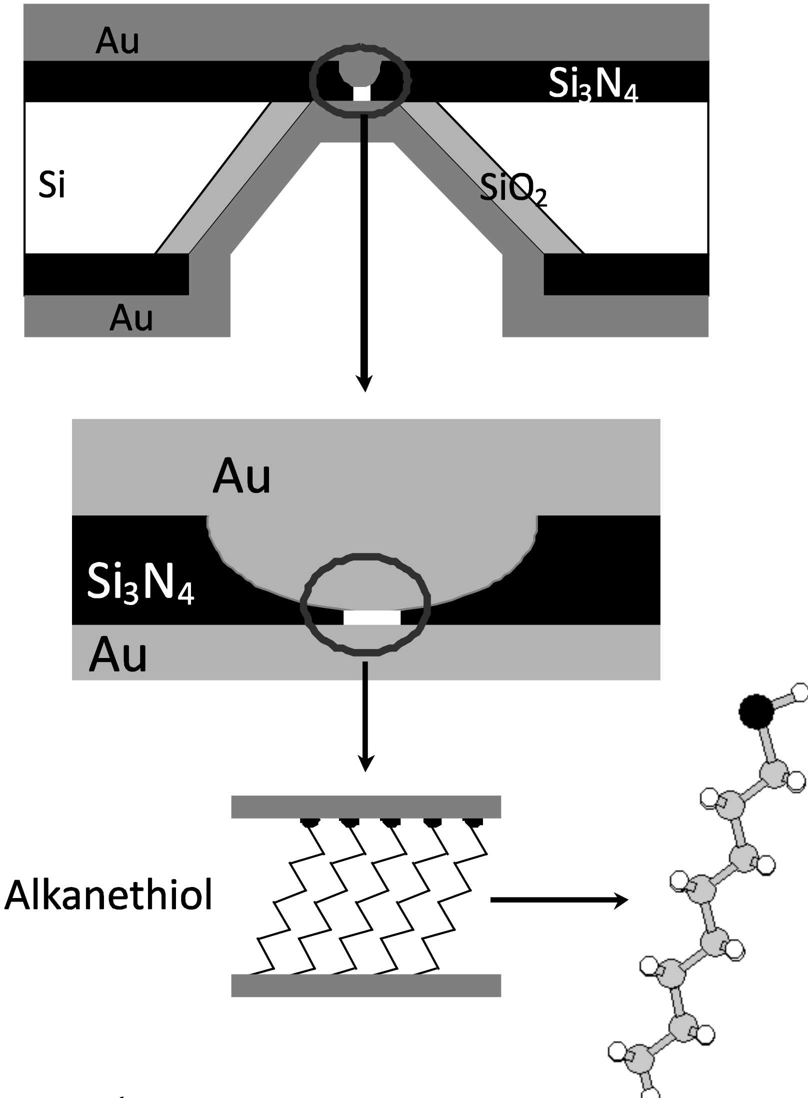
Shadow-mask technique

1. Deposition of gate electrode (Al/AlO_x)
2. Lithographic fabrication of suspended mask (SiN/SiO_2)
3. Evaporation of bottom electrode under an angle
4. Deposition of SAM
5. Evaporation of top electrode under different angle



+ stable three terminal device
- medium yield
- difficult control of contact size
- many artifacts (grain formation, destruction of SAM)

Nanopores in membranes



1. Drilling a hole into a thin membrane by e-beam lithography
2. Evaporation of first electrode
3. Deposition of SAM
4. Evaporation of 2nd electrode

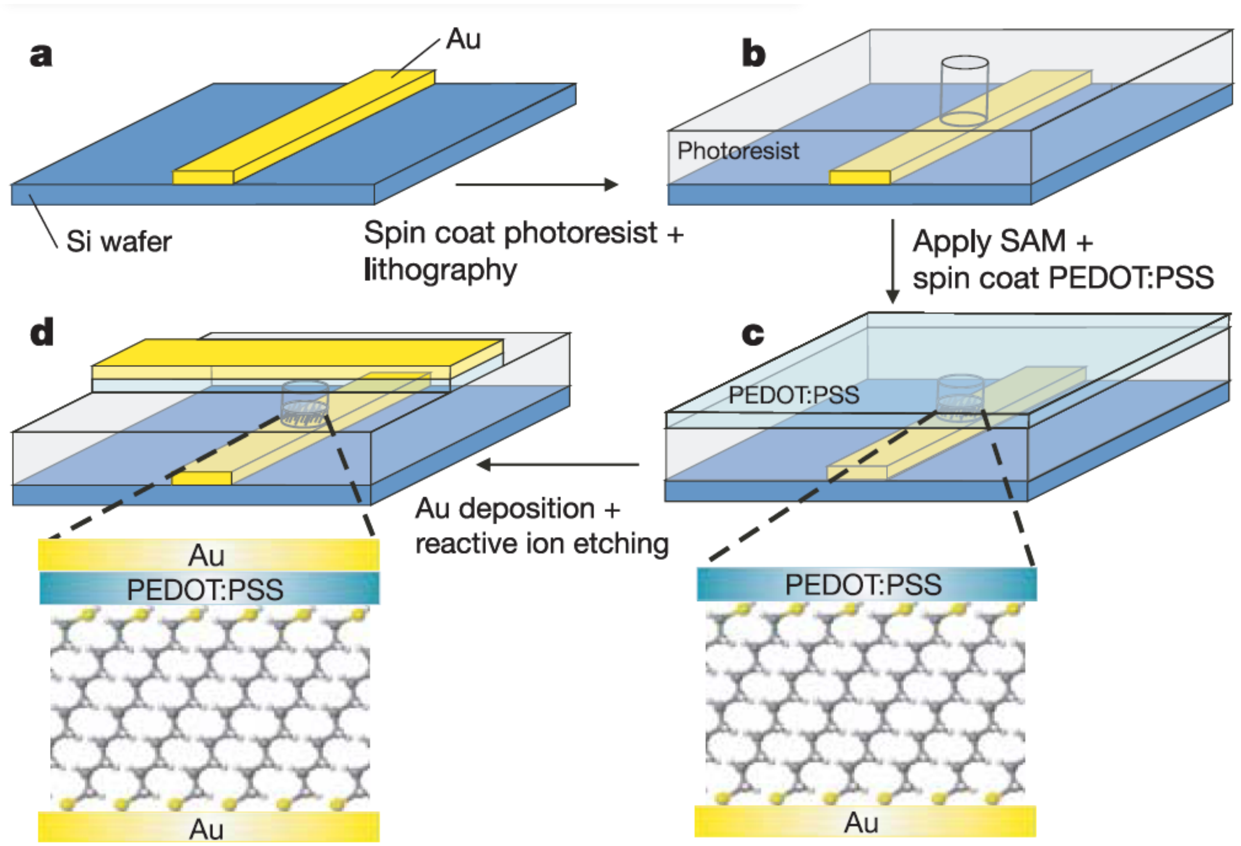
+ stable two-terminal device
- medium yield
- no gate
- difficult measure contact size
+ less artifacts than shadow mask technique
- potentially disordered SAM

Experience: evaporation of top electrode without grains possible for contact sizes up to ~ 50 nm

Wang et al, 2003

Cross-bars with organic semiconductors

Gentle deposition of top electrode by organic semiconductor interlayer (PEDOT-PSS)

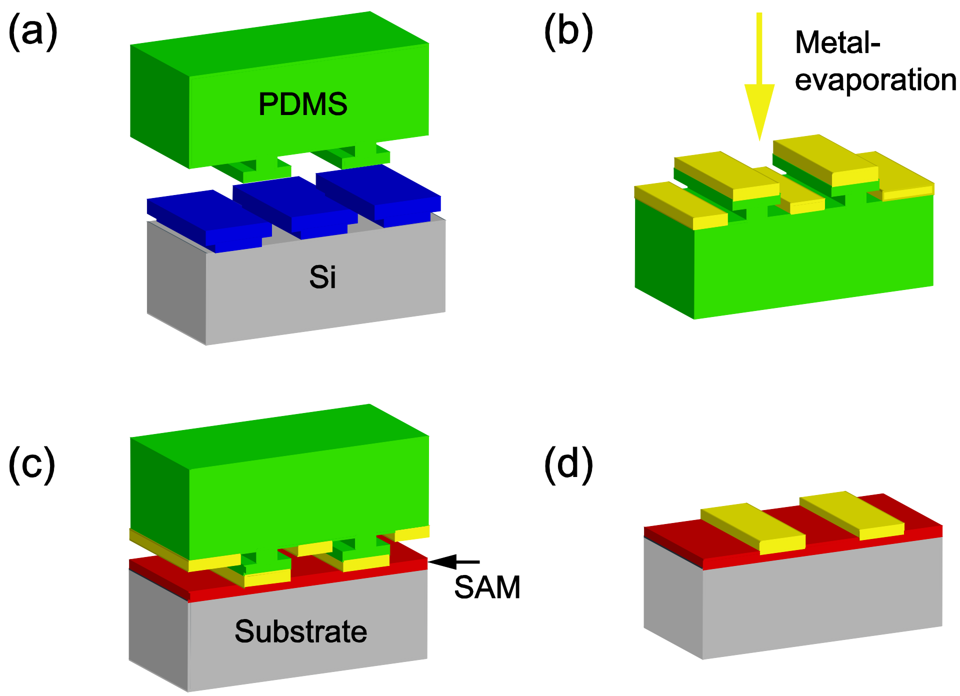


PEDOT-PSS = poly(3,4-ethylenedioxythiophene)–polystyrenesulfonic acid

- Asymmetric contacts –> more complex data analysis required

Nanotransfer lithography

Gentle deposition of top layer by printing the top electrode



(a) Fabrication of the PDMS mold by casting onto a PMMA (blue) mask on Si.
(b) The mold is coated with the metal,
(c) The mold is put in contact with the substrate (GaAs) that is covered with the SAM. The SAM serves also as adhesion layer to promote bonding.
(d) After withdrawal of the mold the metal pattern is transferred to the conducting substrate (GaAs).