Self-Assembled Monolayers of Thiols on Metals: Surface Structures, Defects and Dynamics.

Roberto C. Salvarezza

SPM and Surface Physical Chemistry Laboratory
Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas

PASI 2006, Bariloche, Argentina

Introduction

1) Molecular films in Nanoscience and Nanotechnology

Thiols, silanes and phosphonates on surfaces.

2) Self-Assembly of molecular films on metals and semiconductors.

Clean vs oxidized surfaces, gas phase vs liquid phase preparation.

Driving forces for self-assembly

3) Thiols on Au(111): the model system

i) Alkanethiols on Au(111) vs sulfur on Au(111)

i) Physisorption stage

ii) Lying down phases

iii) Transient surface structures

iv) Stable phases

v) Adsorption sites: theory vs experiments

4) Alkanethiols on Au(111) vs Alkanethiols on Ag(111) and Cu(111).

Surface reconstructions

4) Defects at SAMs.

5) SAMs stability: thermal and electrochemical stability

6) Dynamics at SAMs

7) From nanoparticles to single crystal faces: curved vs planar surfaces

8) Some examples of SAMs applications: Controlling SAM quality

Molecular electronics

Corrosion protection

SAMs as resists for soft lithography

Surface active agents

Redox processes at SAMs covered electrodes

Self-assembly is a branch of nanotechnology in which atoms, molecules, objects, devices, and systems form structures without external prodding

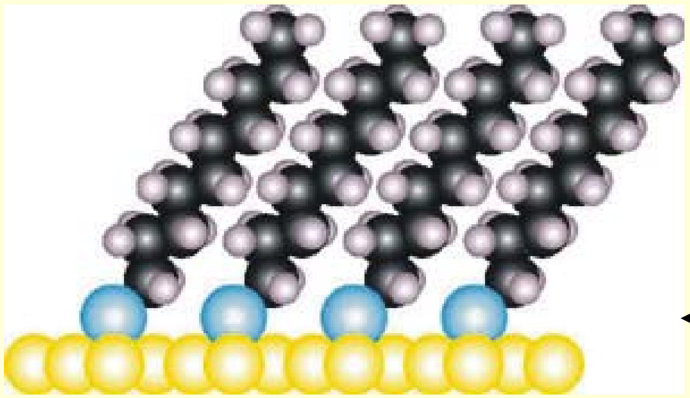
In self-assembly, the individual components contain in themselves enough information to build a template for a structure composed of multiple units.

An example is the construction of a monolayer, in which a single layer of closely-packed atoms or molecules sticks to a surface in an orderly and closely-packed fashion.

Self-assembled monolayers

Molecules

Thiols, silanes, phosphates



Terminal group

Hydrocabon chain

Reactive head (linker)

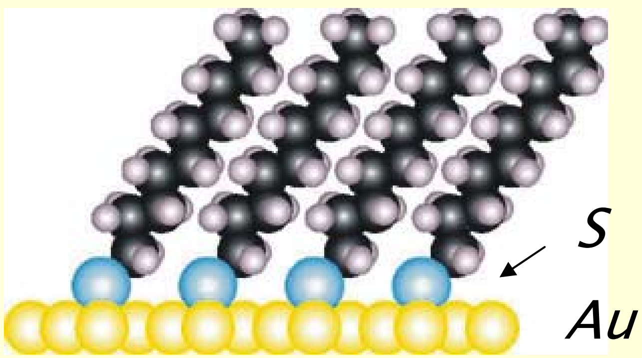
Substrates

metals, semiconductors, oxides

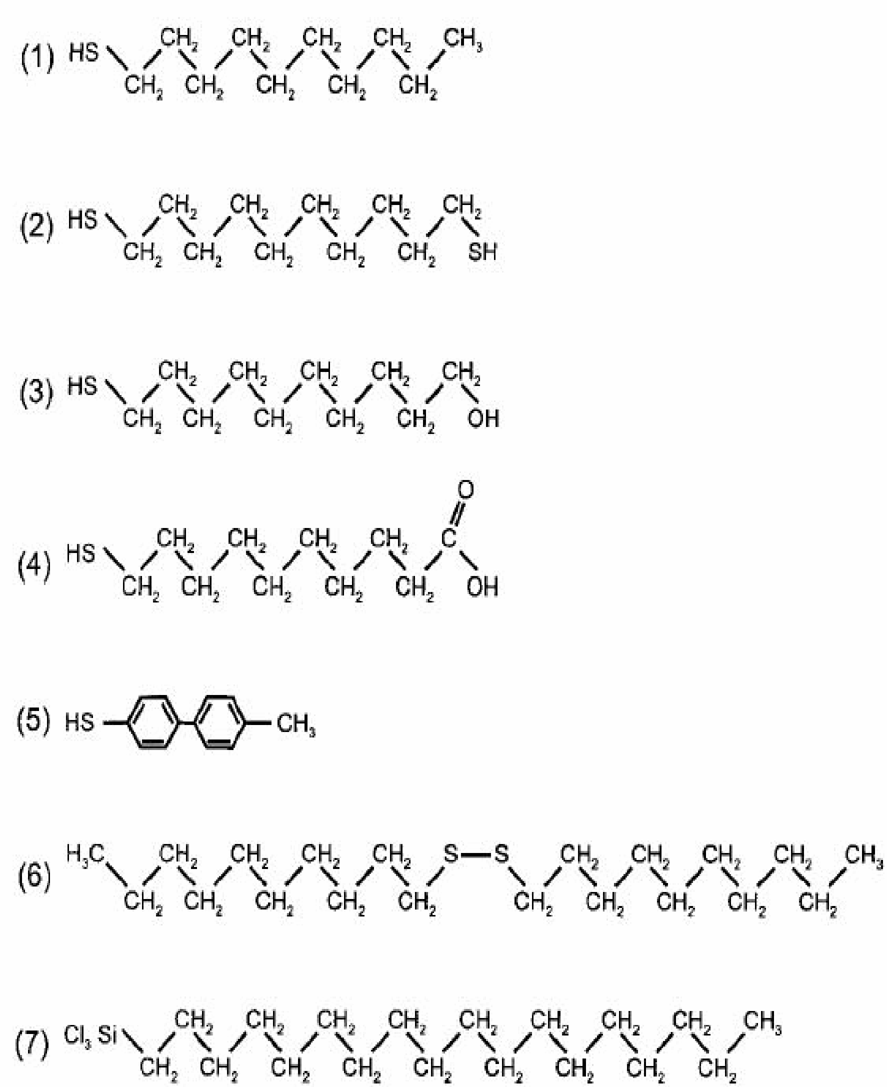
Self-assembly is driven by molecular-substrate, molecular-molecular, molecule-solvent interactions

Self-assembled alkanethiolates on metals (Au,Ag,Cu) are the most popular SAMs.

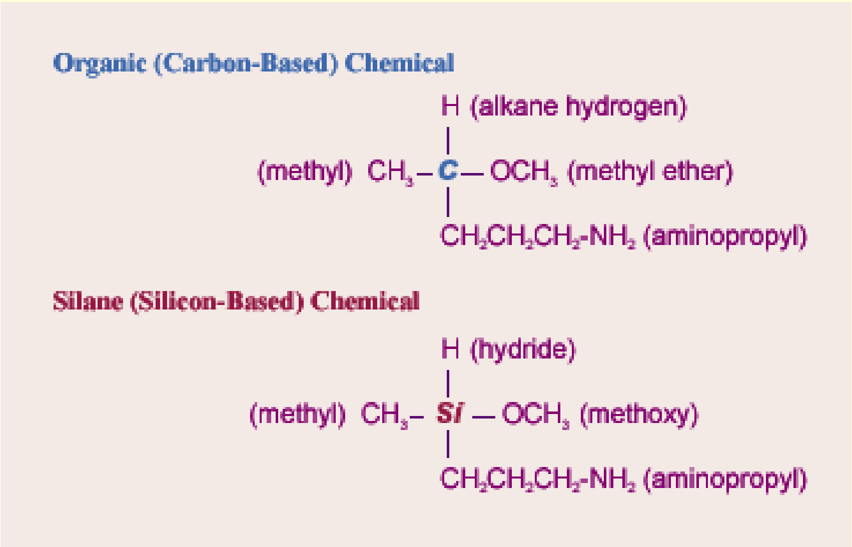
Self-assembly of alkanethiolates on metals requires oxide-free surfaces

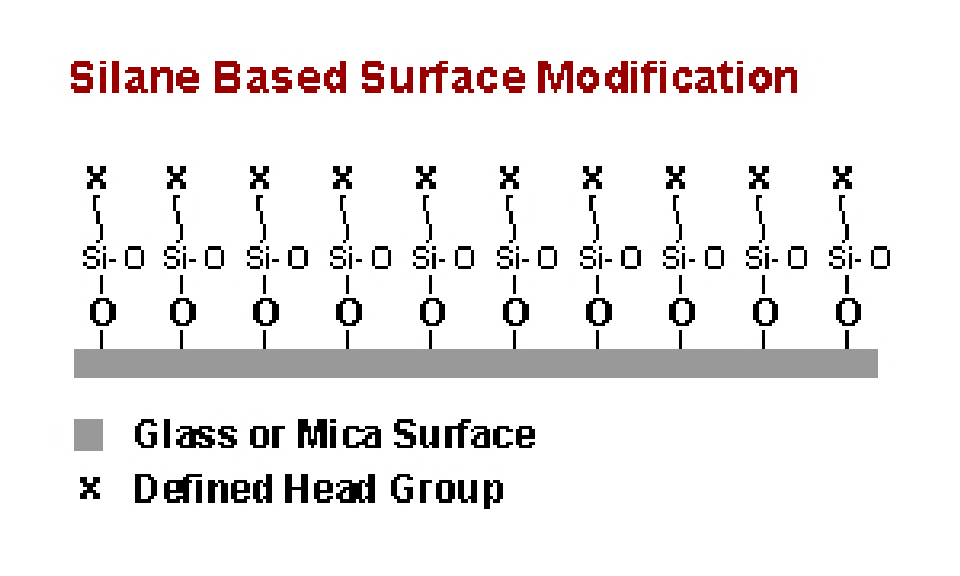


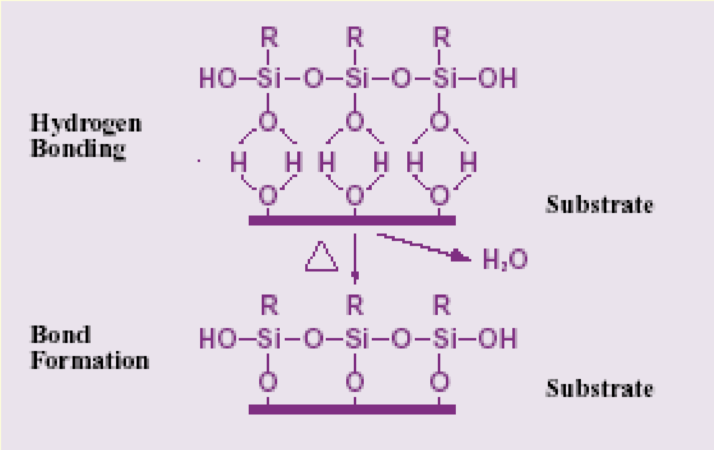
F. Schreiber / Progress in Surface Science 65 (2000) 151–256



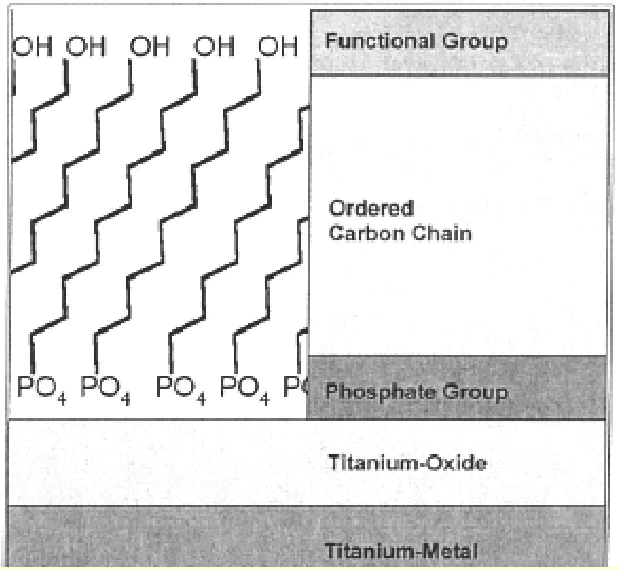
Self-assembled monolayers of silanes are an alternative for surface chemistry modification and nano/microfabrication on oxidized or hydroxilated surfaces

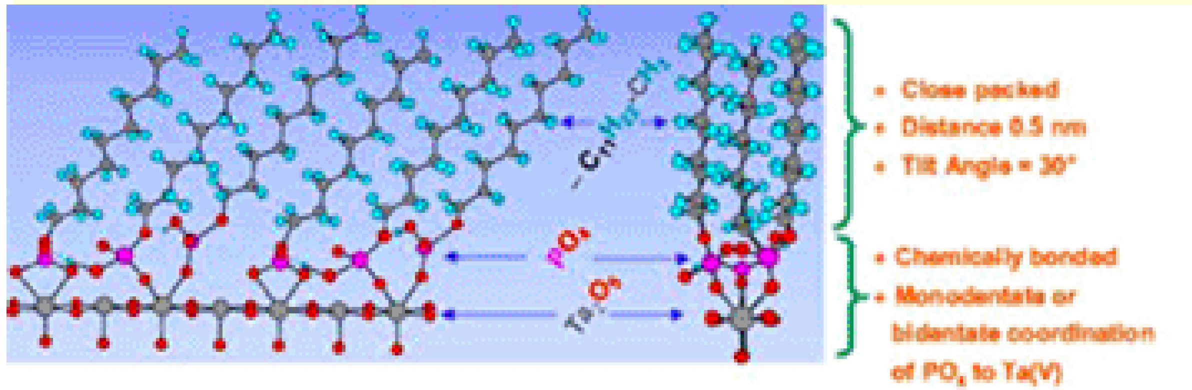




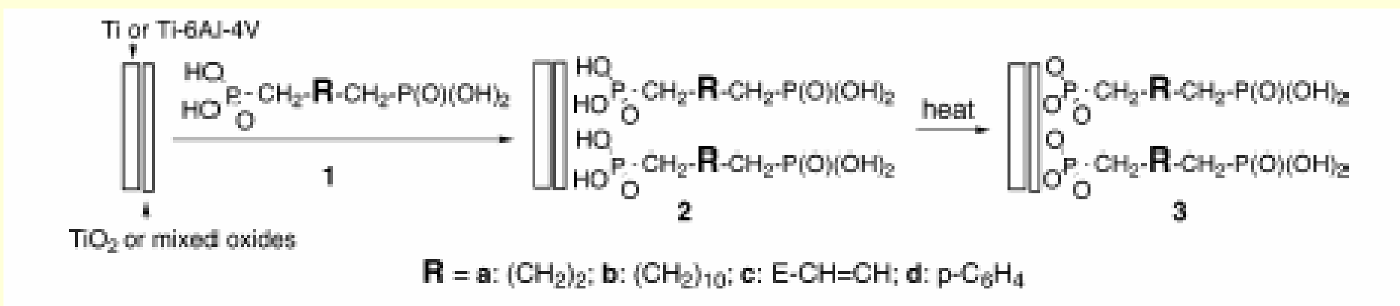


Self-assembled phosphate monolayers for surface chemistry modification of oxidized or hydroxilated surfaces

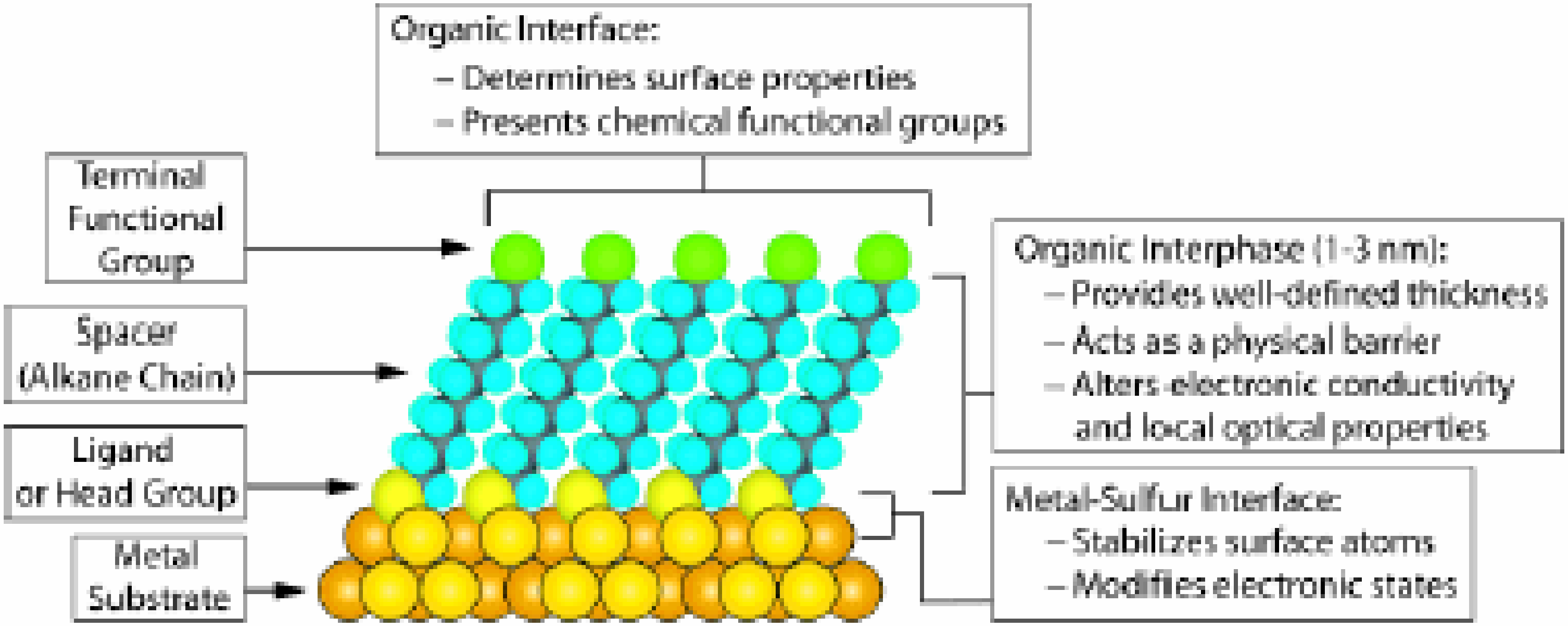




S. Tosatti, R. Michel, M. Textor, N. D. Spencer
Langmuir 2002, *18,* 3537-3548



M.l P. Danahy,,M. J. Avaltroni, K.S. Midwood,
J. E. Schwarzbauer,J. Schwartz
Langmuir 2004, *20,* 5333-5337

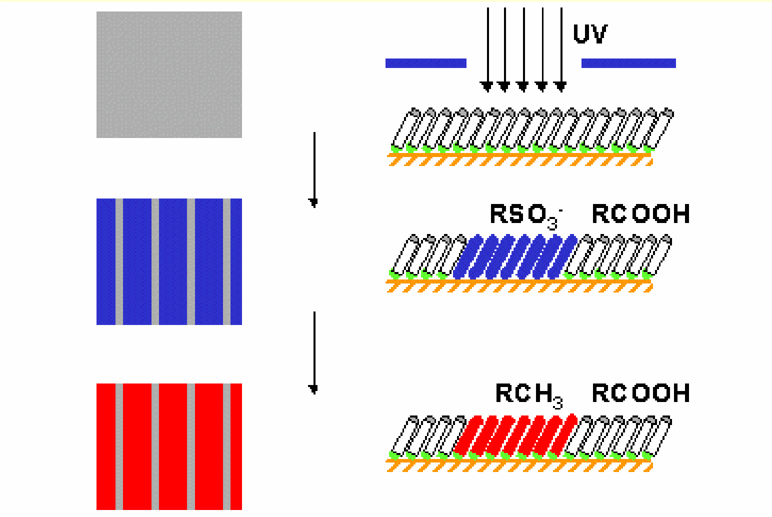


Love, Estroff, Kriebel, Nuzzo,Whitesides
Chemical Reviews, 2005, Vol. 105, No. 4
1121

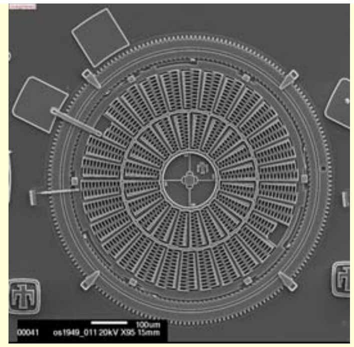
Applications of SAMs

- Protective coating
  - Corrosion and mechanical
- Control of wetting, friction and lubrication, adhesion
  - Tailoring of the headgroup
- Chemical anchors
  - Used to attach other layers of materials
- Bio-related applications
  - Immobilized proteins may be easily characterized (e.g., AFM)
- Molecular electronics
  - Studies of electron transfer/transport though the SAMs
  - Exploitation of SAMs to modify interface properties in a heterostructure

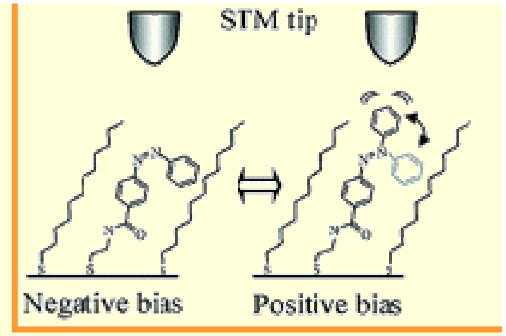
Specific applications:



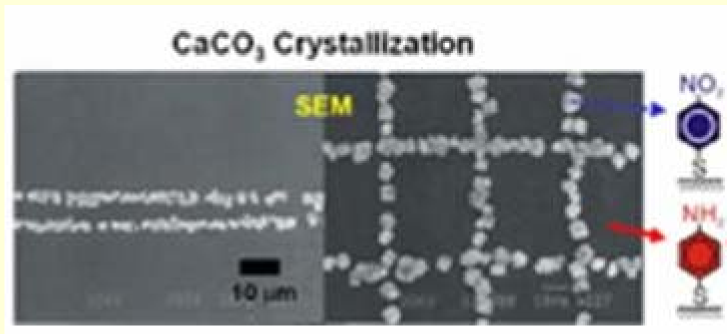
Photoresists



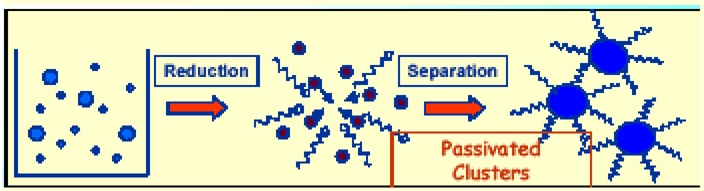
Anti-stiction layers for MEMs



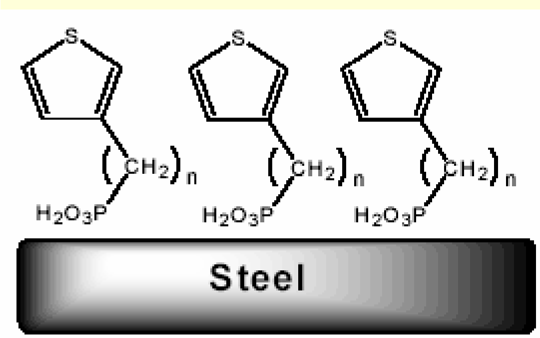
Molecular electronics



Templated crystal growth

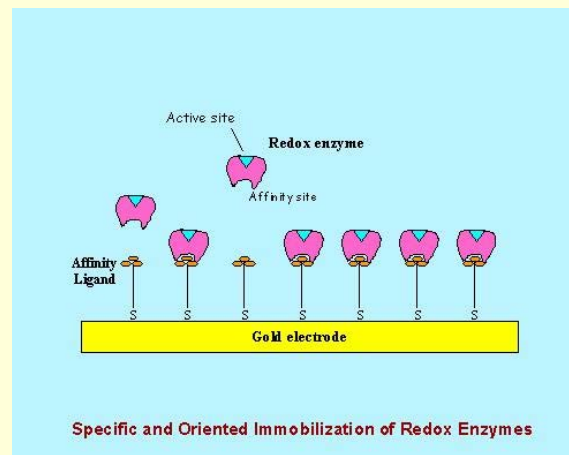


Protection of nanopaticles

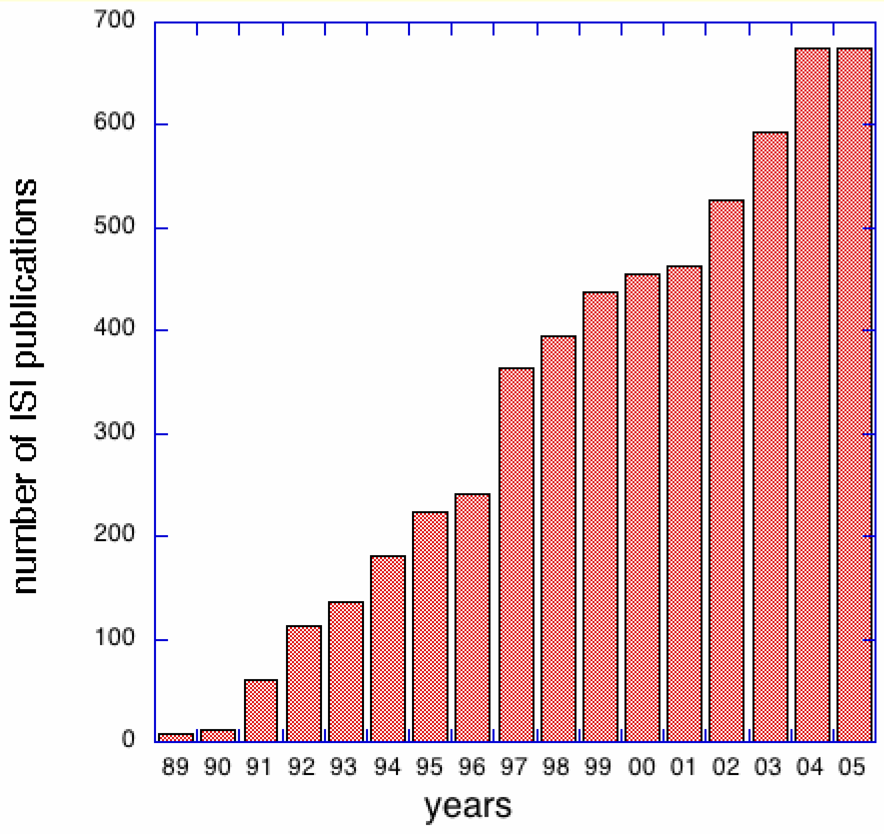


Corrosion protection

Selective enzime binding to surfaces



Number of publications related to SAMs



Techniques for studying self-assembled monolayers of alkanethiols on metal surfaces

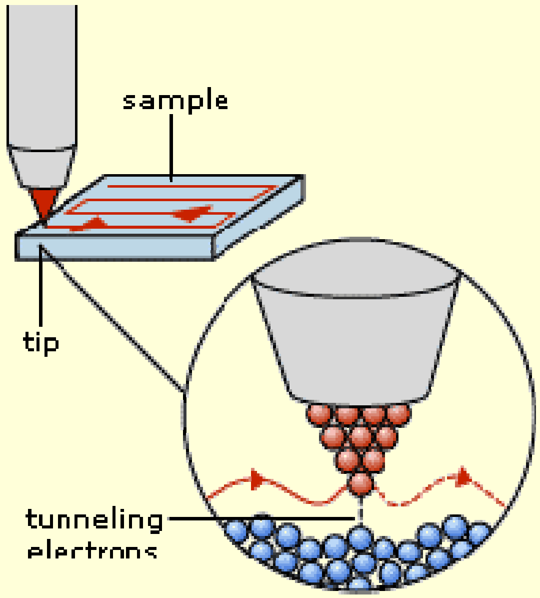
Microscopic techniques	
Scanning Tunneling Microscopy (STM)	Surface topography, surface structure (periodic and non periodic)
Atomic Force Microscopy (AFM)	Surface topography, surface structure (periodic and non periodic)
Scanning Tunneling Spectroscopy (STS)	Local electronic states, single molecule conductance

structural techniques	
Extended X-ray Absorption Fine Structure (EXAFS)	Structural parameters. Atomic distances, molecular orientation, thermal vibrational amplitudes.
Programmed Thermal Desorption (TPD)	adsorption energies and site
Low Energy Electron Diffraction (LEED)	Symmetry of the cell, atomic distances, molecular orientation, thermal vibrational amplitudes (needs periodicity)
Grazing incidence X-ray diffraction (GIXRD)	Symmetry of the cell, atomic distances, molecular orientation, thermal vibrational amplitudes (needs periodicity)
Ion Scattering Spectroscopy (ISS) Time of Flight-Direct Recoil Spectroscopy (TOF-DR)	surface structure, composition, H detection

X-ray photoelectron diffraction (XPD or phD)	Structural parameters
Infrared spectroscopy (IR) Infrared Reflection-Absorption Spectroscopy (IRAS)	specific chemical groups, adsorption site, molecular tilt
Surface Plasmon Enhanced Raman Spectroscopy (PSPR) (SERS?)	adsorbate vibration, surface phonons, molecular tilt
Low Energy Atom Diffraction (LEAD)	Structure
X Ray Standing Waves	Distance of the bonding, adsorption site

Electronic techniques	
Auger Electron Spectroscopy (AES)	Surface elemental composition, growth mode, coverage
X-ray photoemission spectroscopy (XPS)	elemental composition, chemical state, impurities
Ultraviolet photoemission spectroscopy (UPS)	valence band, density of occupied states, bonding nature, band dispertion
X-ray absorption near edge spectroscopy (XANES)	Conduction band, density of empty electronic states, molecular orientation, bonding nature
High Resolution Electron Energy Loss Spectroscopy (HREELS)	adsorbate vibrations, phonons, adsorption sites

Scanning Tunneling Microscopy
(invented in 1981)



Gerd Binnig y Heinrich Rohrer,
IBM Research Laboratory, Zurich,
Nobel Prize in Physics 1986

Topographic (real space) images
Spectroscopic (electronic structure, density of states) images

Atomic resolution, several orders of magnitude better than the best electron microscope

Quantum mechanical tunnel-effect of electron

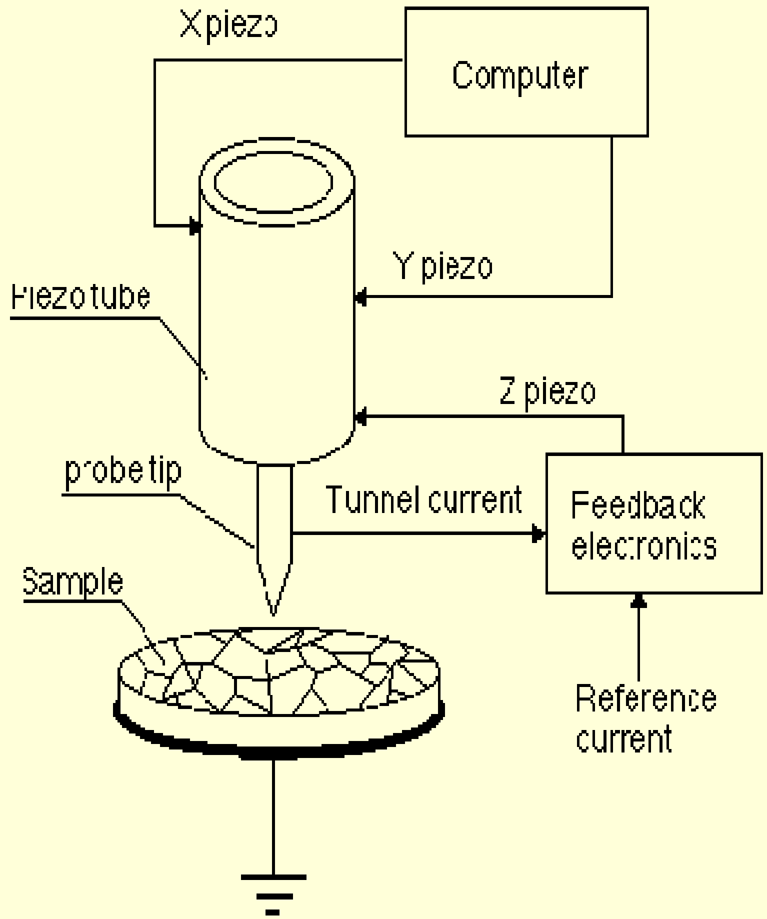
In-situ: capable of localized, non-destructive measurements or modifications material science, physics, semiconductor science, metallurgy, electrochemistry

Scanning Probe Microscopes (SPM): designed based on the scanning technology of STM

Experimental methods

Basic Set-up

- the *sample* you want to study
- a sharp *tip* mounted on a piezoelectric crystal tube to be placed in very close proximity to the sample
- a mechanism to control the location of the tip in the x-y plane parallel to the sample surface
- a *feedback* loop to control the height of the tip above the sample (the z-axis)

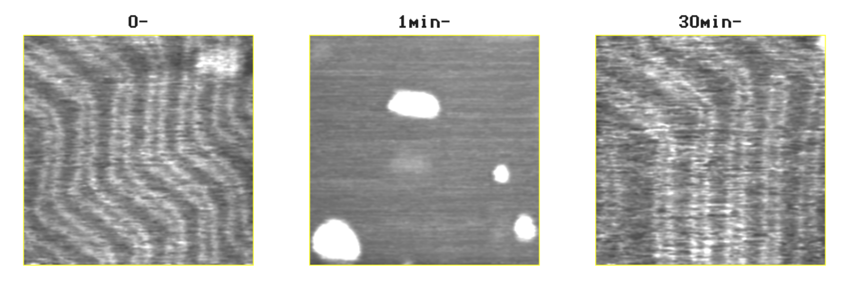


STM

conductors or semiconductors

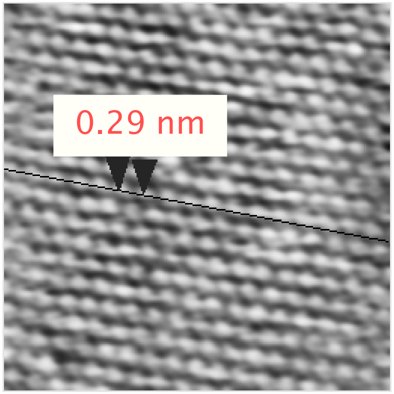
$I \propto Ve^{-ks}$

I tunneling current
V bias voltage
S tip-sample distance
k local barrier heigth
STM operates in UHV, air, liquids

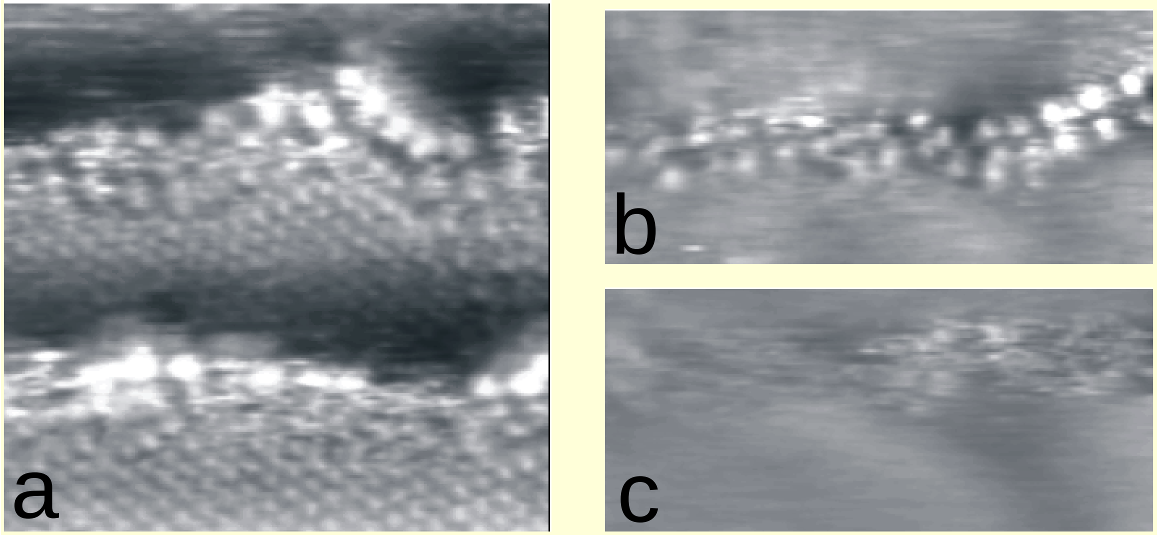


22x√3 (1x1) 22x√3

Atomic and molecular resolution, real time
Imaging of reactions



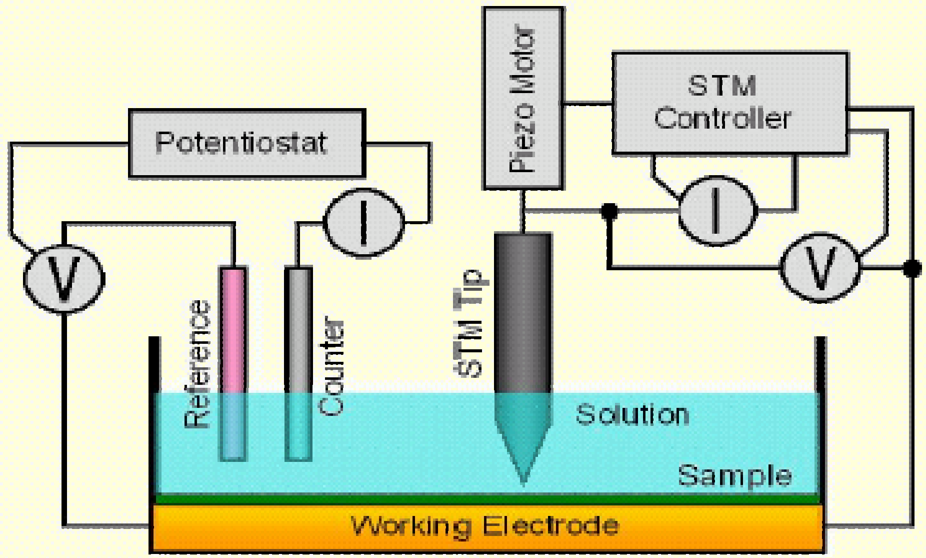
Au(111)



S electrodesorption from Au(111) 0.1 M NaOH

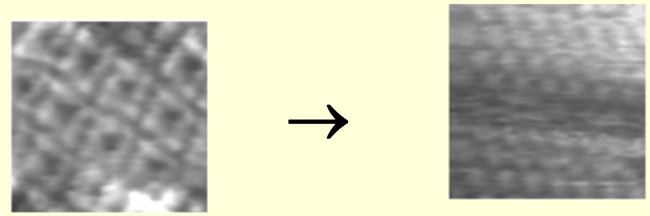
G. Andreasen, C. Vericat, M.E. Vela and R.C. Salvarezza Journal of Chemical Physics, 111, 9457-9460 (1999).

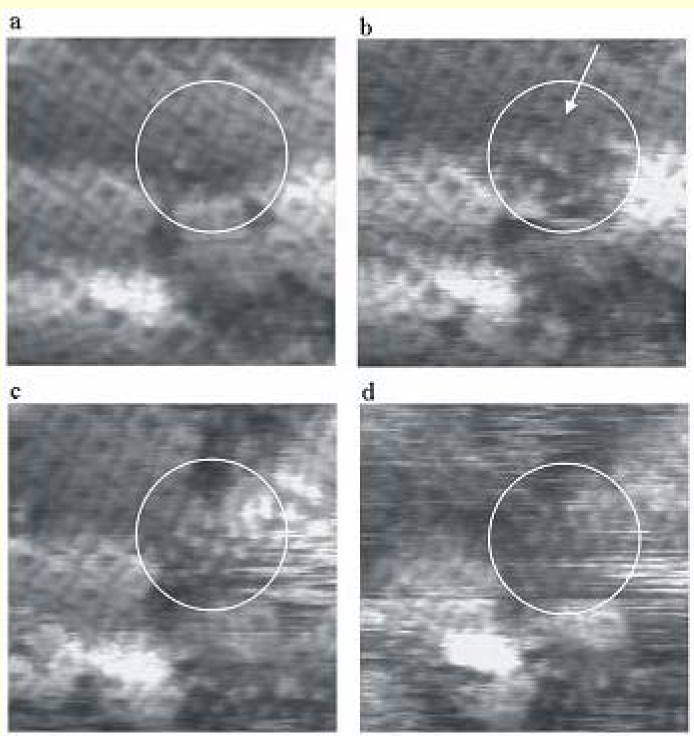
ECSTM

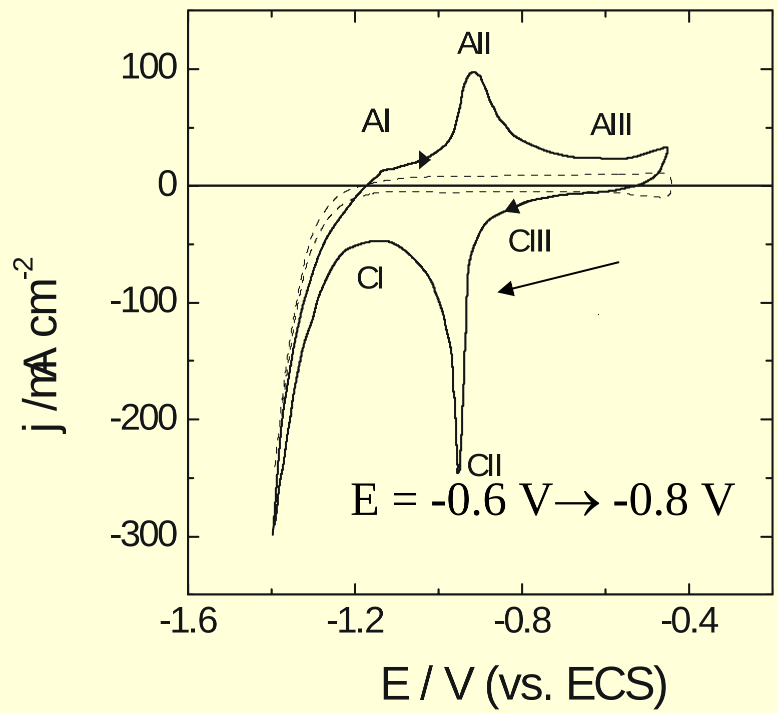


Jingpeng Wang, University of Guelph

$S_n \rightarrow \sqrt{3}x\sqrt{3}$ R30°

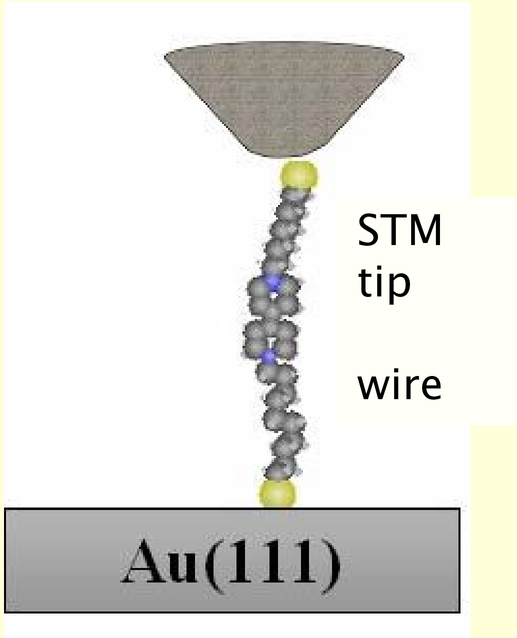






G. Andreasen, C. Vericat,M.E. Vela,R.C. Salvarezza, J. Chem. Phys. ***111,*** *9457 (1999).*

Scanning Tunneling Spectroscopy (STS)



Single molecule conductance

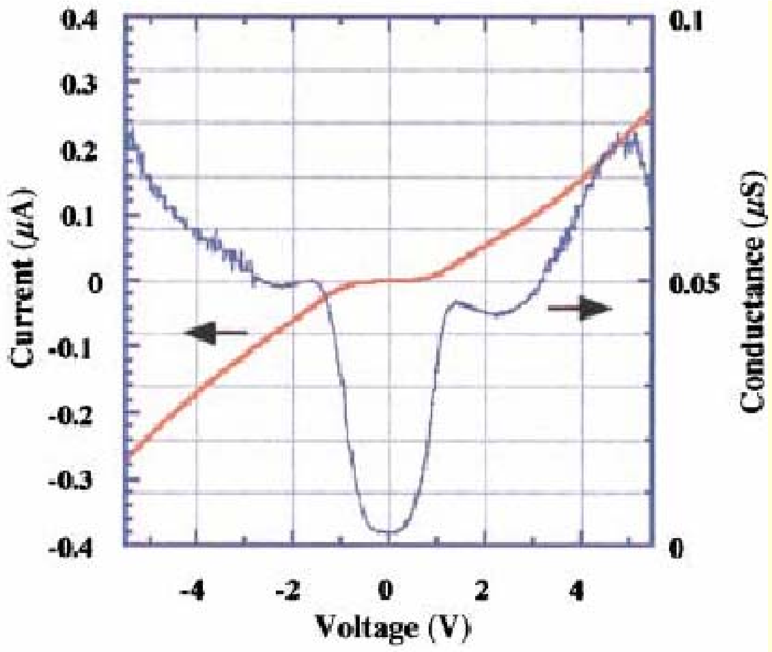
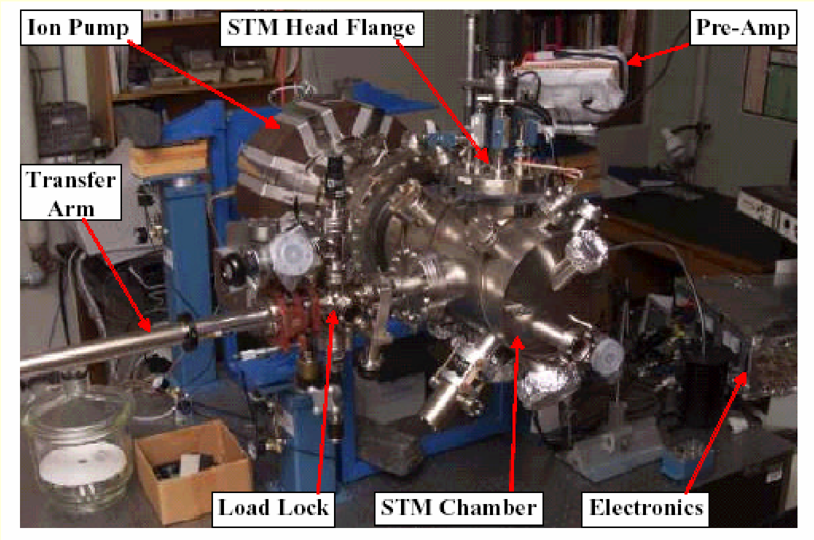
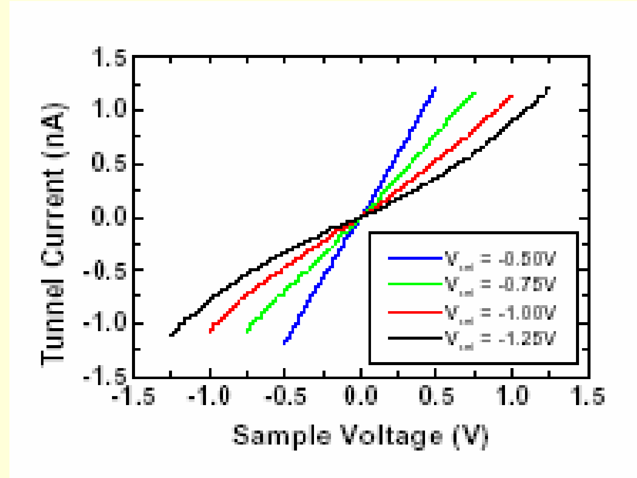


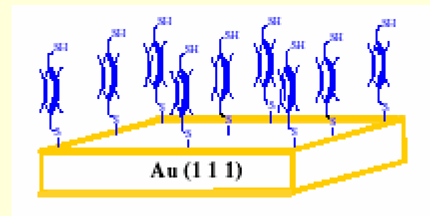
Figure 11. The I-V (red) and G-V (blue) characteristics of a single molecule.

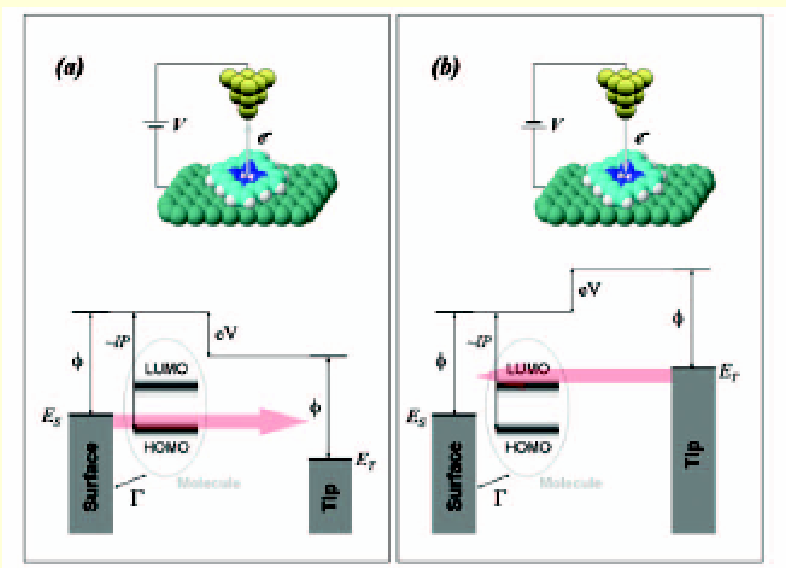
MRS BULLETIN/FEBRUARY 2001

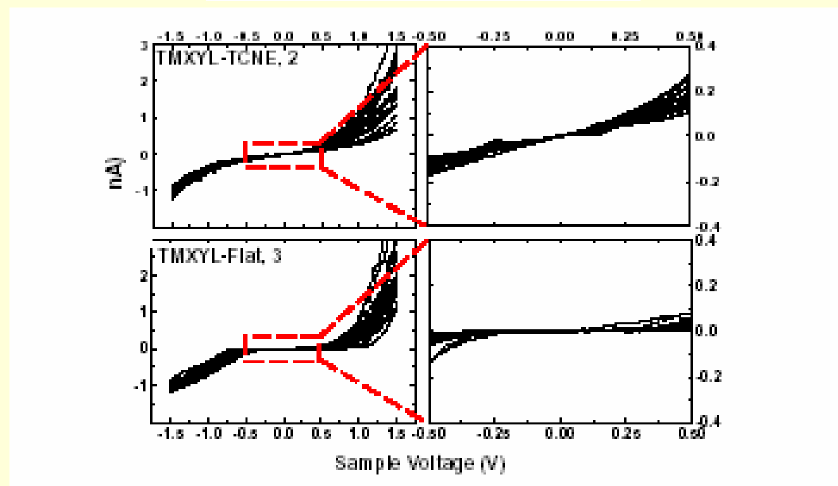
Spectroscopy (STS):
By varying the potential difference between tip and sample, one can measure I(V) spectra as well as the differential conductance dI/dV(V). In a very simple but realistic model, the differential conductance reflects directly the local electronic density of states (LDOS).









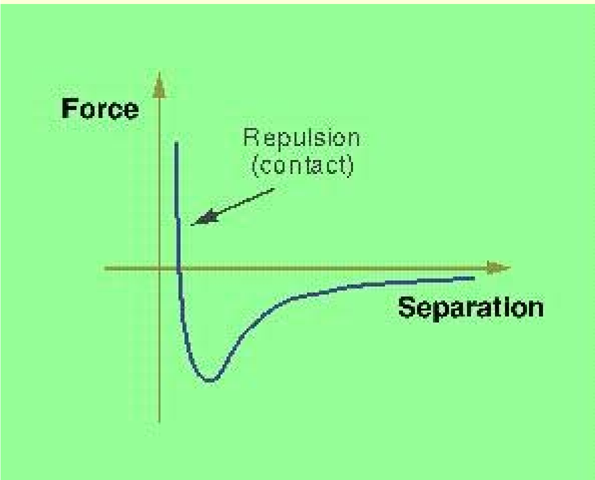


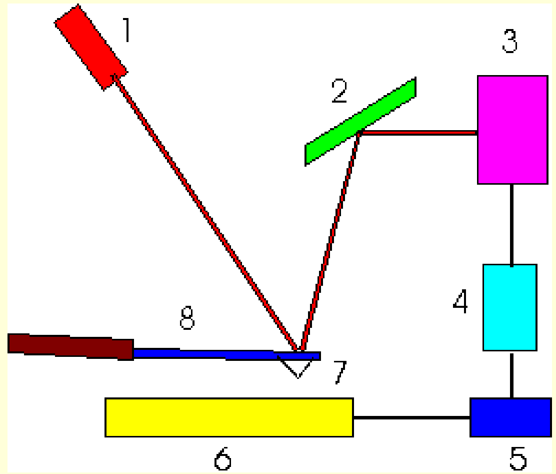
Reifenberger et al, Pardue University

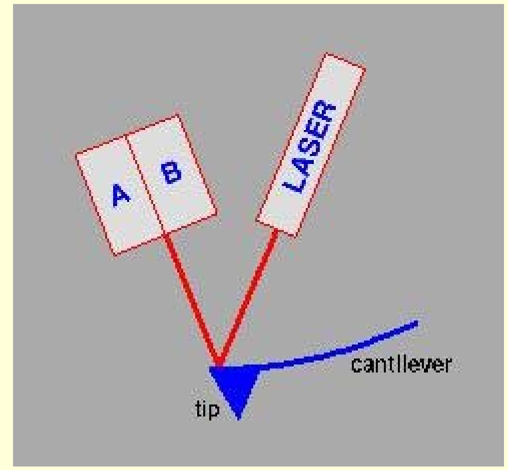
Atomic Force Microscopy

(all materials)

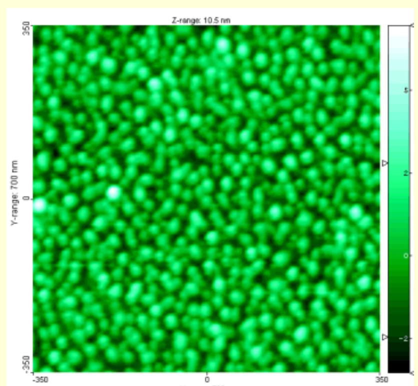
Binnig, Quate and Gerber, 1985



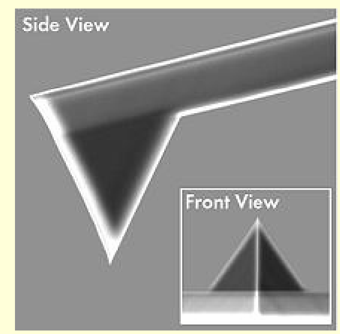




Repulsive
Attractive
Capillary
Magnetic…

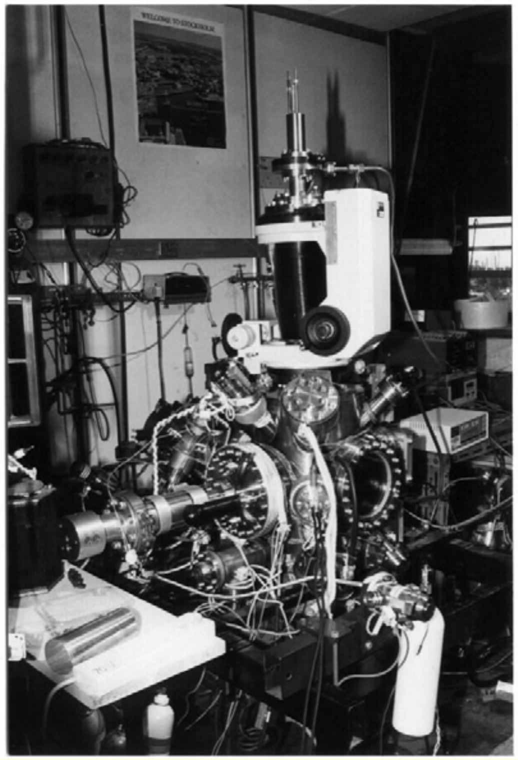


Azurin on mica



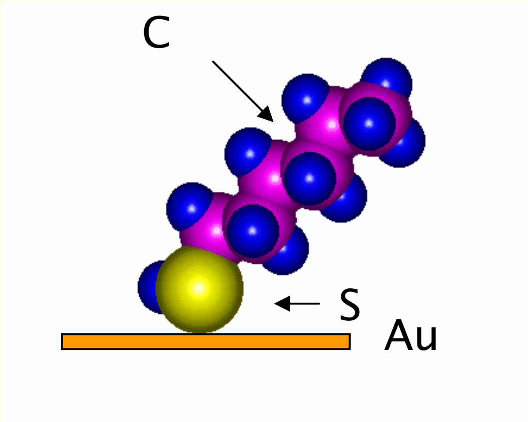
Ultra High Vacuum Techniques

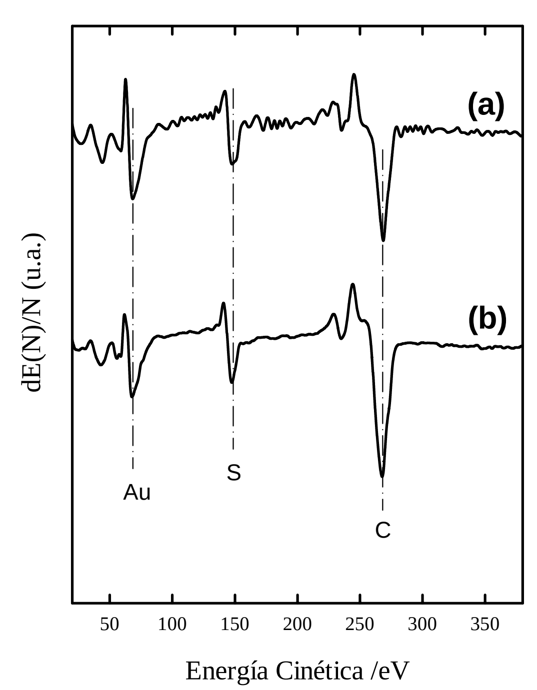
Auger Electron Spectroscopy (AES) 1960s



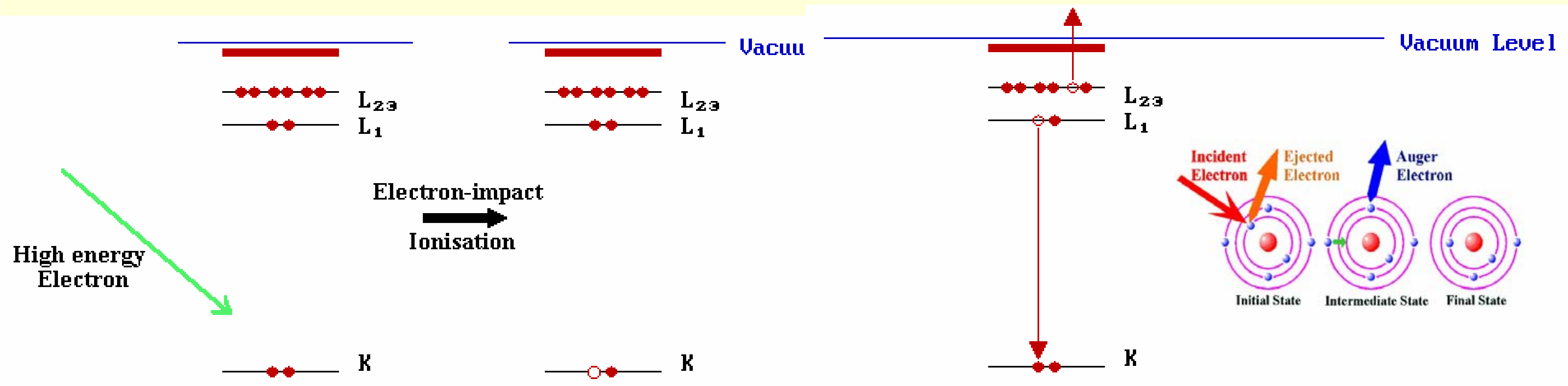
Elemental composition,

AES
Hexanethiol on Au



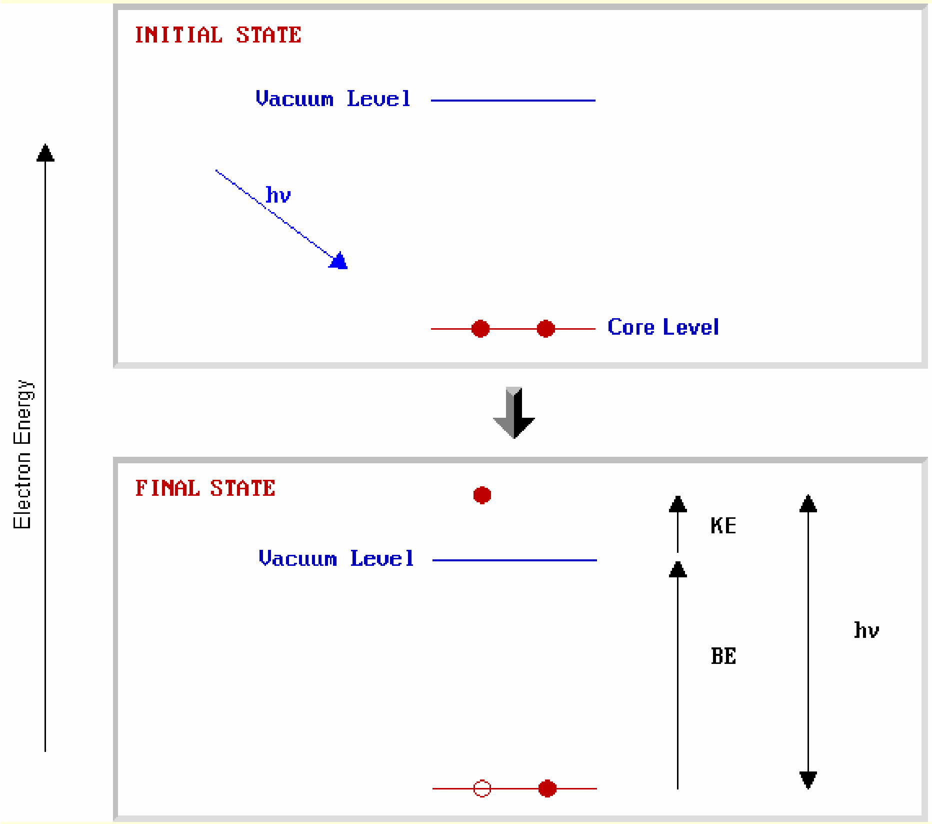


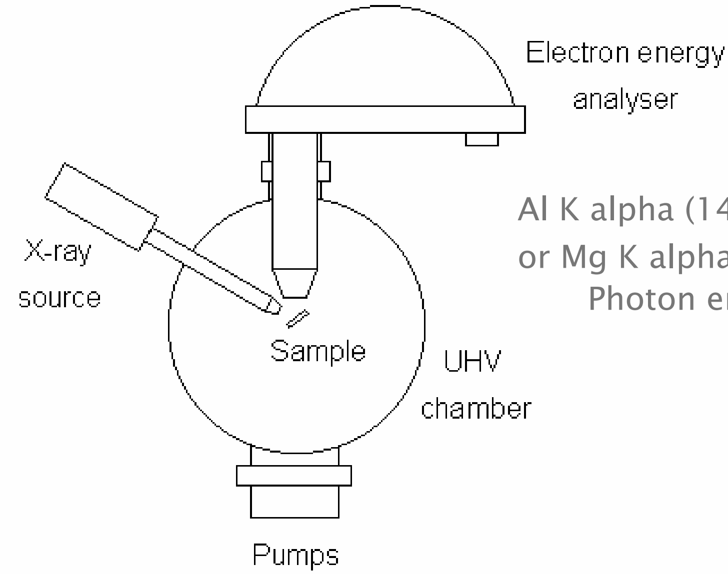
3-20 KeV



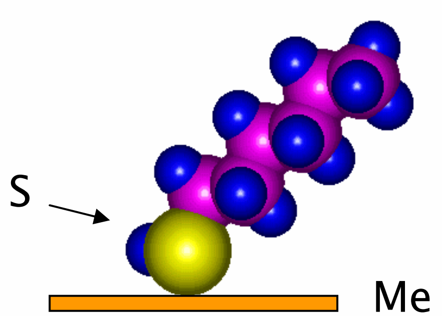
X-ray Photoelectron Spectroscopy (XPS)

1960s by K. Siegbahn, Nobel Prize for Physics in 1981

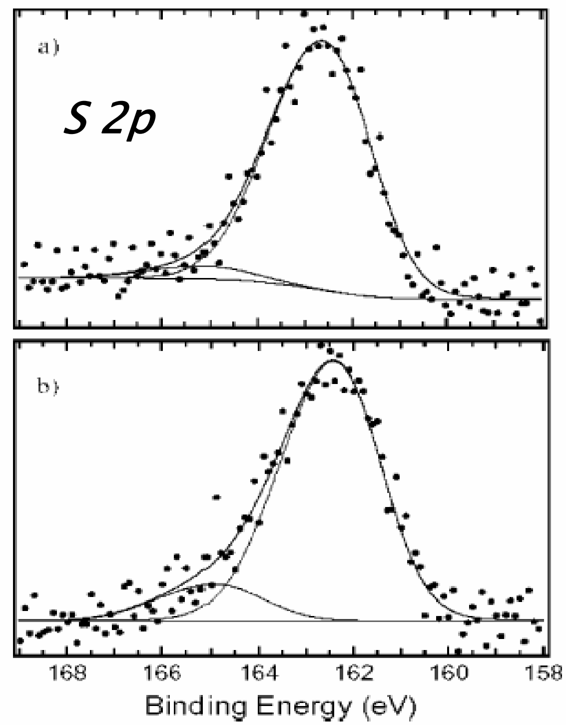




Al K alpha (1486.6eV) or Mg K alpha (1253.6eV)
Photon energyy



XPS
Dodecanethiol on Ni



chemical nature of compounds

SAMs preparation

Solution deposition

Inmersion

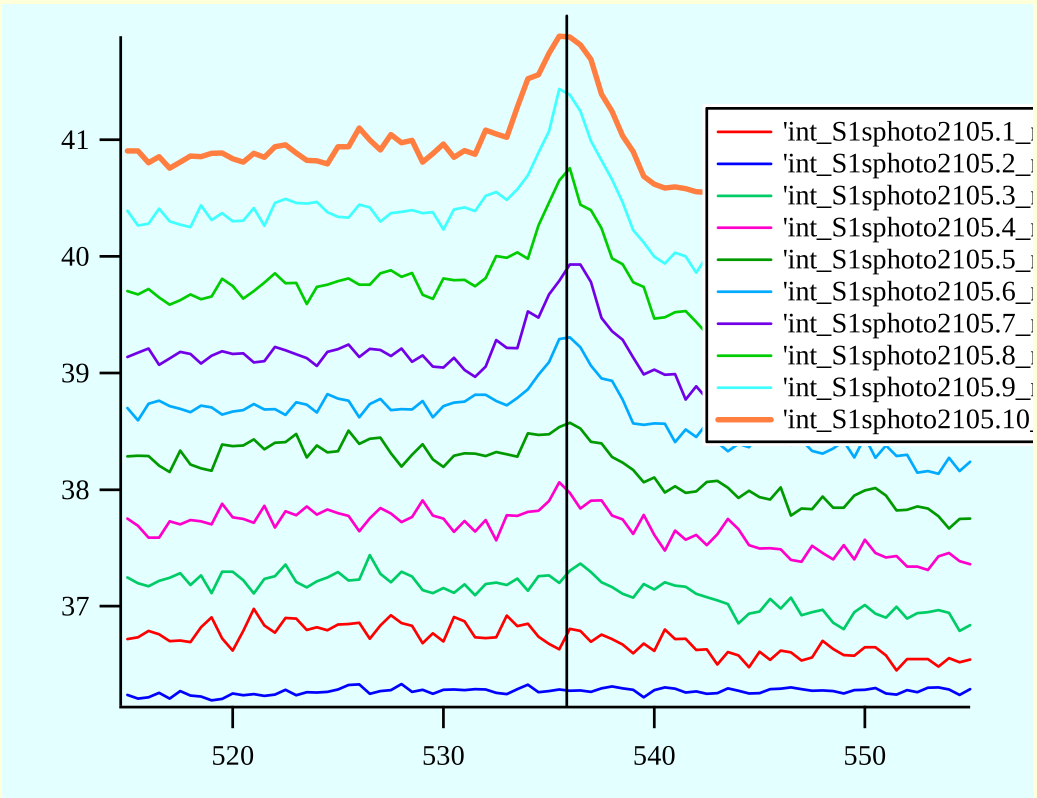
Electrochemistry

Gas phase deposition

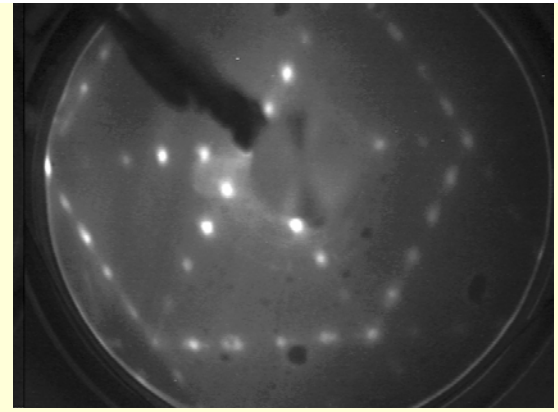
Solution deposition: an easy and low cost method

GAS PHASE DEPOSITION

D.P.Woodruff et al



Substrate bombarding (1KeV),annealing 530 C,30 min

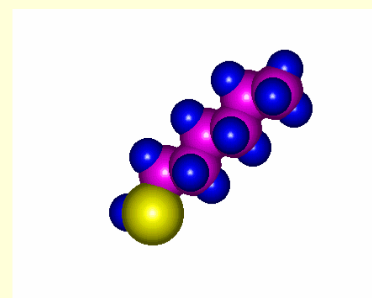


$p(\sqrt{3}\times 5\sqrt{3})R30$

o

300-9000 Langmiur

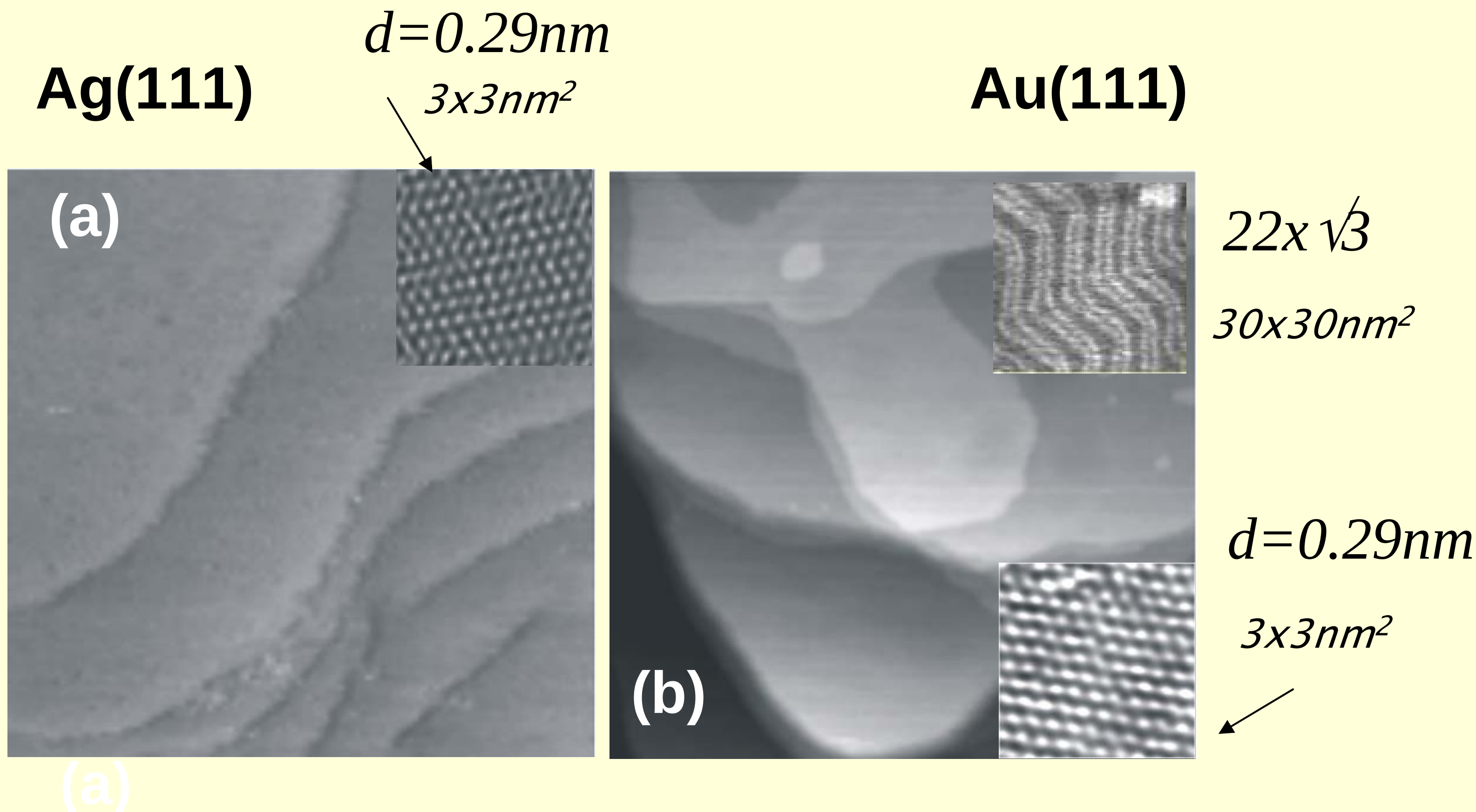
XPS Results for S 1s photo peak hexanethiol on Au(111)



$CH_3-(CH_2)_n-H_2CSH + M \longrightarrow CH_3-(CH_2)_n-H_2CS-M + 1/2H_2$

Solution deposition of alkanethiolate SAMs

Clean Metal Substrates



200x200 nm² STM images

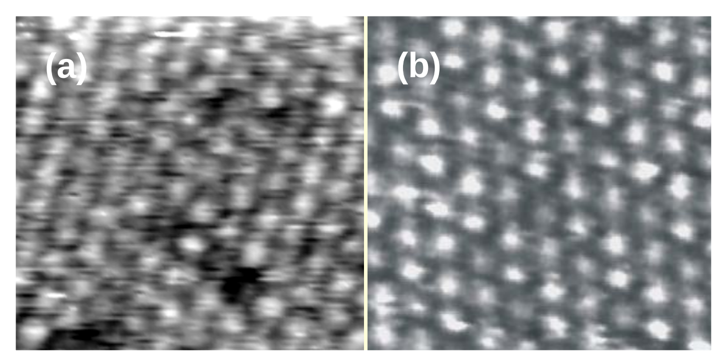
Solution deposition

Au, Ag, Cu

Solvent: ethanol, toluene, etc

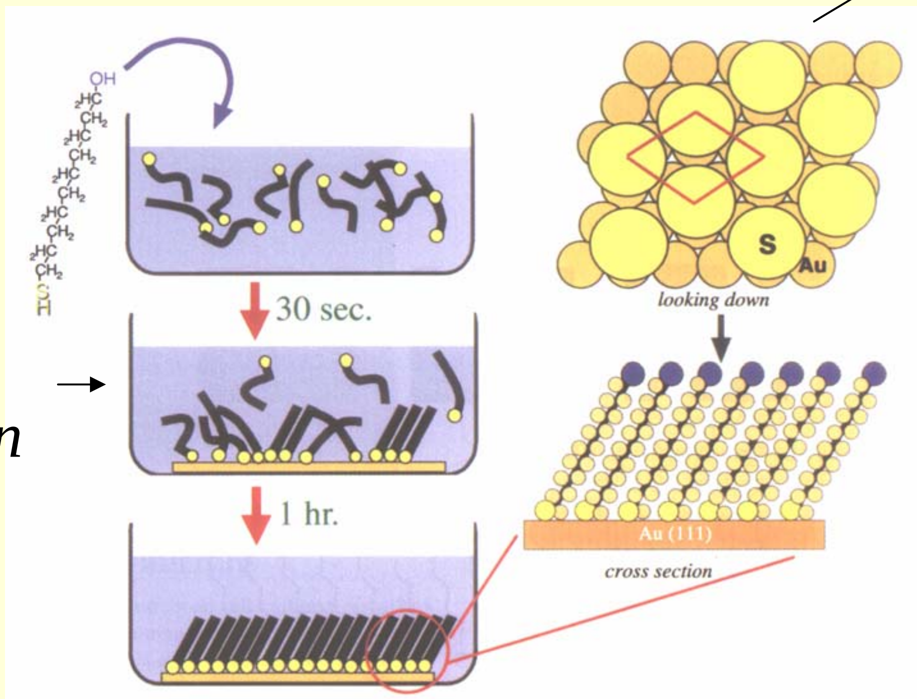
STM 4x4 nm2

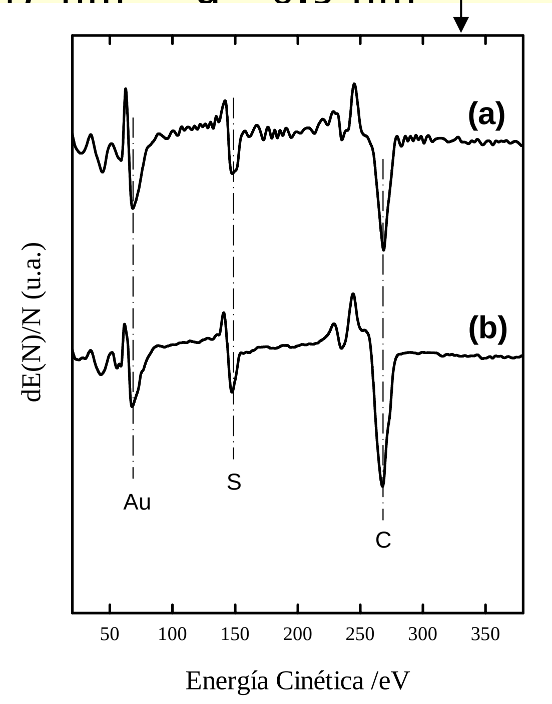
Propanethiol on Ag(111) *hexanethiol on Au (111)*



d=0.47 nm d= 0.5 nm

Substrate immersion





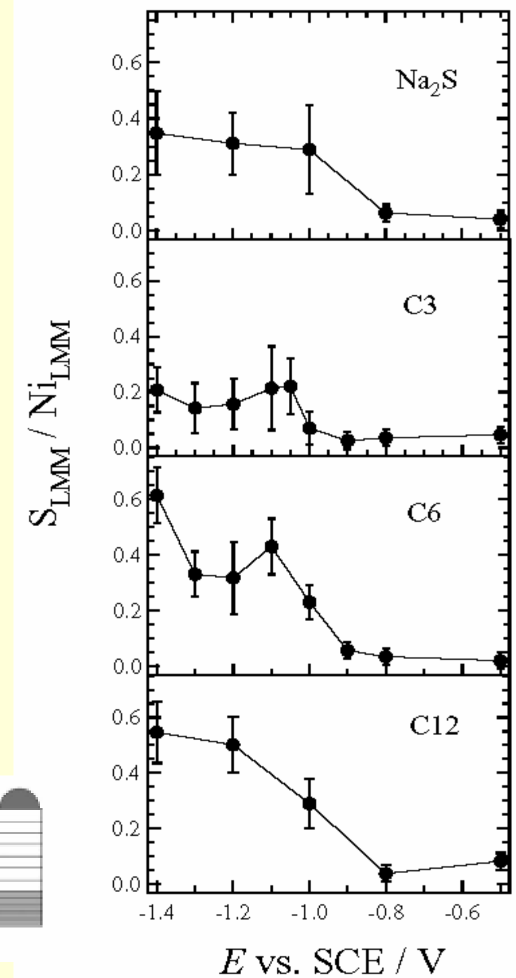
$CH_3\text{-}(CH_2)_n\text{-}H_2CSH + Me \longrightarrow CH_3\text{-}(CH_2)_n\text{-}H_2CS\text{-}Me + 1/2H_2$

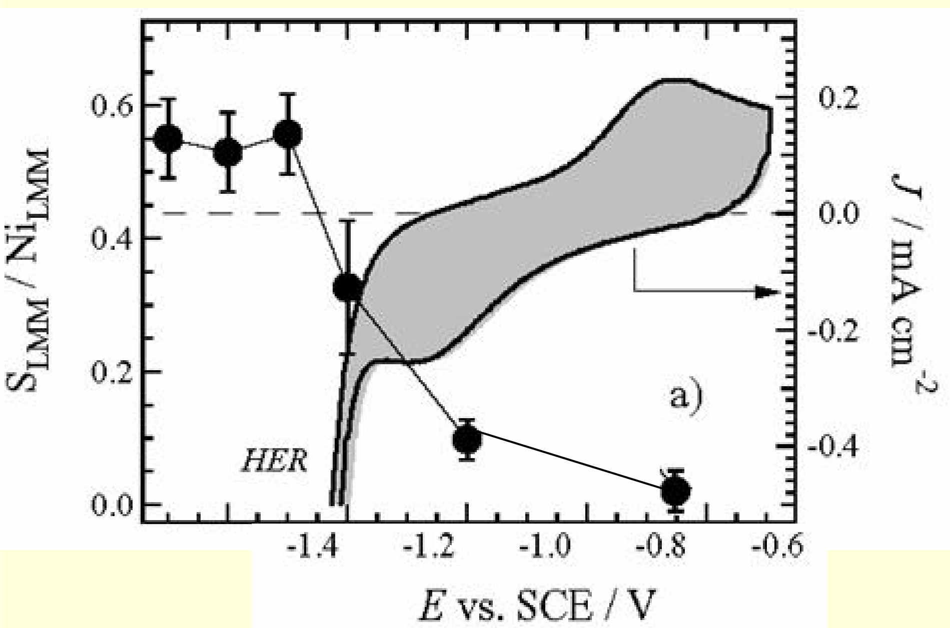
Electrochemical-induced dodecanethiolate self-assembly on Ni(111)

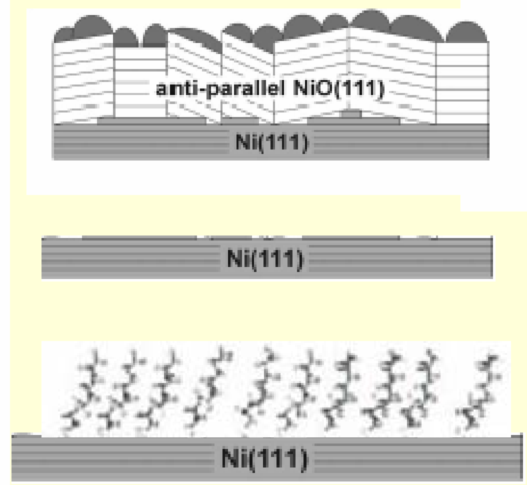
$$NiO + 2e^- + H_2O \longrightarrow Ni + 2OH^-$$

dodecanethiol-saturated aqueous 1 M NaOH

$$R\text{-}S^- + Ni \longrightarrow R\text{-}S\text{-}Ni + e^-$$





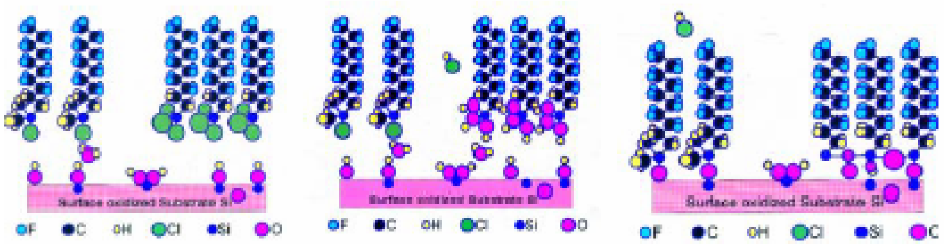


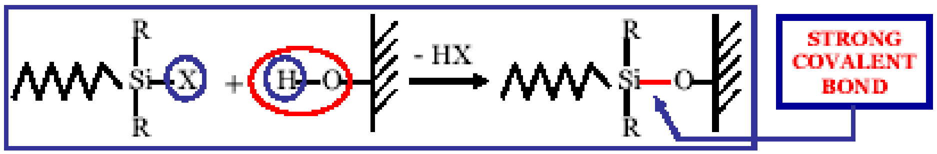
Ni poly

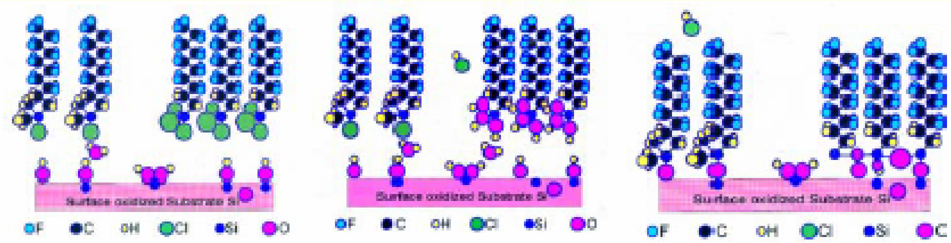
Bengió, Fonticelli,Benítez, Hernández Creus, Carro, Ascolani, Zampieri, Blum, Salvarezza,
J. Phys. Chem. B **2005,** *109*, 23450-23460

$$R_nSiX_{4-n} + SiOH \rightarrow SiOSiR_n + 4 - nHX$$

$$n = 1 - 3 \quad X = Cl, OR, NH_2, NR_2$$ R=Alkyl, functional chain







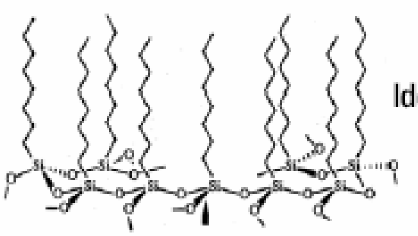
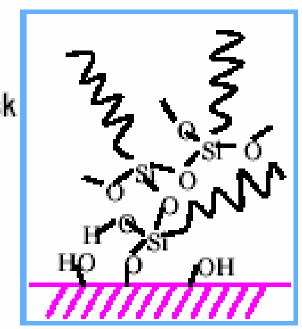
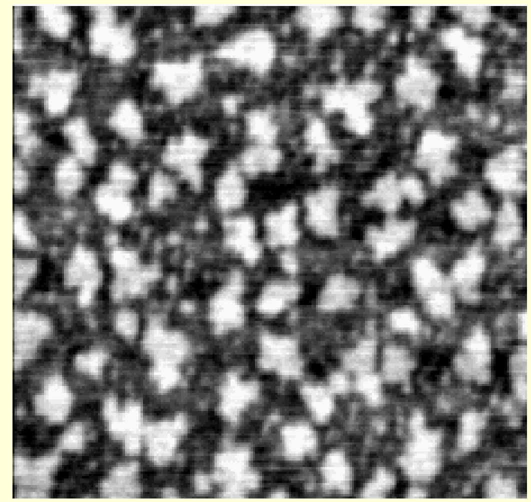


Figure 3.14. A schematic description of a polysiloxane at the monolayer-substrate surface. The arrow points to an equatorial Si–O bond that can be connected either to another polysiloxane chain or to the surface.

Ideal and risk



Solution deposition of self-assembled silanes monolayers

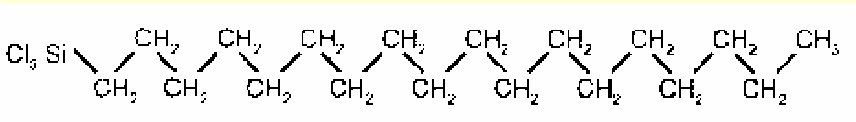


4 micron x 4 micron image taken with a scanning probe microscope from an assembled monolayer of silanes with two different chain lengths.

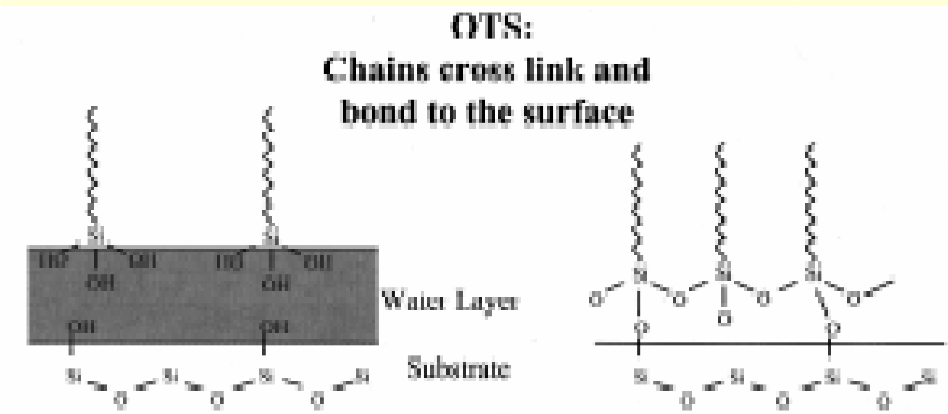
Jeffrey J. Weimer

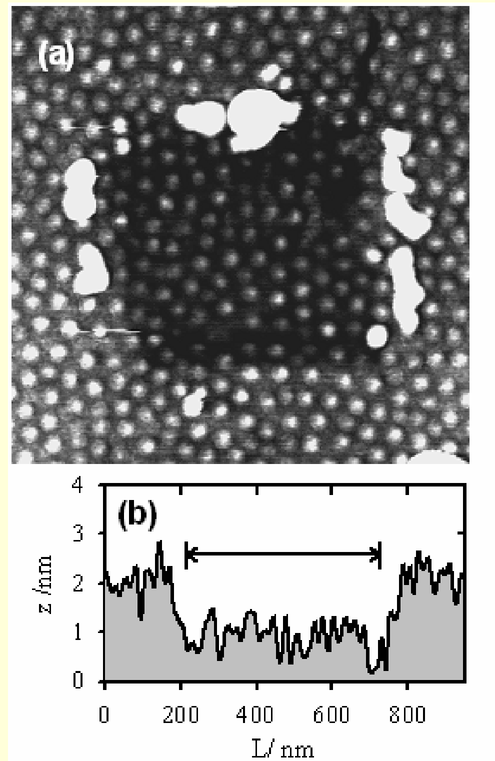
Uniform and robust self-assembled silane monolayers on Si Surfaces

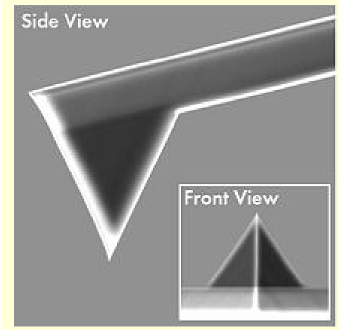
1) Fully hydroxylated Si by treatment in piranha solution
2) OTS under strict anhydrous conditions (hexane)
3) Cross-linking



Octadecyltrichlorosilane (OTS) C=18

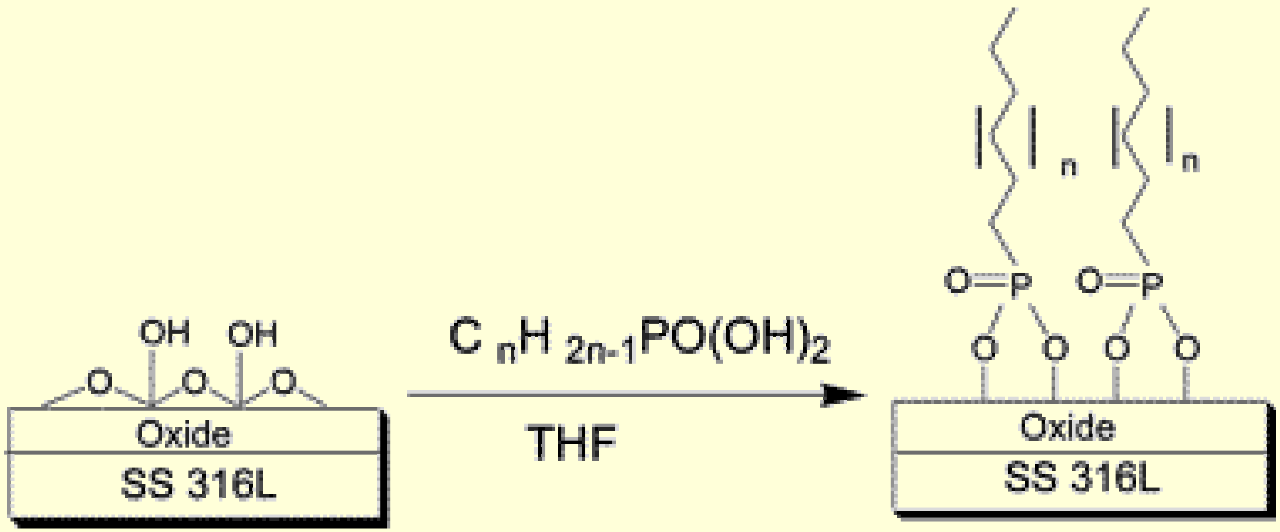






Surfaces, prepared in the presence of moisture, exhibit nonuniform topological and mechanical properties.

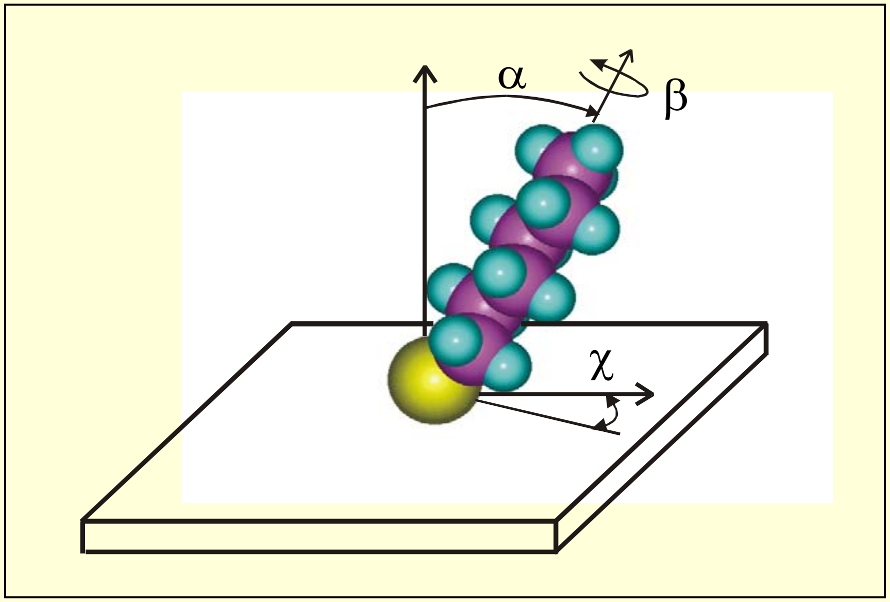
Solution deposition of phosphonate SAMs

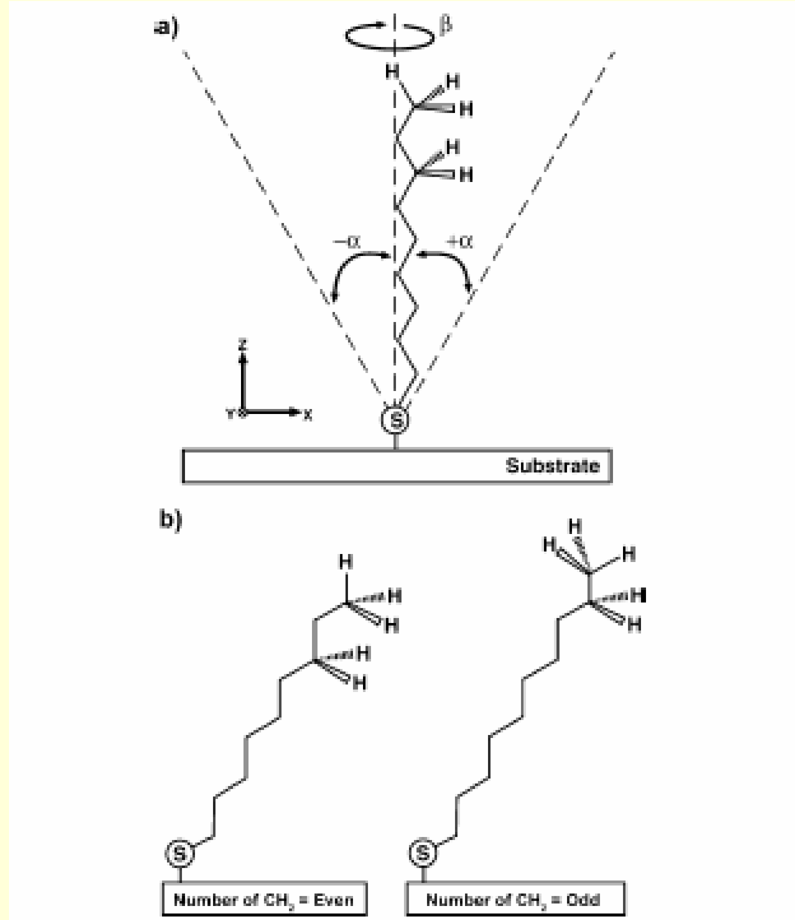


Formation of Self-Assembled Monolayers of Alkylphosphonic Acid on the Native Oxide Surface of SS316L

The cleaned room-temperature substrates were dipped in a 1 mM solution of octadecylphosphonic acid (ODPA) or octylphosphonic acid in dry tetrahydrofuran

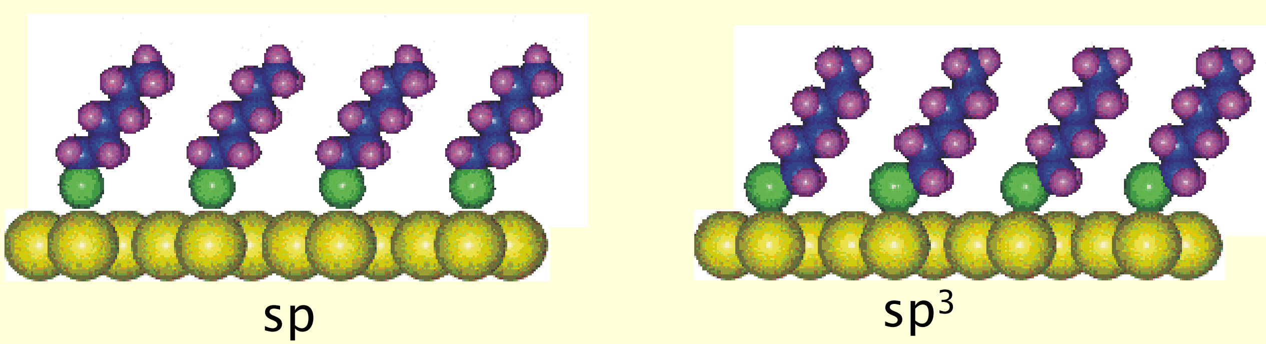
A. Raman, M. Dubey, I. Gouzman, E. S. Gawalt
Langmuir 22, 6469 – 6472, 2006





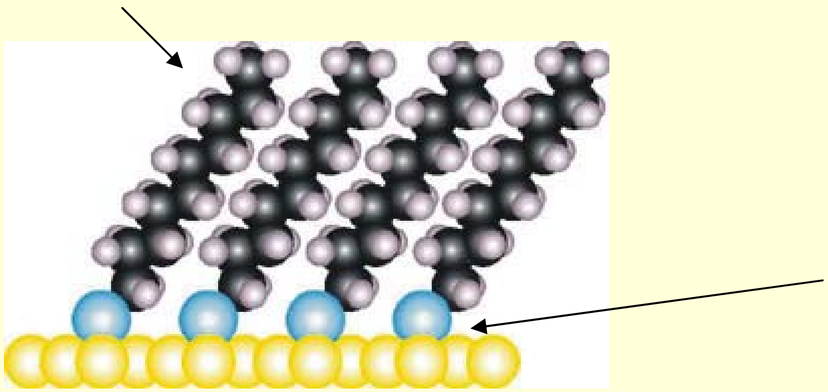
Thiols on Au(111)

$\alpha = 30°$
$\beta = 55°$
$\chi = 14°$



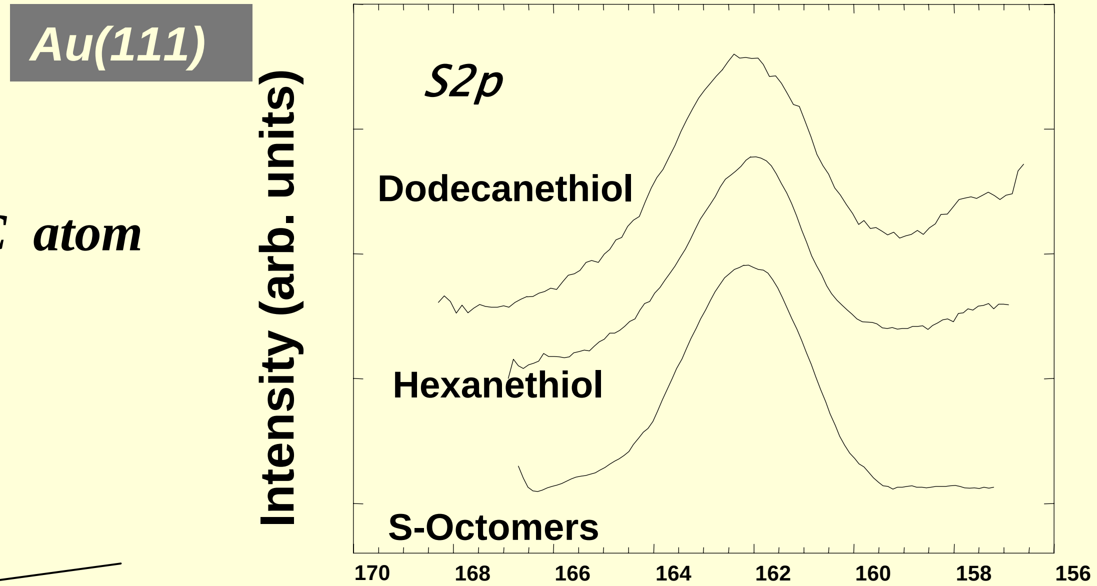
MAIN FORCES FOR SELF-ASSEMBLY:

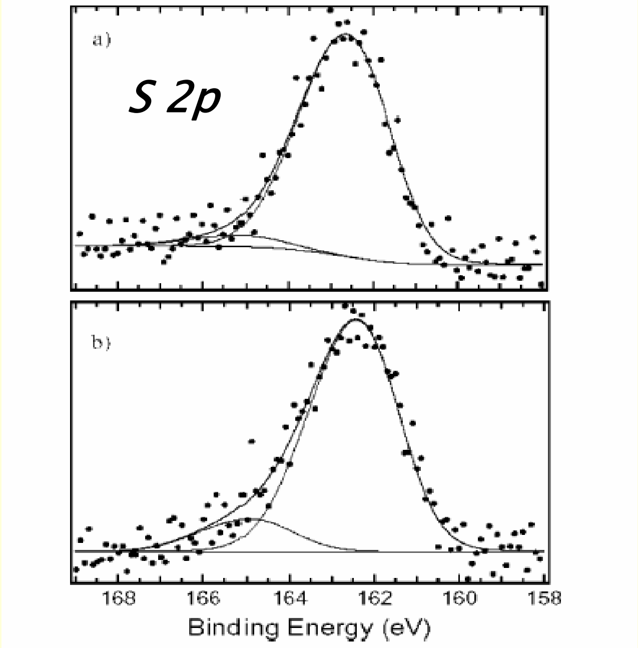
alkanethiolate-alkanethiolate interactions 1 Kcal mol^{-1} per C atom



S-Me bond: thiolate 40-60 Kcal mol^{-1}

XPS

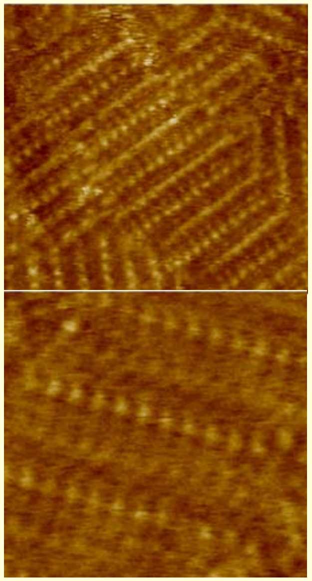


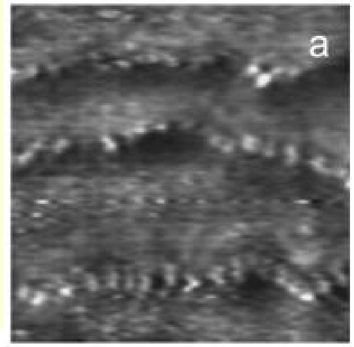


Dodecanethiol on Ni(111) and Ni poly

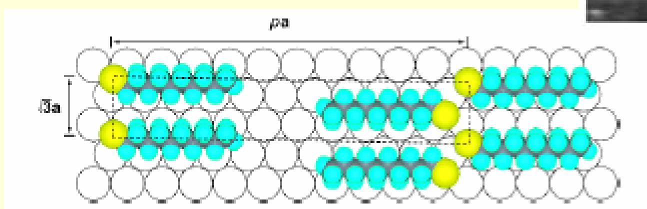
*C. Vericat, M.E. Vela, G. Andreasen, R.C. Salvarezza, L. Vázquez and J.A. Martín-Gago Langmuir, **17**, 4919-4924 (2001)*

Self-assembly: Low-coverages and transients alkanethiolate phases on Au(111)

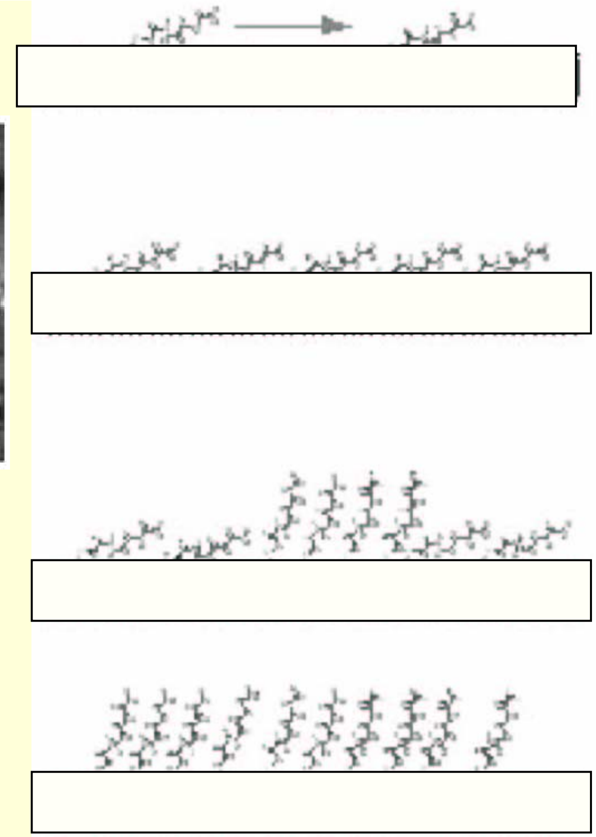




1) Adsorption at defects



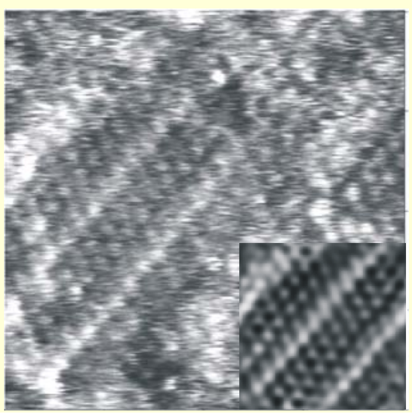
2) Parallel configuration



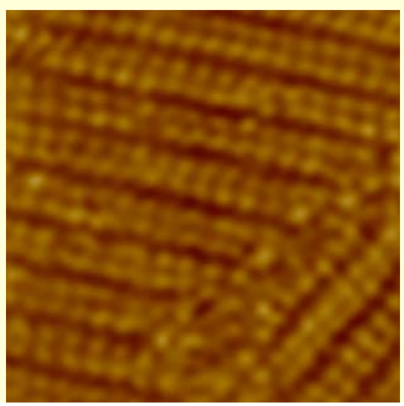
C. Vericat, M.E. Vela , R.C. Salvarezza Physical *Chemistry Chemical Physics, 7, 3258 (2005)*

3) Vertical configuration

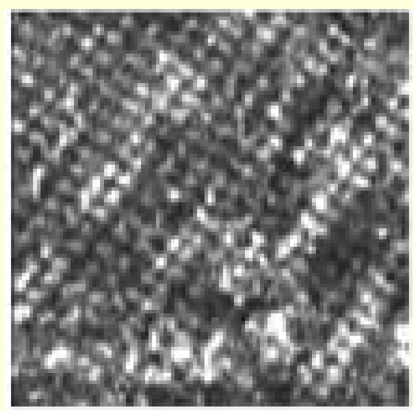
(6×√3) Tilt 30º



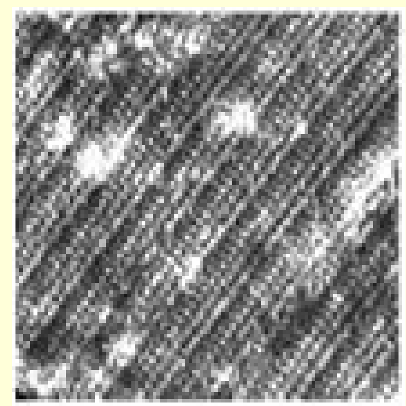
(4×√3) Tilt 50º



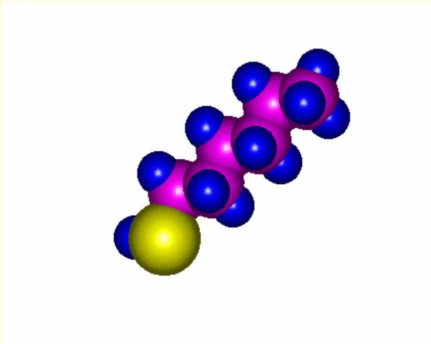
(2×√3) Tilt 50º



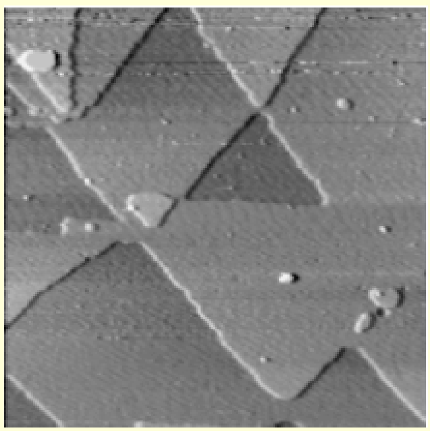
PinstripeTilt 30º



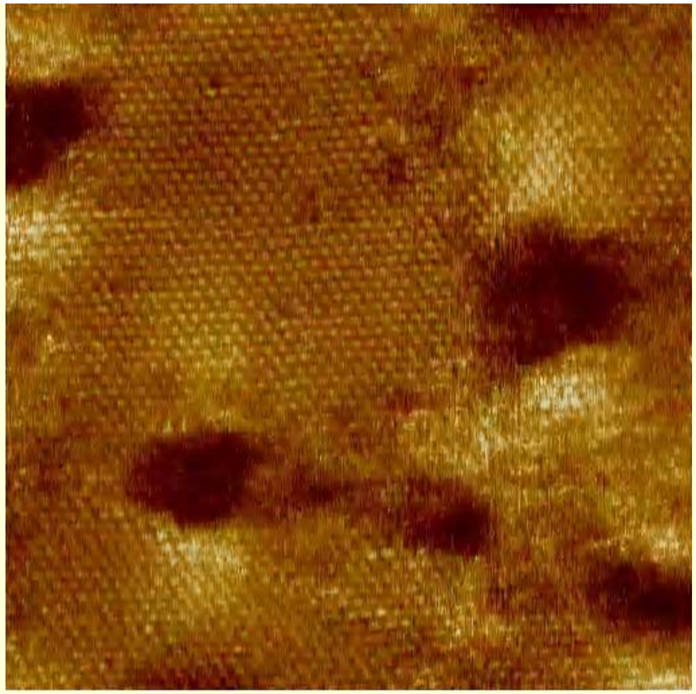
Stable phases

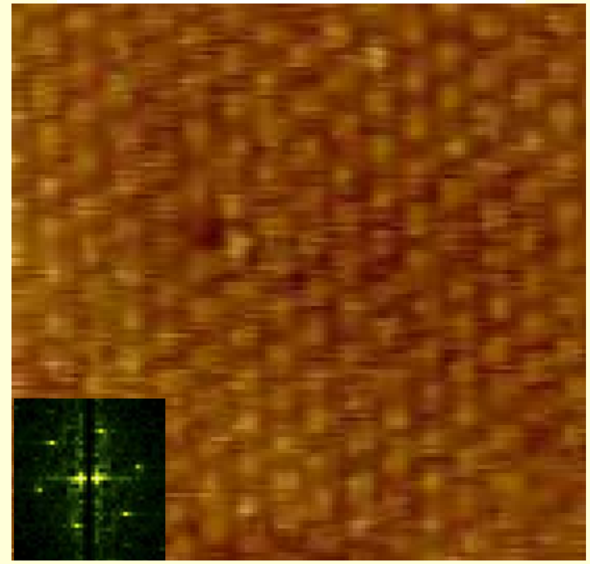


hexanethiolate on Au(111)

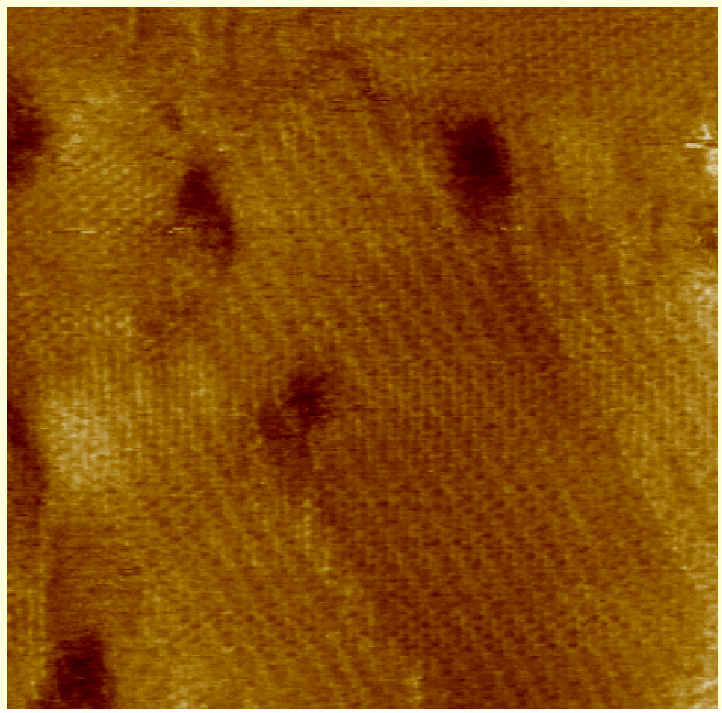


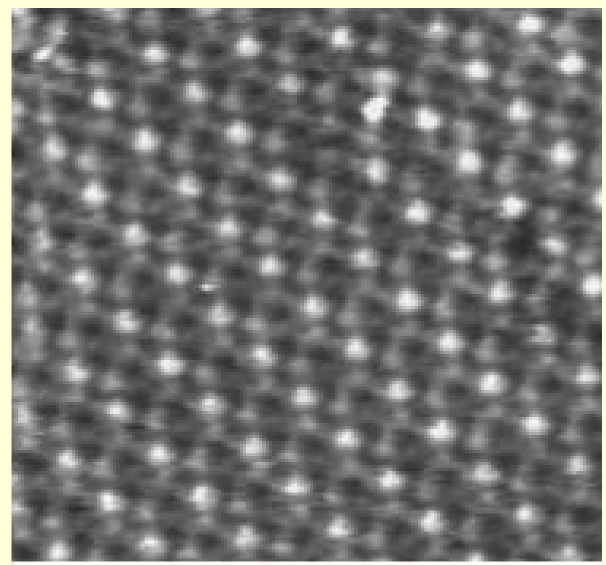
Adsorption time: 24 hs





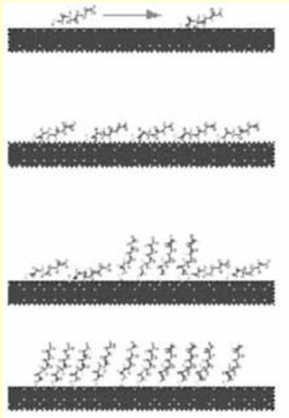
$\sqrt{3} \times \sqrt{3}$ R30°





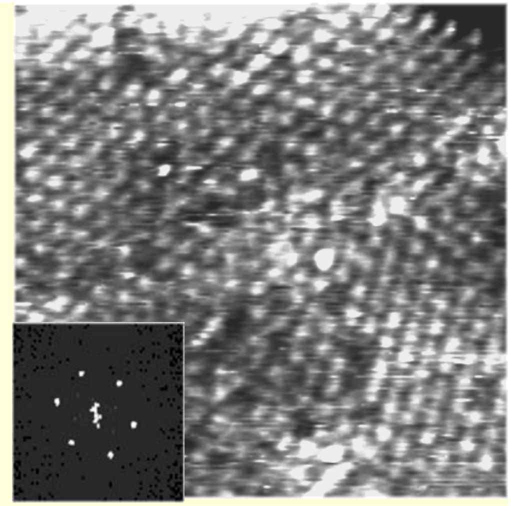
rectangular c(4x2)

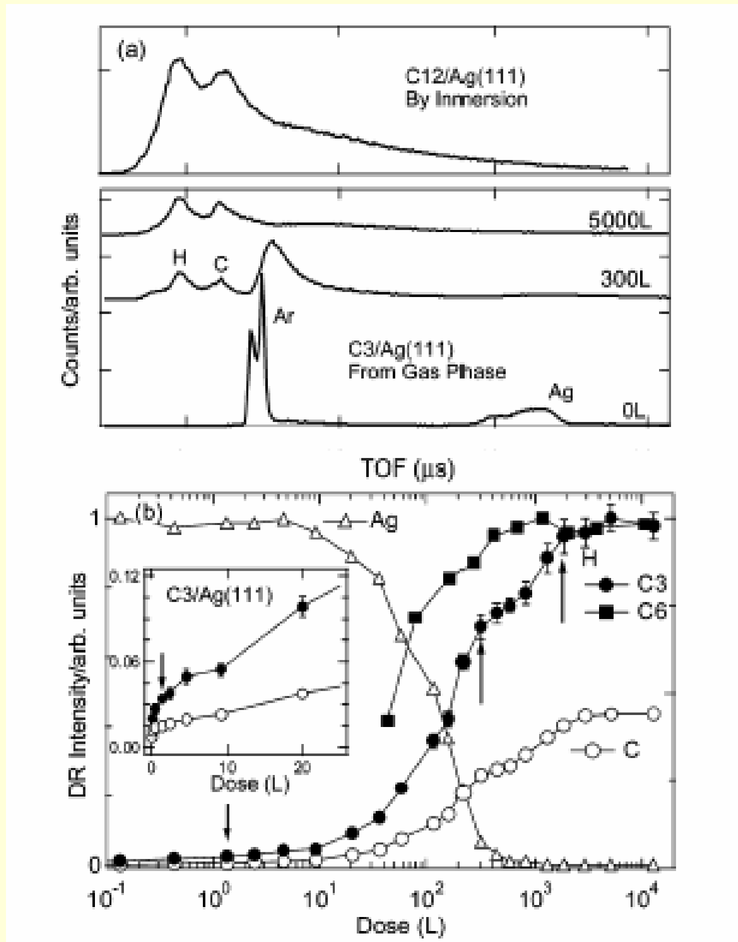
Alkanethiol self-assembly on Ag(111)

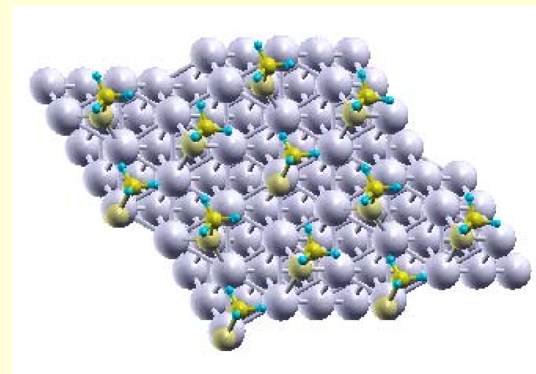


??

√7 x √7 R 19.1° propanethiolate lattice







TOF-DRS spectra for clean and thiol-coveredAg(111) surfaces.

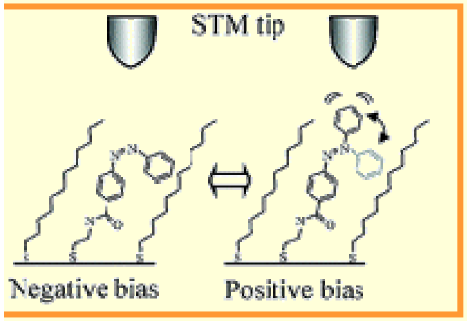
Recoil intensities for Ag, H, and Cvs C3 dose. 1.Inset: span of the lower range in linear scale. Arrows indicate major changes in sticking

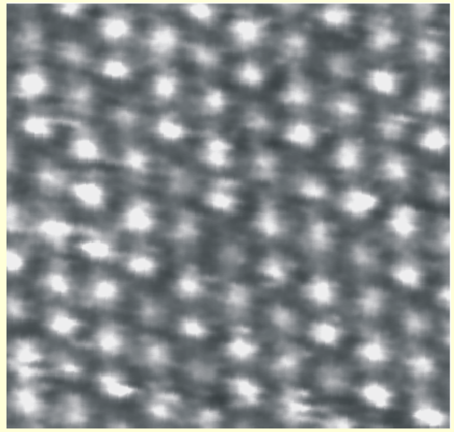
Luis M. Rodriguez, J. Esteban Gayone, Esteban A. Sanchez, Oscar Grizzi, Barbara Blum, Roberto C. Salvarezza

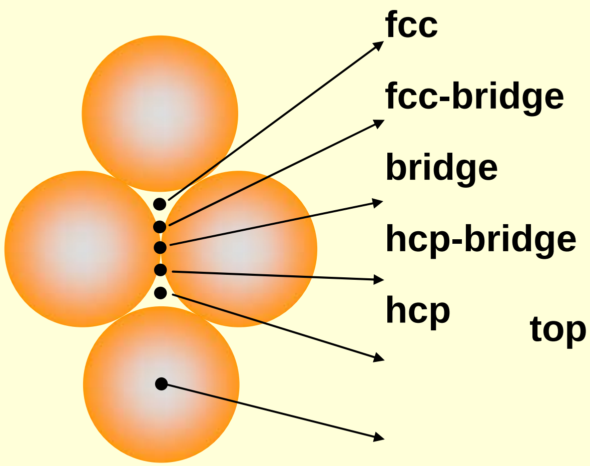
THE JOURNAL OF PHYSICAL CHEMISTRY B LETTERS

110, 7095-7097 **2006**

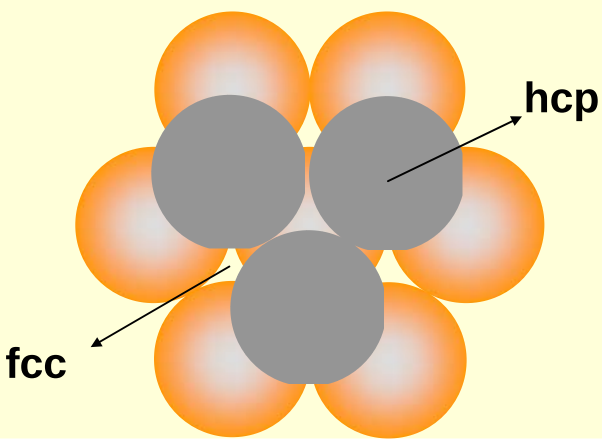
Adsorption sites





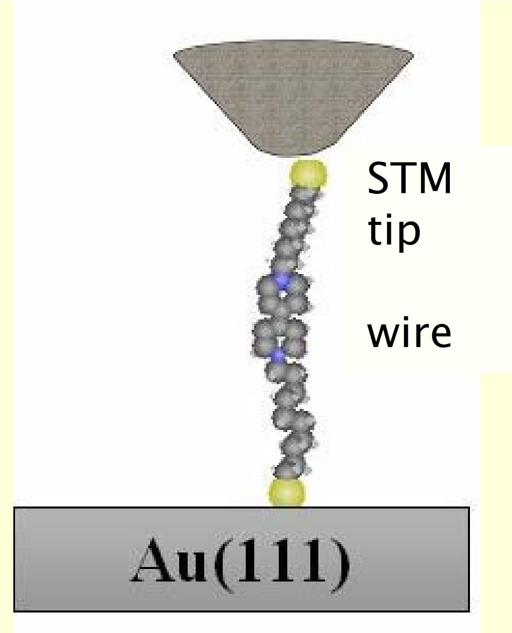


√3x√3 R30°



DFT: bridge or fcc

Standing waves/ Photoelectron diffraction: top



Single molecule conductance

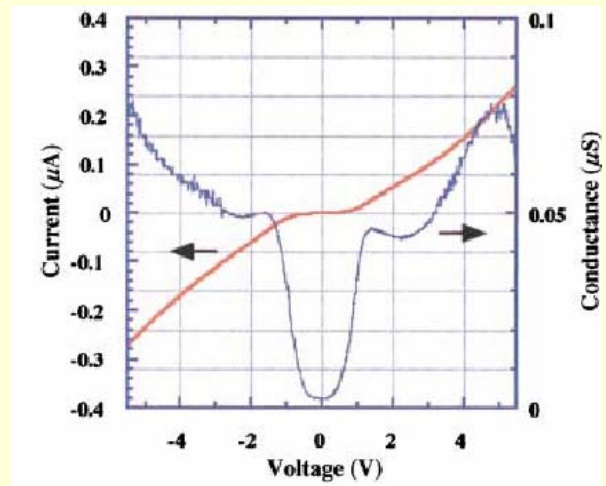


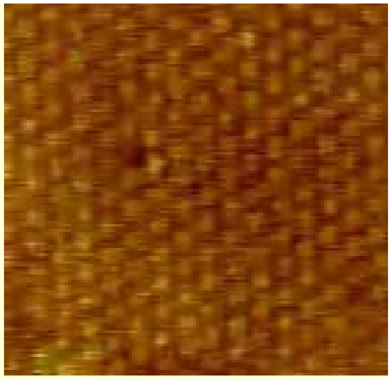
Figure 11. The I-V (red) and G-V (blue) characteristics of a single molecule.

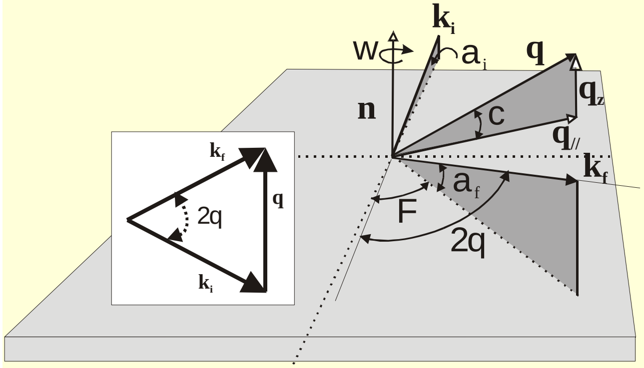
MRS BULLETIN/FEBRUARY 2001

Mark A. Reed

Dodecanethiol on Au(111)

√3√x3 R30°



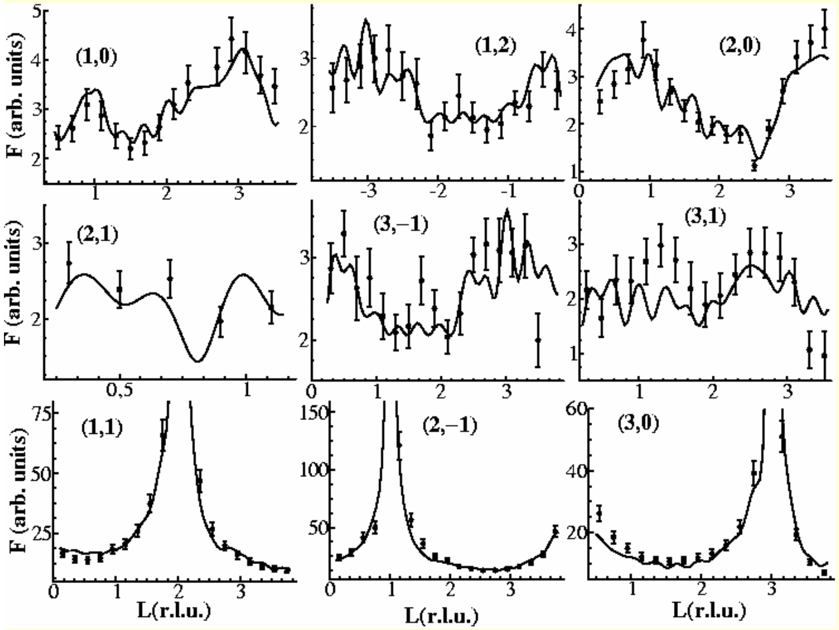


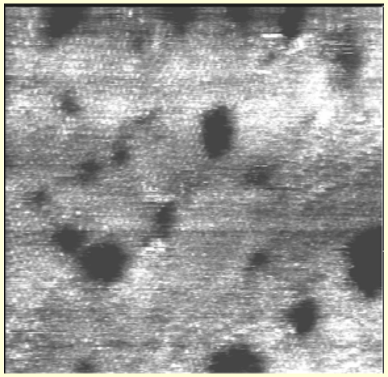
Only one adsortion site?

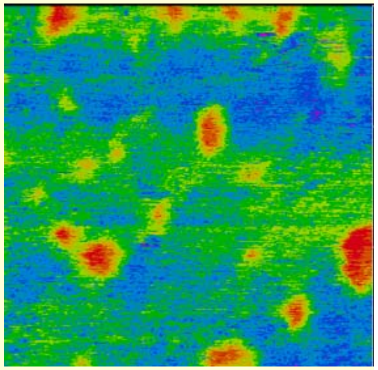
S–Au = 0.23 nm
S–Au= 0.24 nm
42 % top
58 % fcc

STM
two sites?

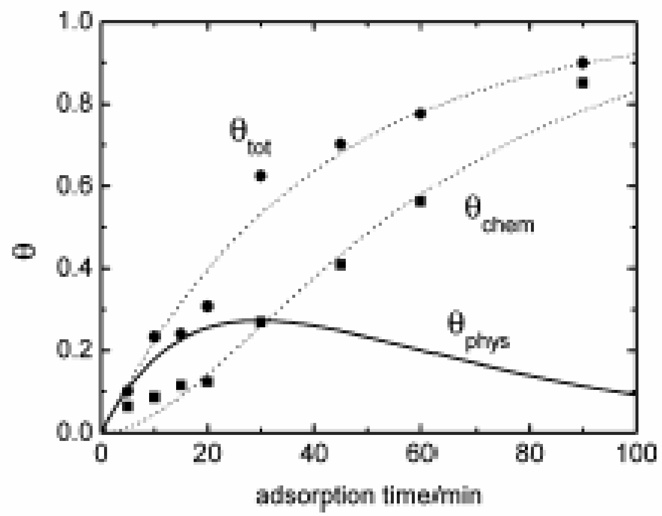
GIXRD (CTRs)
ID32 Sincrotron Grenoble







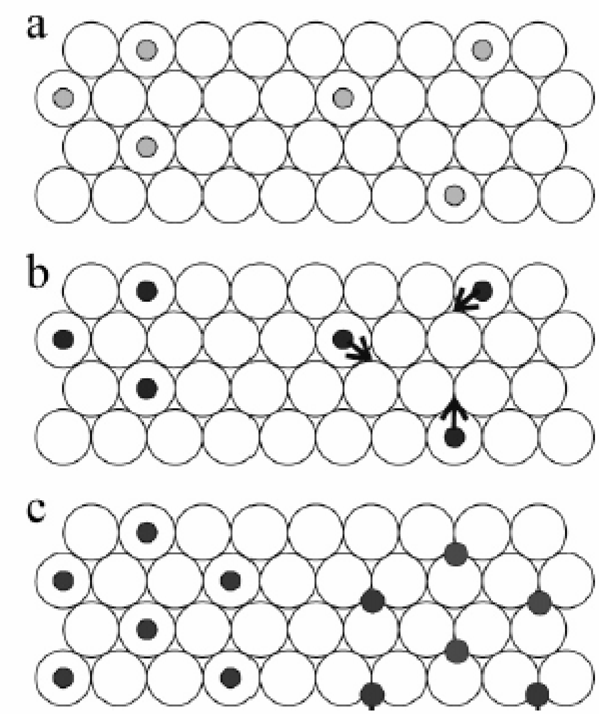
X Torrelles,C Vericat, M Vela, M. Fonticelli, M Daza Millone,R Felici,T-L Lee,| J Zegenhagen,|G Muñoz,J Gago,R C. Salvarezza, *J. Phys. Chem. B* **2006,** *110*, 5586-5594

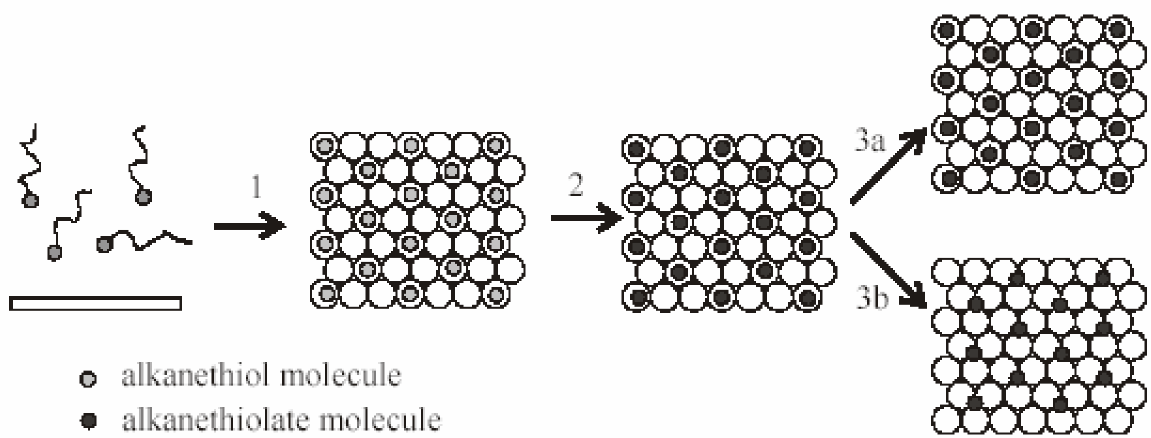


physisortion

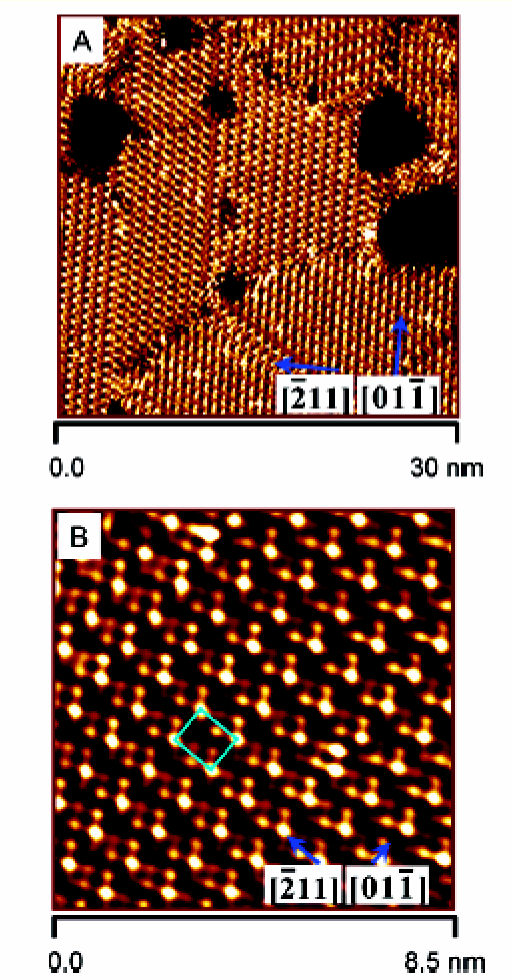
H_2

chemisorption





c(4x2)



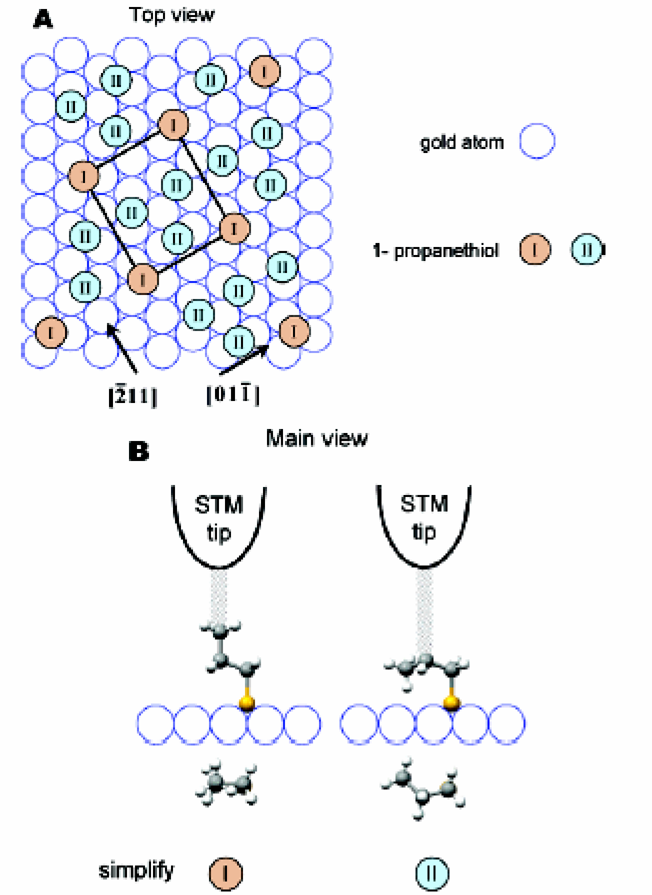


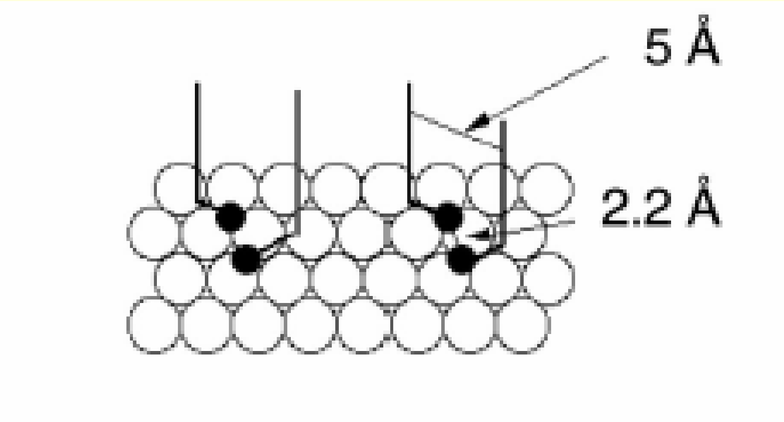
Figure 9. (A) Possible surface model for a $(2\sqrt{3} \times 3)$ R30° unit cell containing four 1-propanethiol molecules, and (B) a proposed illustration of two configurations of adsorbed 1-propanethiol and corresponding tunneling pathways.

Jingdong Zhang,* Qijin Chi, and Jens Ulstrup, Langmuir published in the web

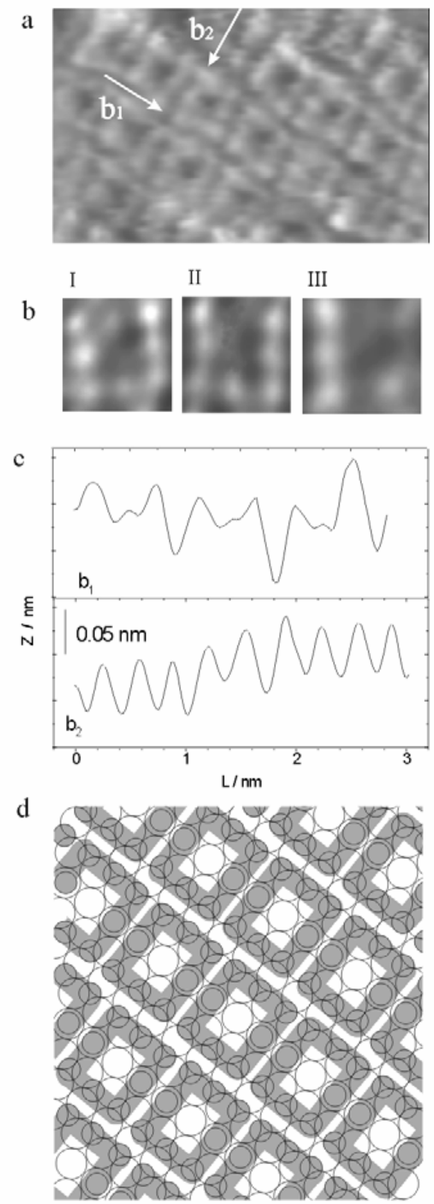
D. **Anselmetti** et al., Europhys. Lett. 23, 421 (1993).

S on Au(111)

c(4x2)



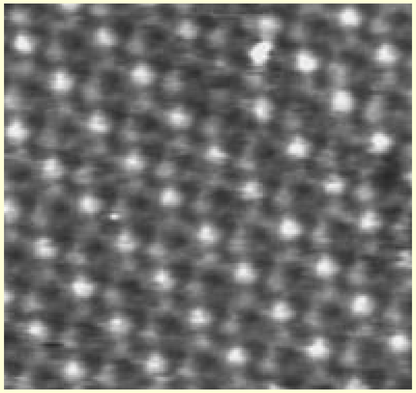
P. Fenter, A. Eberhardt, P. Eisenberger, "n-Alkyl Thiols Self-Assembled as Disulfideson Au(111)", Science, 266, 1216-1218 (1994)

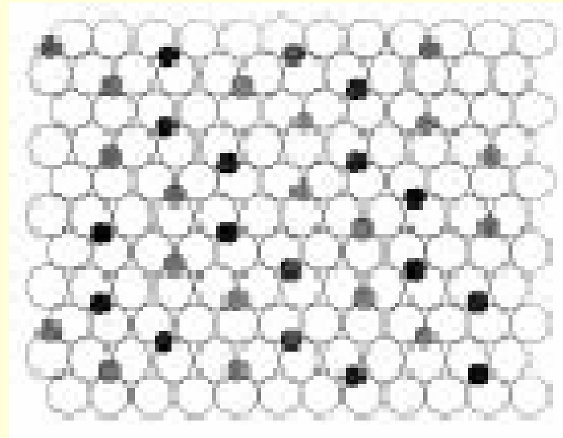


C. Vericat, G. Andreasen, M.E. Vela, R.C. Salvarezza, J. Phys. Chem. B ***104***, *302 (2000).*

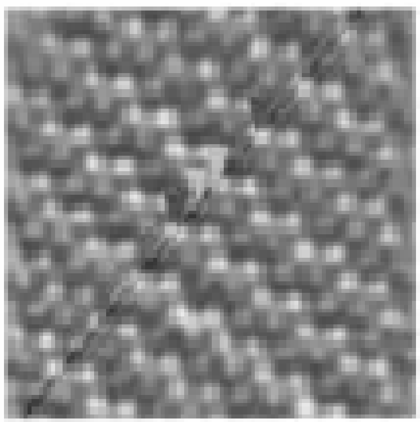
S-S distance ≈ 0.3 nm

C(4x2)

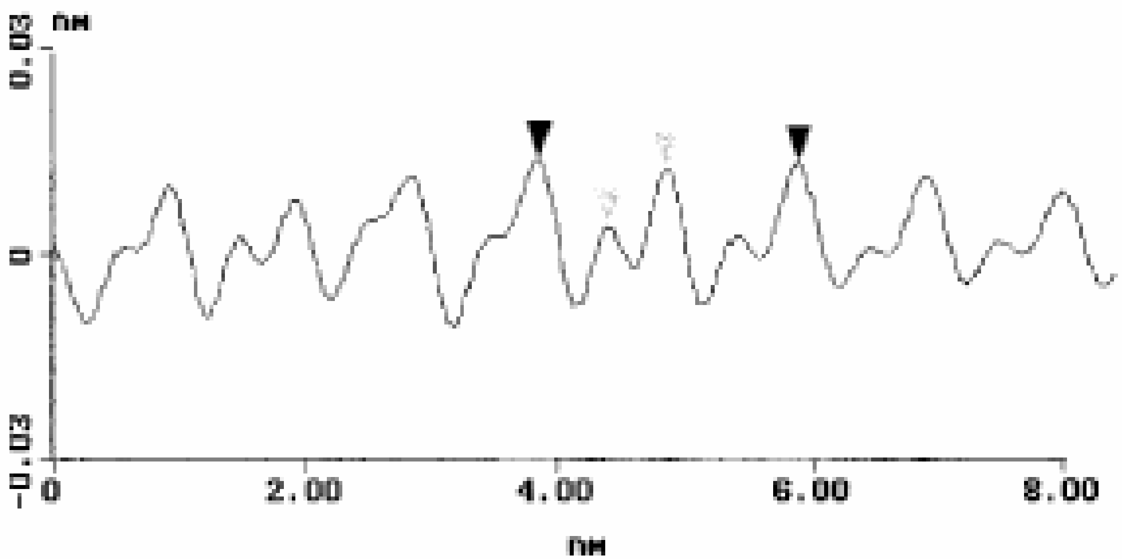




Rectangular
Zig-zag



a



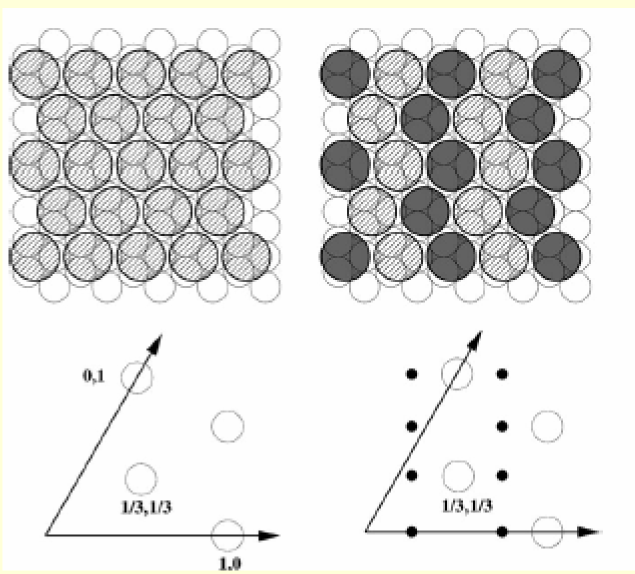
F. Teran Arce, M. E. Vela, R. C. Salvarezza, A. J. Arvia
Langmuir 1998, *14,* 7203-7212

S-S distance/nm	Reference
0.5	172
0.45	53
0.37	126
0.32	176
0.22	62

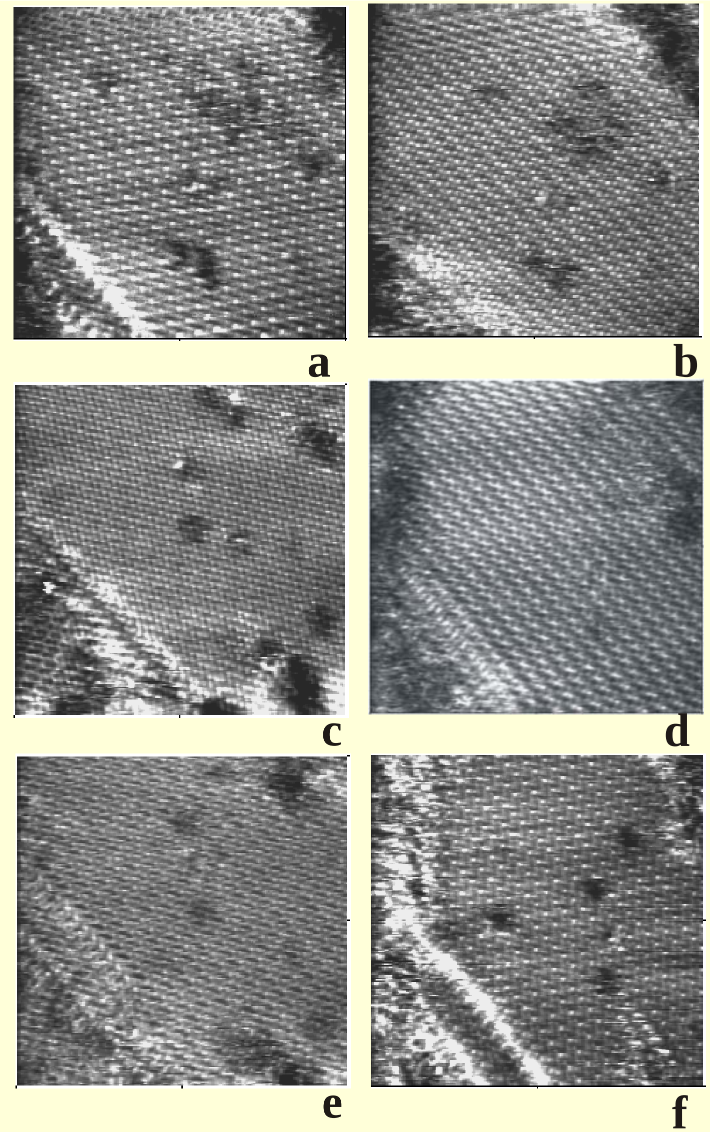
STM: S vs methylene group

DFT calculations: methylene group

Diffraction techniques and IR in liquids: disorder in the terminal groups



Maria Jos Capitan, Jesus Alvarez, Juan Jos Calvente, Rafael Andreu Angewandte Chemie, in press

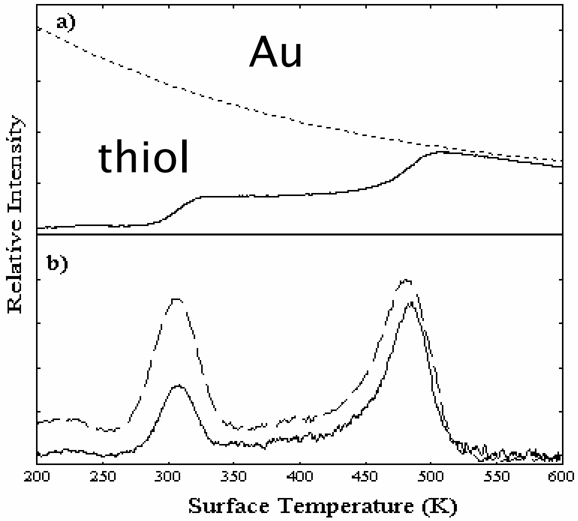


(20x20 nm2) sequential in situ STM images c(4x2) ⇔ √3x√3 R30°transitions 0.1 M NaOH

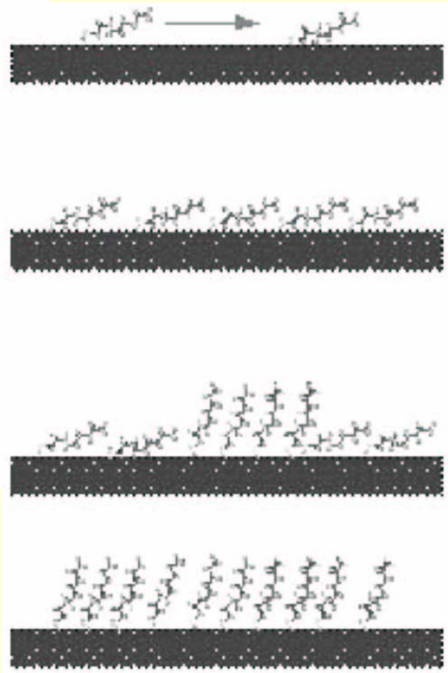
C. Vericat, G. Andreasen, M.E. Vela, H. Martin, R.C. Salvarezza Journal of Chemical Physics, 115, 6672-6678 (2001).

Thermal Stability of Self -Assembled Monolayers

Alkanethiolates Au(111)

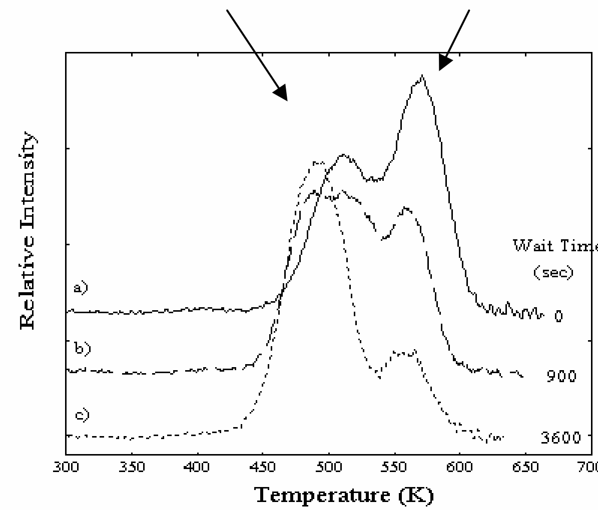


Physisorbed chemisorbed



standing-up phase → Alkyl disulfides R-S-S-R

low-density flat-lying phase → thiolate radicals R-S•



Thermal Programmed Desorption

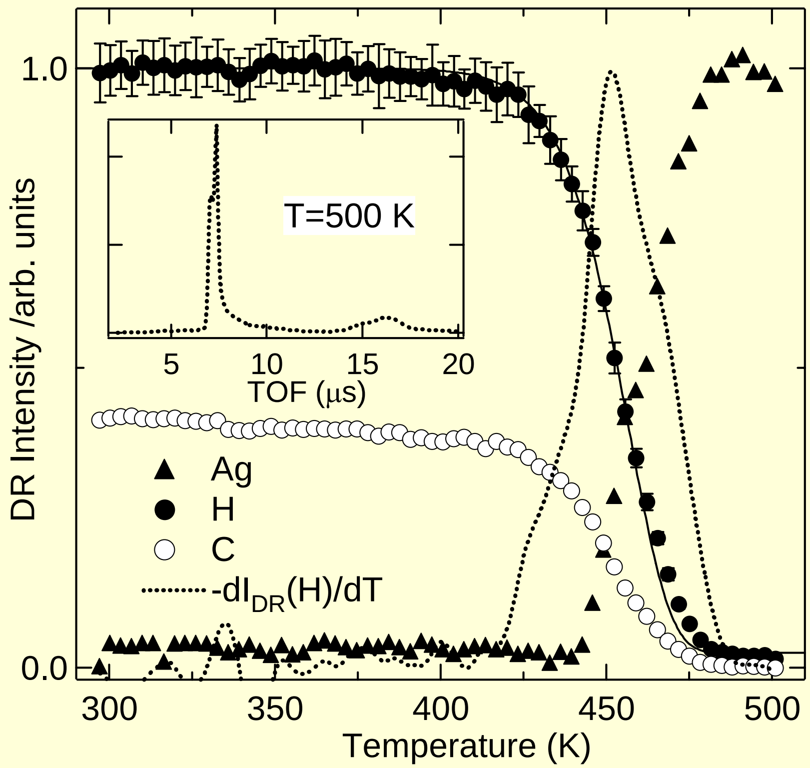
Scoles et al. J .Phys. Chem. B 102, 3456 (1998)

SAMs are stable below 80-90° C

Thermal Stability of Self -Assembled Monolayers

Alkanethiolates Ag(111)

Time-of-flight direct recoiling spectroscopy (TOF-DRS)



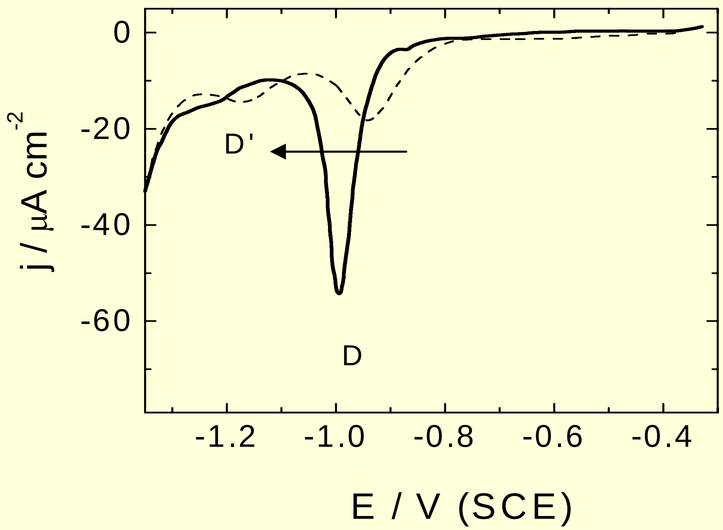
Propanethiol on Ag (111)

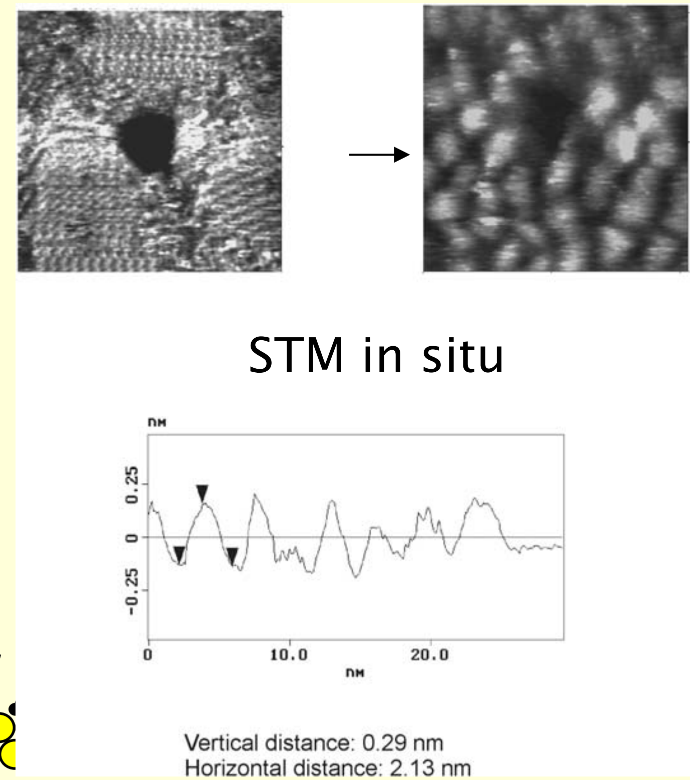
Ag, H and C recoil intensities vs. sample temperature.
The full line is a fit to the H recoil intensity with a first order desorption model. The derivative -dIDR(H)/dT of the H data (dotted line) is included.

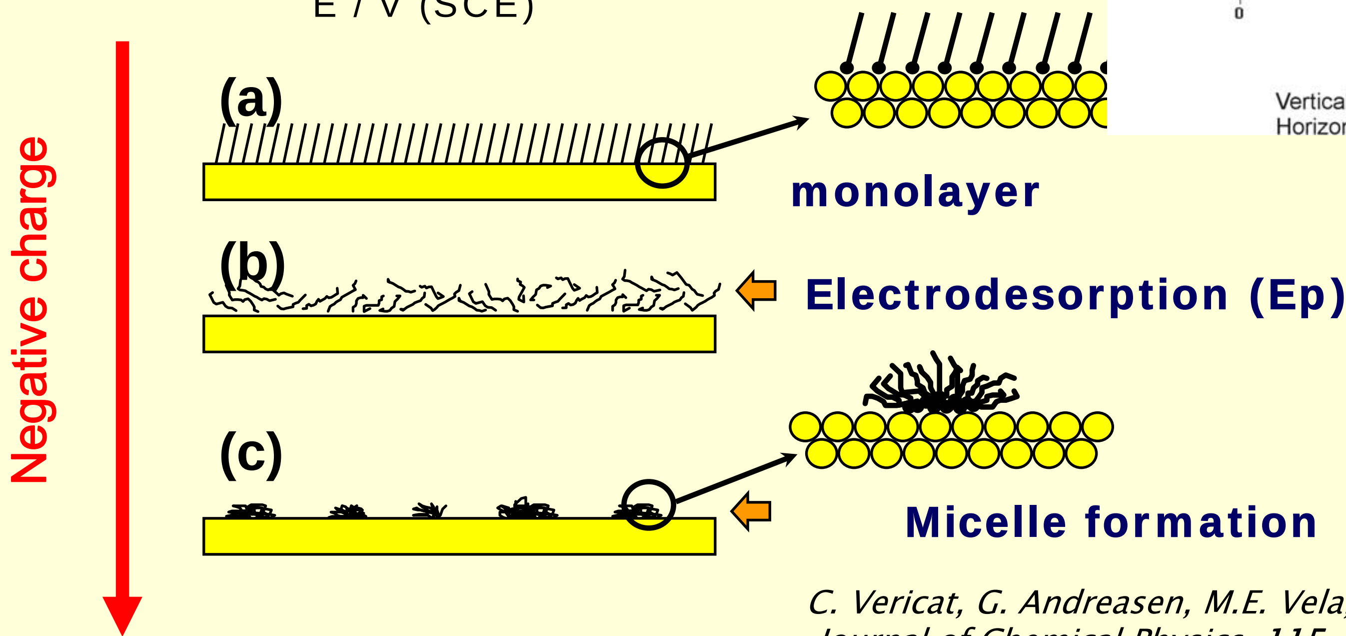
O. Grizzi et al

Electrochemical stability

R–S–Au(111) + e = Au(111) + RS⁻



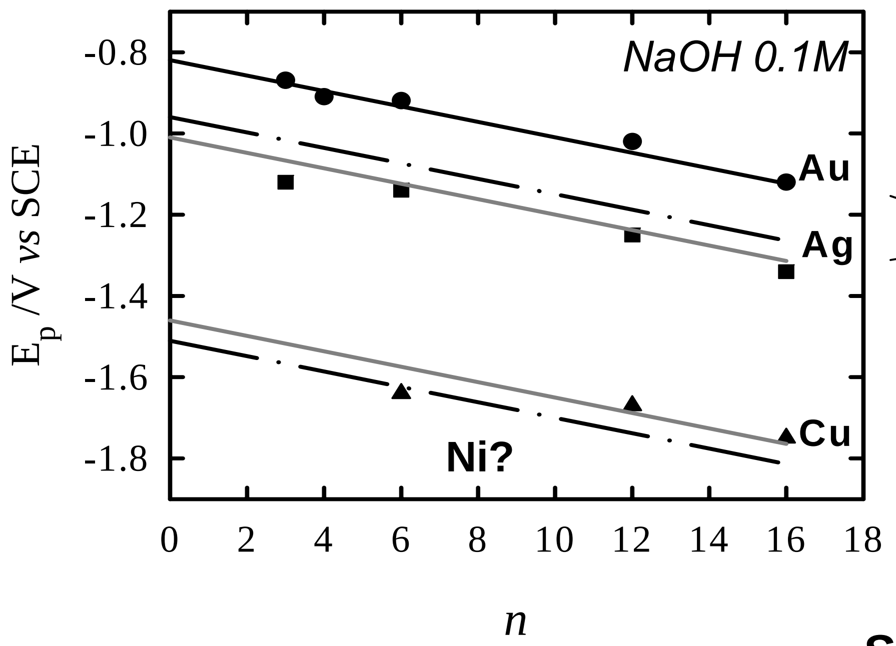




C. Vericat, G. Andreasen, M.E. Vela, H. Martin, R.C. Salvarezza
Journal of Chemical Physics, 115, 6672-6678 (2001)

Selecting the SAM: hydrocarbon chain length effect

Dependence of the peak potential for alkanethiol electrodesorption on the number of carbon units (n)



Solid line: experimental data

Dashed line: estimated from DFT

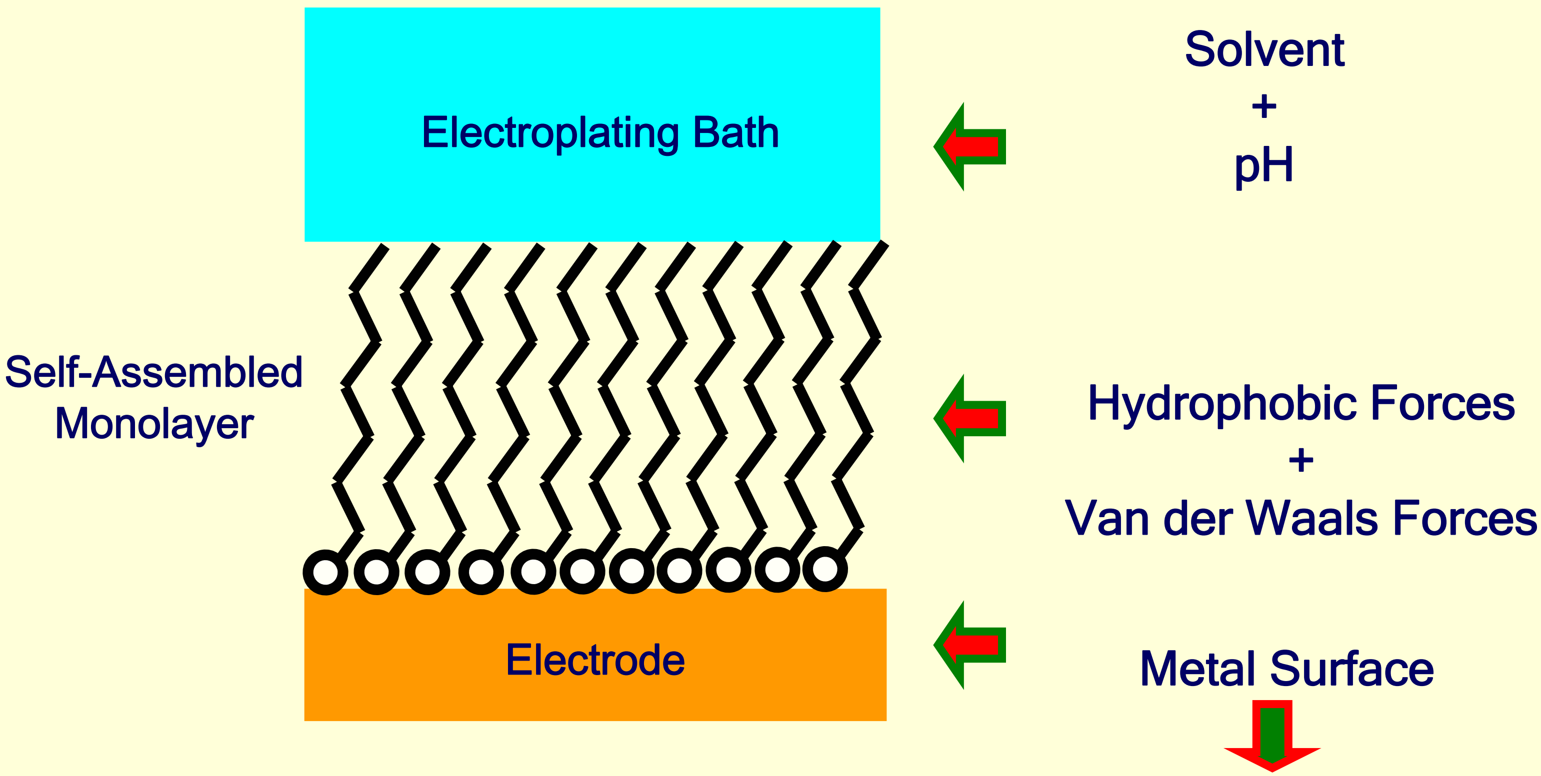
Voltammetric determination of E_p

Rotanting ring-disc+AES

Slope : 3.5 kJ mol^{-1} / C unit
Van der Waals + hydrophobic forces

O.Azzaroni, M.E. Vela, M. Fonticelli, G. Benitez, P. Carro, B. Blum, R.C. Salvarezza
*J.Phys.Chem.B **107** 13446 (2003)*

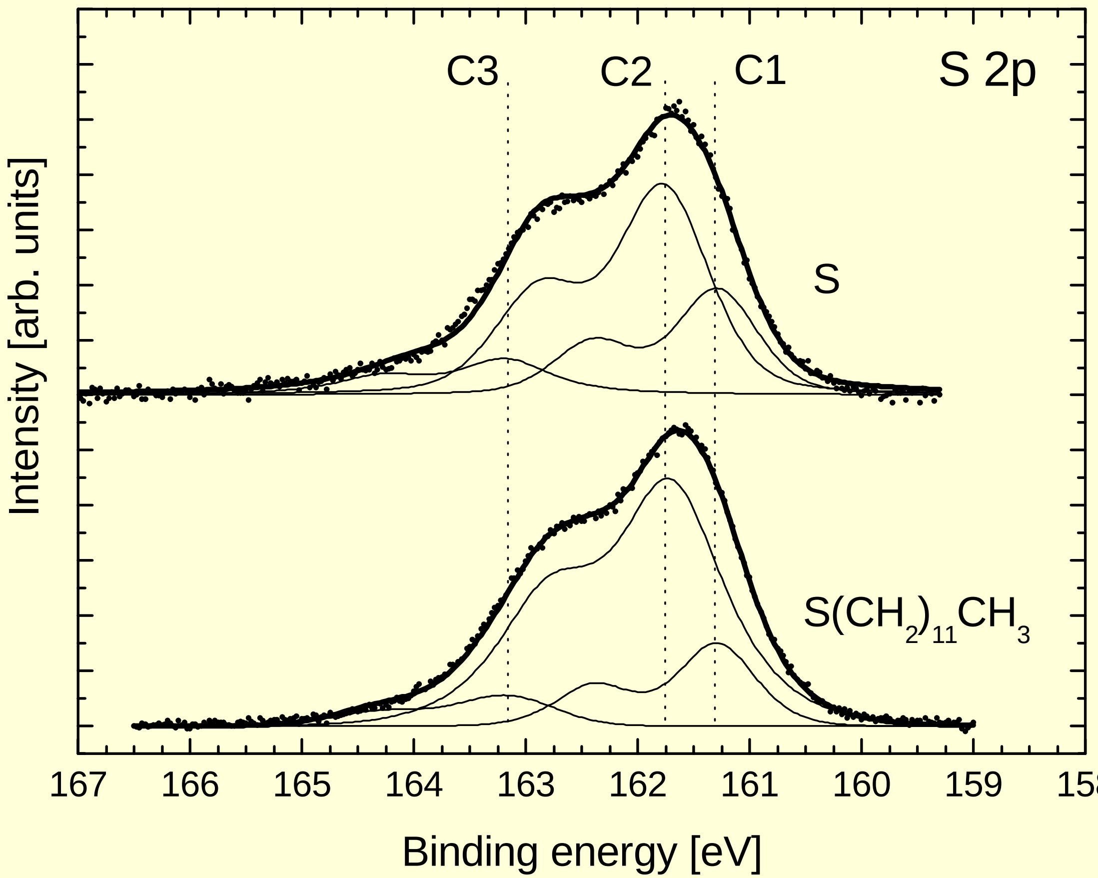
Main factors ruling the stability of SAMs in electrochemical environments



The Electrochemical Stability of SAMs is Extremely Sensitive to the Nature of the Metal Surface !!!

Fonticelli, Azzaroni, Benitez, Carro Salvarezza
Journal of Physical Chemistry B, 108 1898 (2004).

Alkanethiolate SAM composition

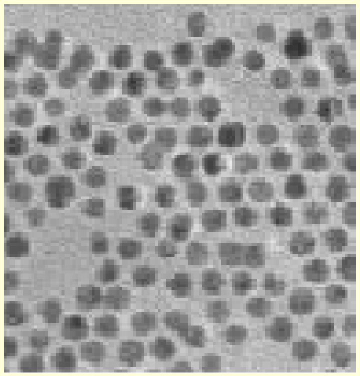


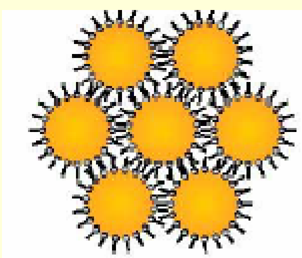
Thiol-Au bond difficult to distinghish from Sulfur-Au bond
Sulfide contamination?
Free thiol molecules physisorbed on SAMs?

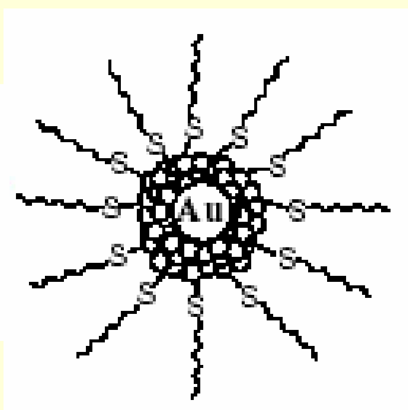
Physisorbed Thiols

(More important for curved surfaces)

Thiol capped
Au nanoparticles







???

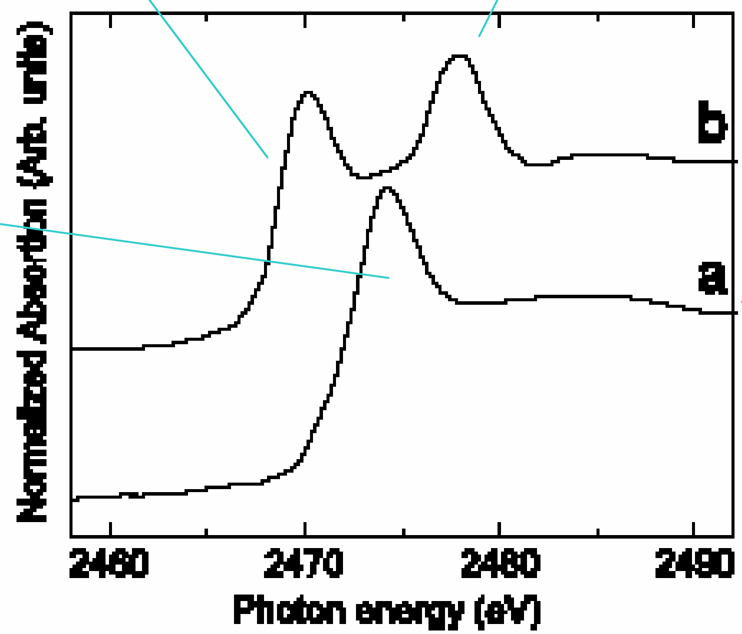
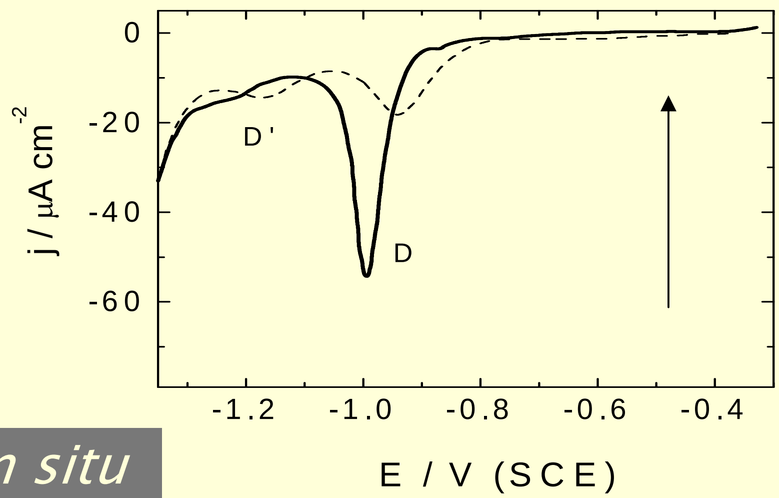


FIG. 1. Sulfur *K*-edge XANES spectra of 1.5-nm Au nanoparticles capped with hexanethiols. (a) Before and (b) after washing in dichloromethane. Weakly bound molecules dominate the spectrum in (a). These molecules are removed by washing in dichloromethane, leaving only the molecules covalently bound to the gold in (b).

J. M. Ramallo-López, L. J. Giovanetti, F. G. Requejo, S. R. Isaacs,Y. S. Shon, M. Salmeron
PHYSICAL REVIEW B **74**, 073410 2006

Dynamics: In situ STM study of hexanethiolate SAM on Au(111)



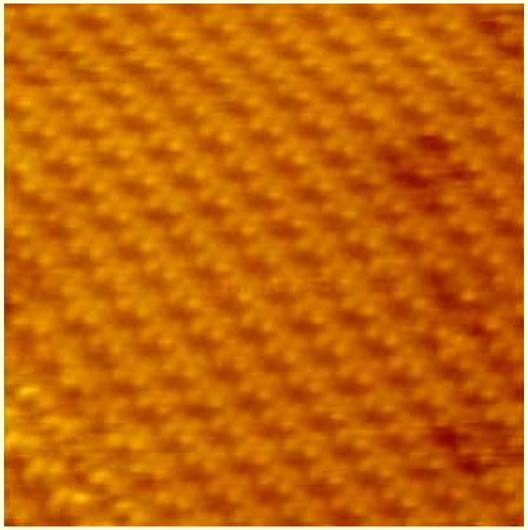
Cathodic polarization curve of hexanethiol-covered Au(111)

Electrolyte 0.1 M NaOH
Solid line first scan, dashed line second scan

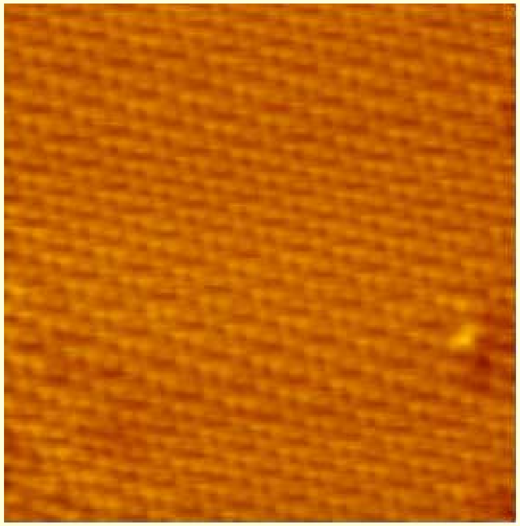
($20x20\ nm^2$) in situ STM images

c(4x2) ⇔ √3x√3 R30° transitions

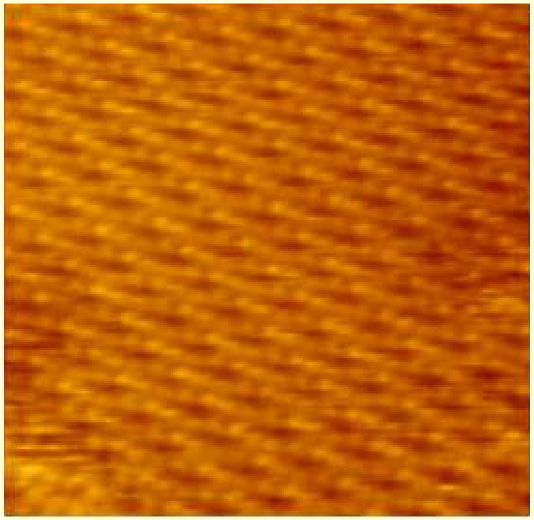
1 min



5 min



10 min



*Vericat, Andreasen, Vela, Martin, Salvarezza Journal of Chemical Physics, **115**, 6672-6678 (2001)*

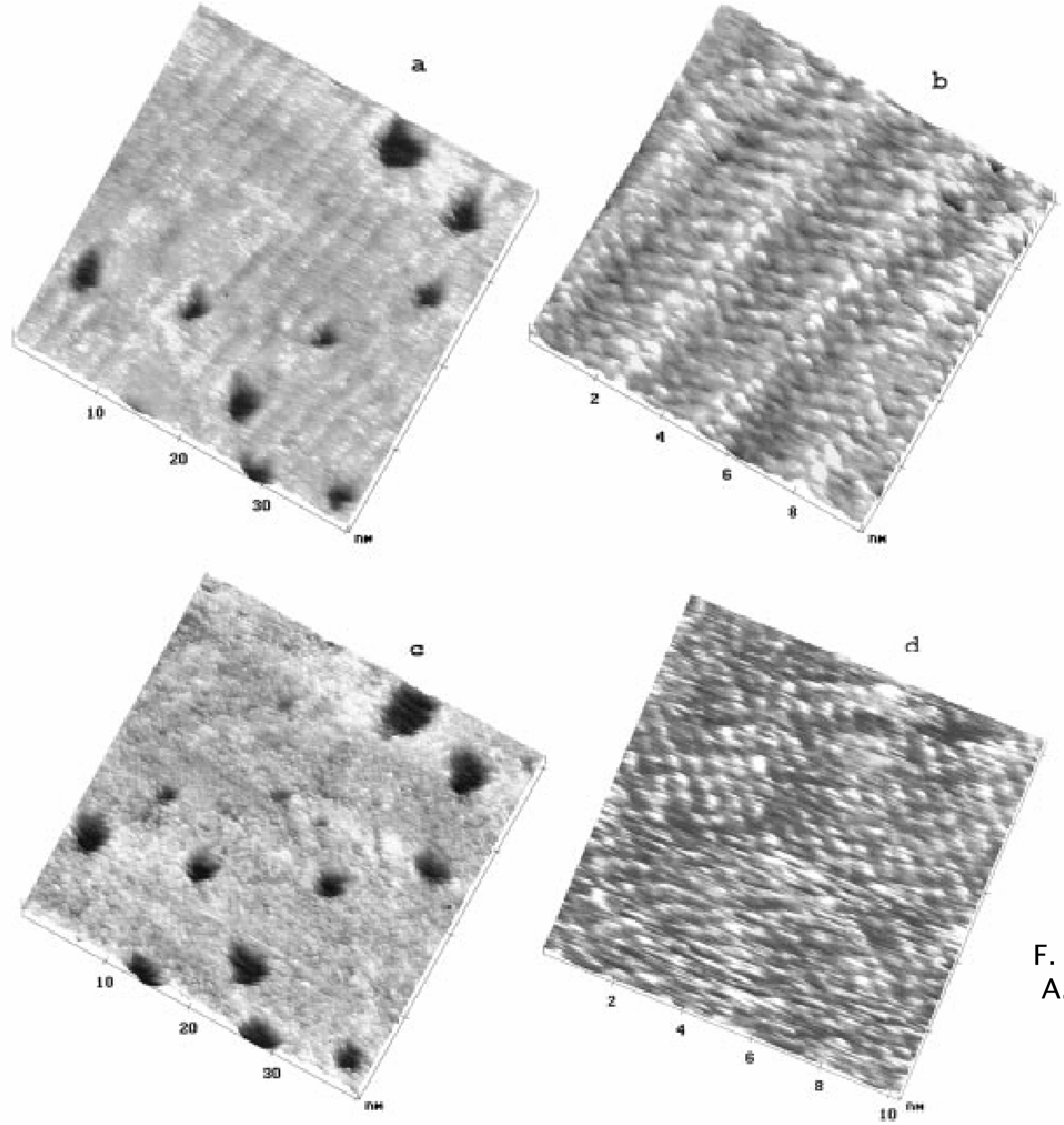
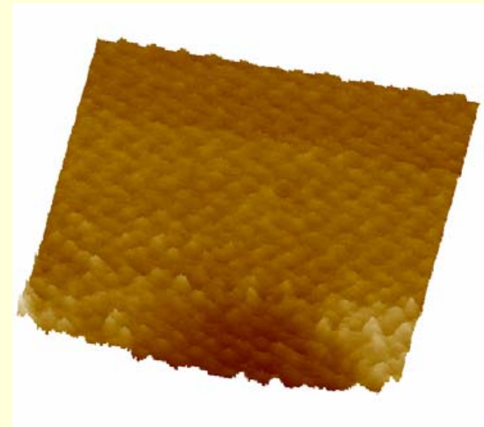


Figure 4. In situ STM images of 1-dodecanethiol-covered Au(111) at 298 K showing the spontaneous change occurring at ordered adlayer domains. (a) Stripelike pattern resulting from $t = 3$ h. (b) High-resolution image of the image shown in part a. The p(6×1) lattice can be observed. (c) Image of the same domain shown in part a for $t = 3$ h 4 min. (d) High-resolution image of the image shown in part c. The ($\sqrt{3}\times\sqrt{3}$)R30° lattice can be observed.



F. Teran Arce, M. E. Vela, R. C. Salvarezza, A. J. Arvia*Langmuir* 1998, *14,* 7203-7212

Substrate mobility: hole coalescence

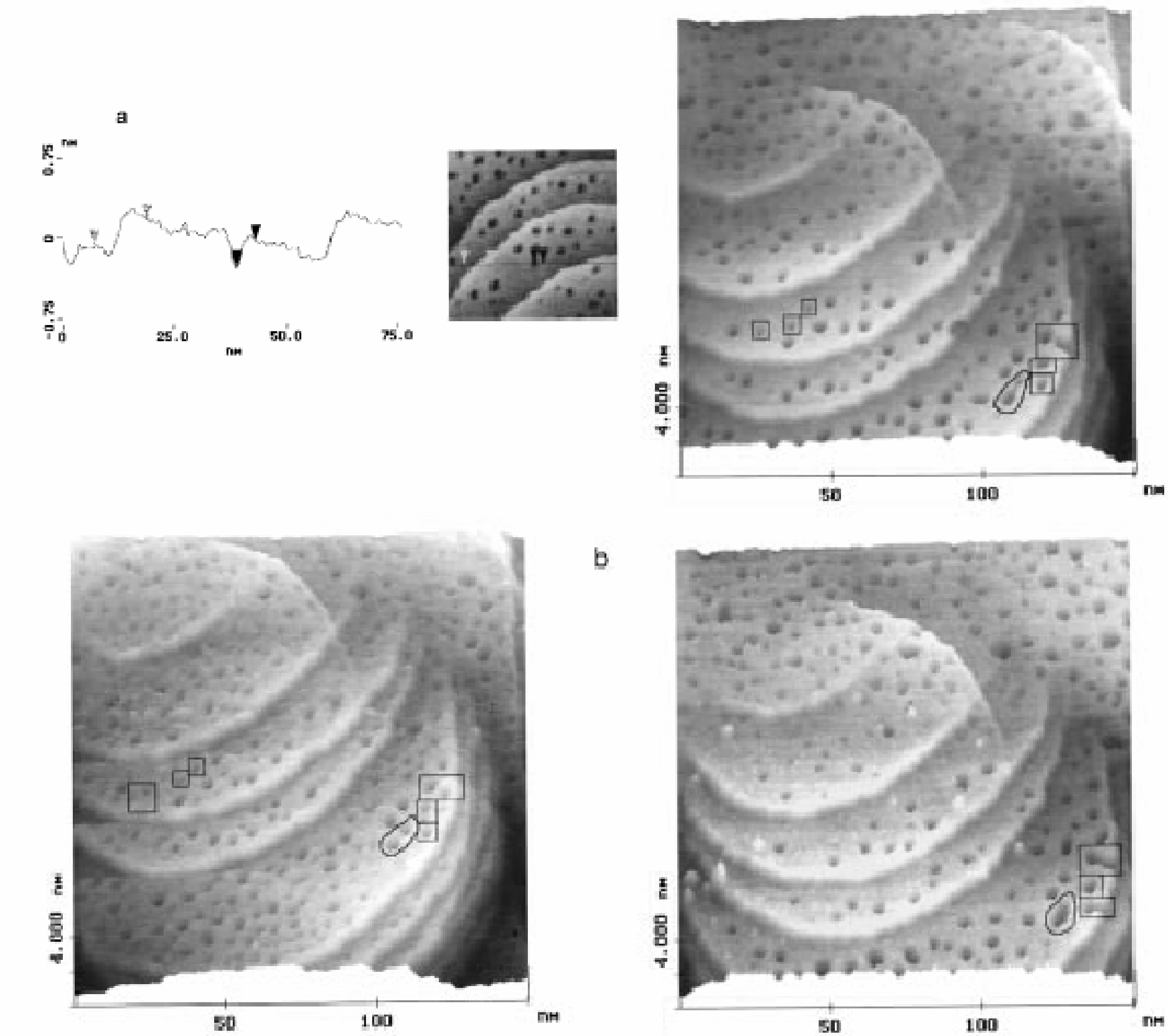
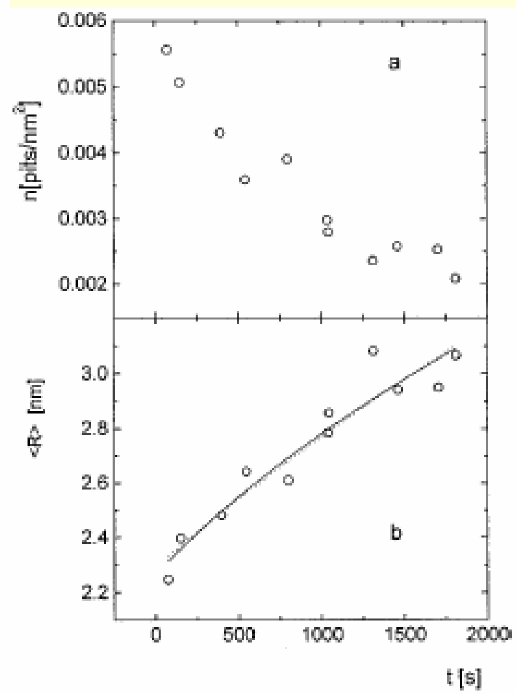
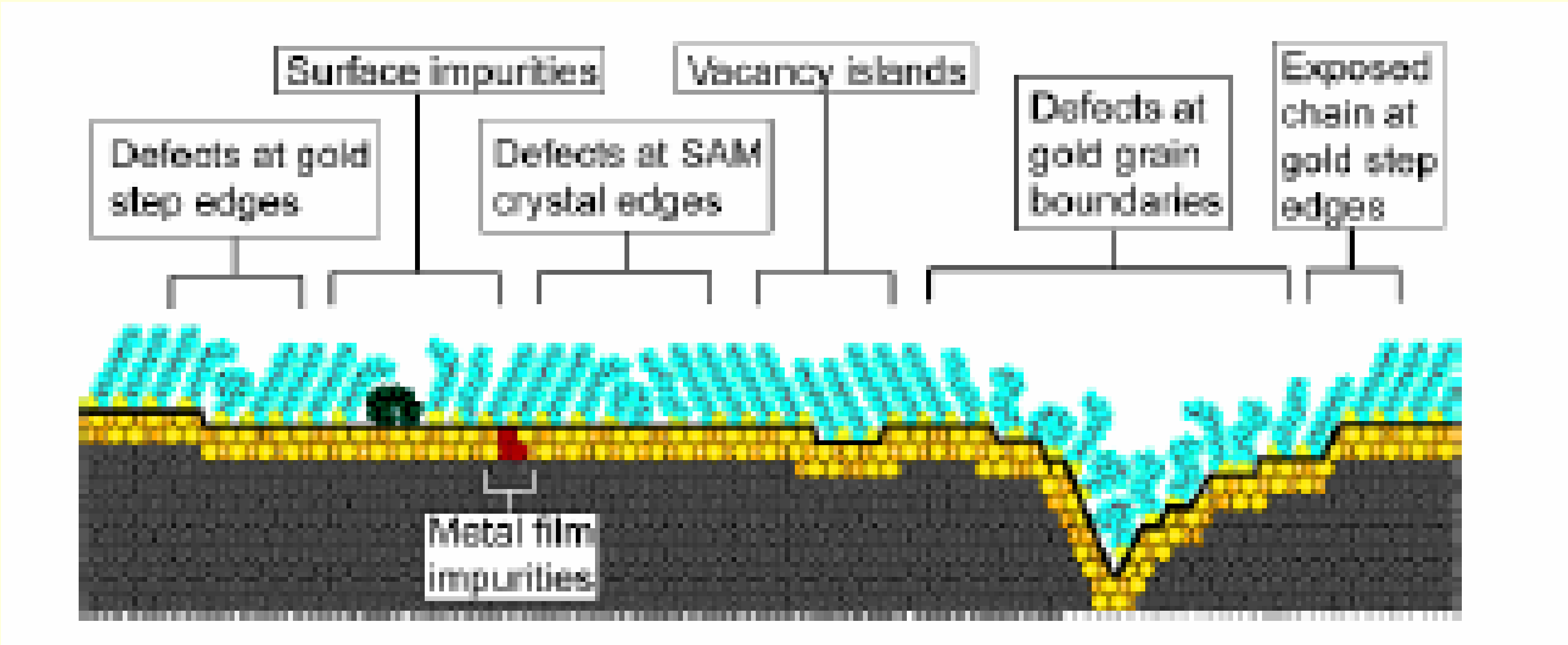


Figure 1. In situ STM images of 1-dodecanethiol-covered Au(111) at 298 K. (a) Cross section showing terraces separated by monatomic high steps and monatomic deep pits. (b–d) STM images of the same domain taken for different Au(111)/pure 1-dodecanethiol contacting times t: (b) $t = 9$ min 6 s; (c) $t = 21$ min 54 s; (d) $t = 30$ min 12 s.

Mass transport surface diffusion coefficient gold adatoms (thiol-covered) $\approx 10^{-18}$ cm^2 s^{-1}
Clean gold $\approx 10^{-15}$ cm^2 s^{-1}

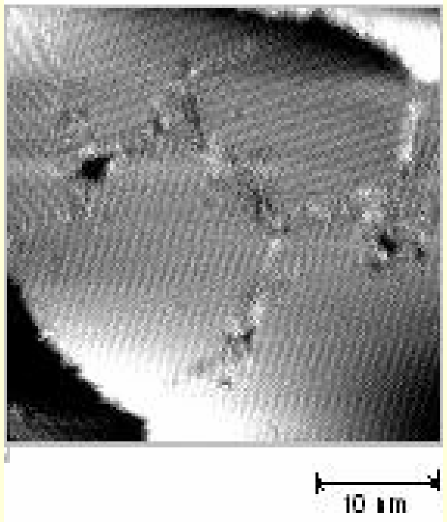


SAMs quality: defects

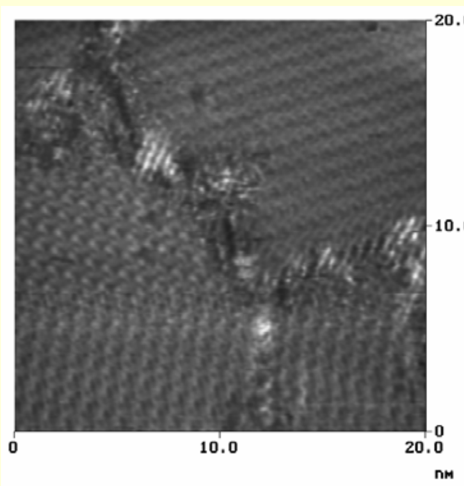


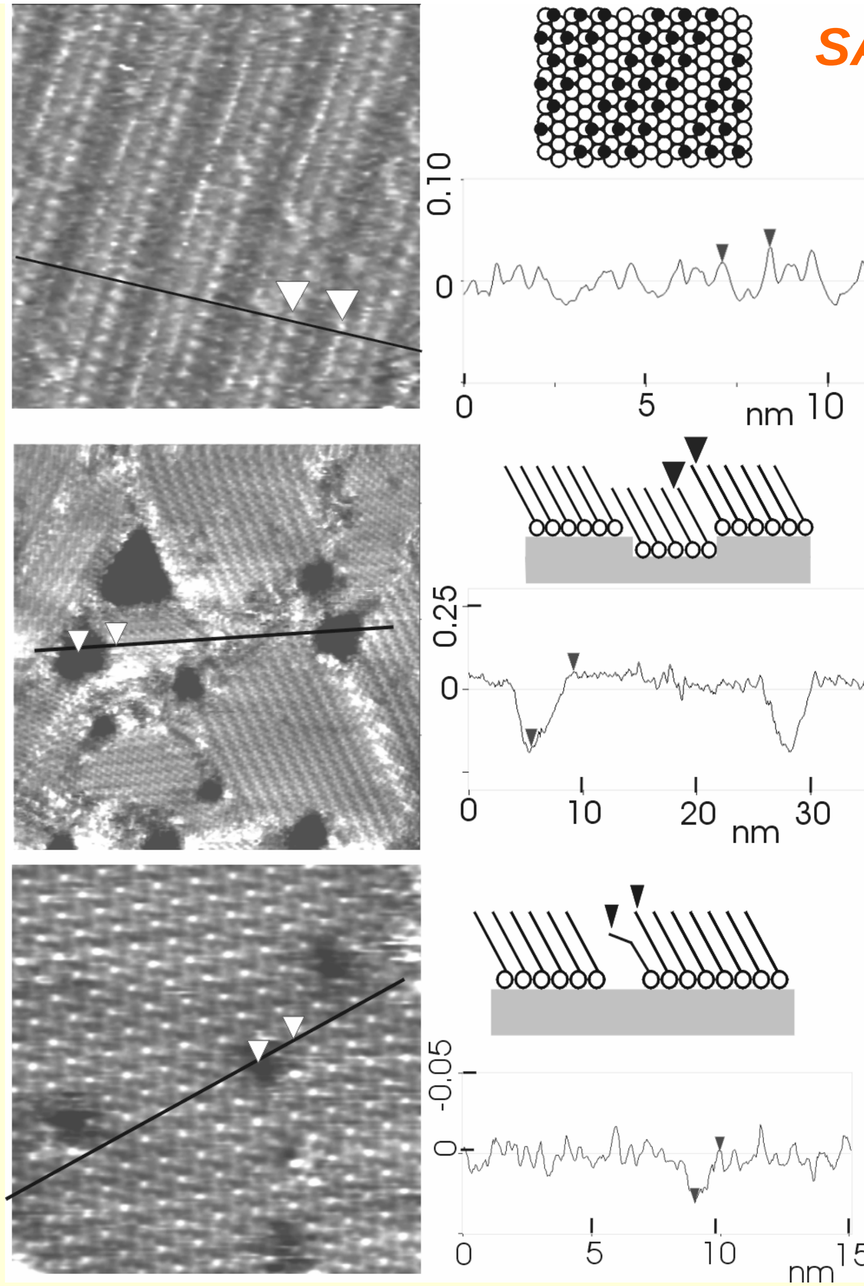
Love, Estroff, Kriebel, Nuzzo,Whitesides
Chemical Reviews, 2005, Vol. 105, No. 4 1121

SAMs quality: defects



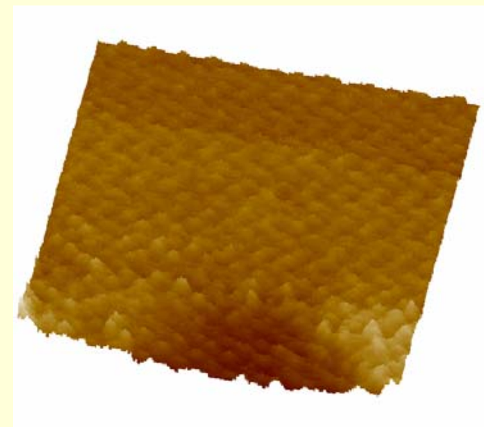
Domain boundaries





Missing rows in √3 x√3 R30

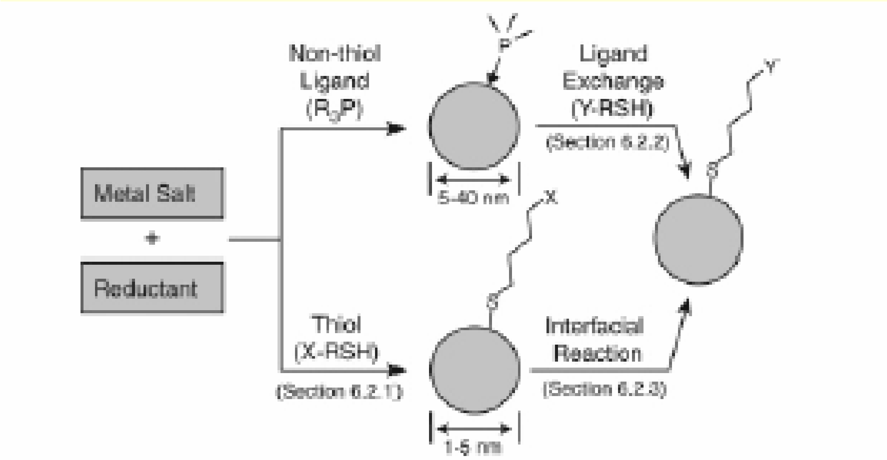
Depressions



Molecular defects

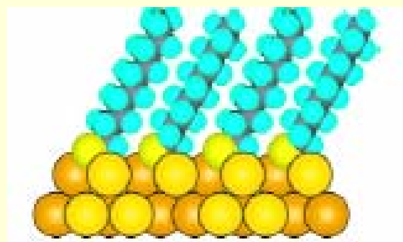
Benítez, Vericat, Tanco, Remes Lenicov, Castez, Vela, Salvarezza Langmuir **20** 5030 (2004)

SAMs on curved surfaces: Nanoparticles

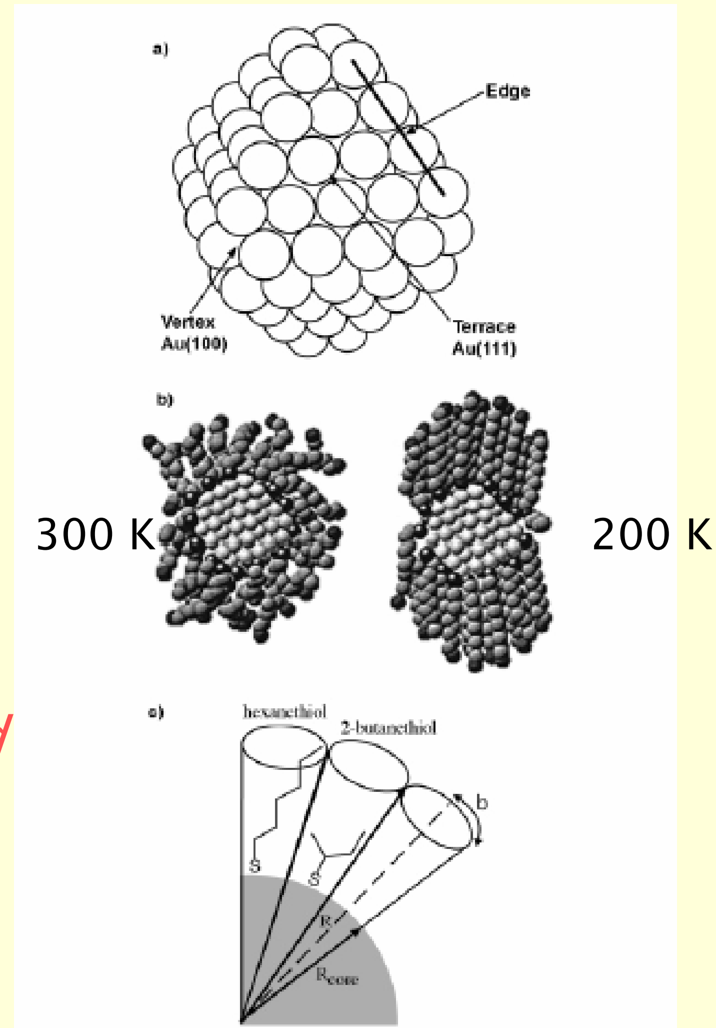


$$AuCl_4^- \text{ (toluene)} + RSH \rightarrow (-Au^ISR-)_n\text{(polymer)} \quad (2)$$

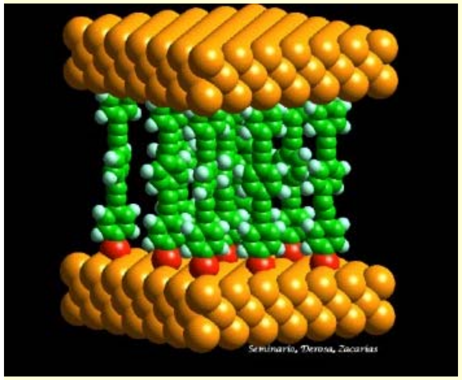
$$(-Au^ISR-)_n + BH_4^- \rightarrow Au_x(SR)_y \quad (3)$$



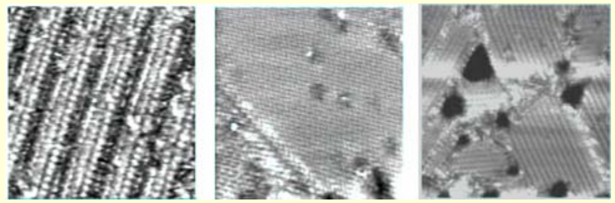
planar vs curved surfaces



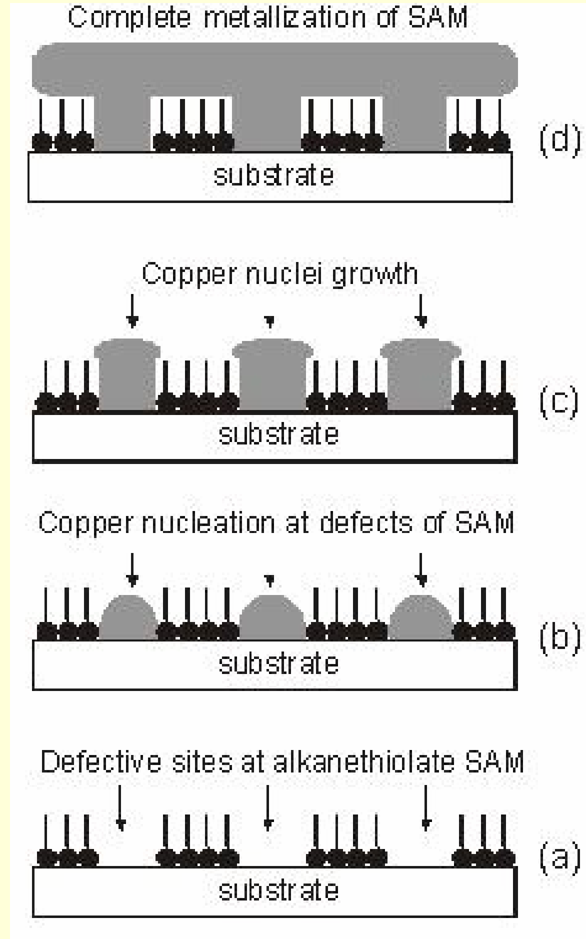
Love, Estroff, Kriebel, Nuzzo,Whitesides
Chemical Reviews, 2005, Vol. 105, No. 4 1121



Defects at SAMs



Metal penetration into SAMs



One of the biggest problems with molecule-based devices is poor yield. Often the overall device yield will be significantly less than 10 %, sometimes less than 1 %. Most of the degradation occurs at the final metallization step, which it is called the "top contact problem".

Decrease defect density (annealing)
Use functionalized thiols (-COOH, -OH, -OCH_3)
Induce cross-linking in phenyl thiol by electron irrediation

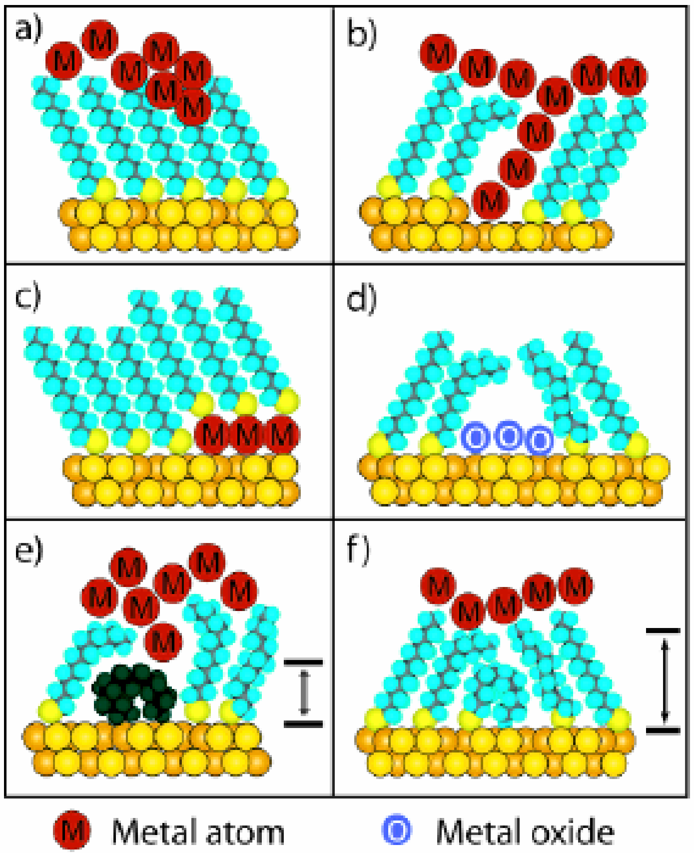


Figure 17. Schematic illustration of the types of defects in SAMs that can influence the rate of electron transfer in two-terminal (or three-terminal) devices. (a) Chemical reaction with the organic component of SAMs during evaporation of metal films. (b) Formation of metallic filaments during evaporation or operation of the device. (c) Deposition of adlayers of metal on the surface of the substrate supporting the SAM. (d) Formation of oxide impurities on the surface. (e) Organic (or organometallic) impurities in the SAM. (f) Thin regions in the SAM resulting from conformational and structural defects. In e and f the dimension normal to the surface that is denoted by the black arrows indicates the approximate shortest distance between the two metal surfaces; note that these distances are less than the nominal thickness of the ordered SAM.

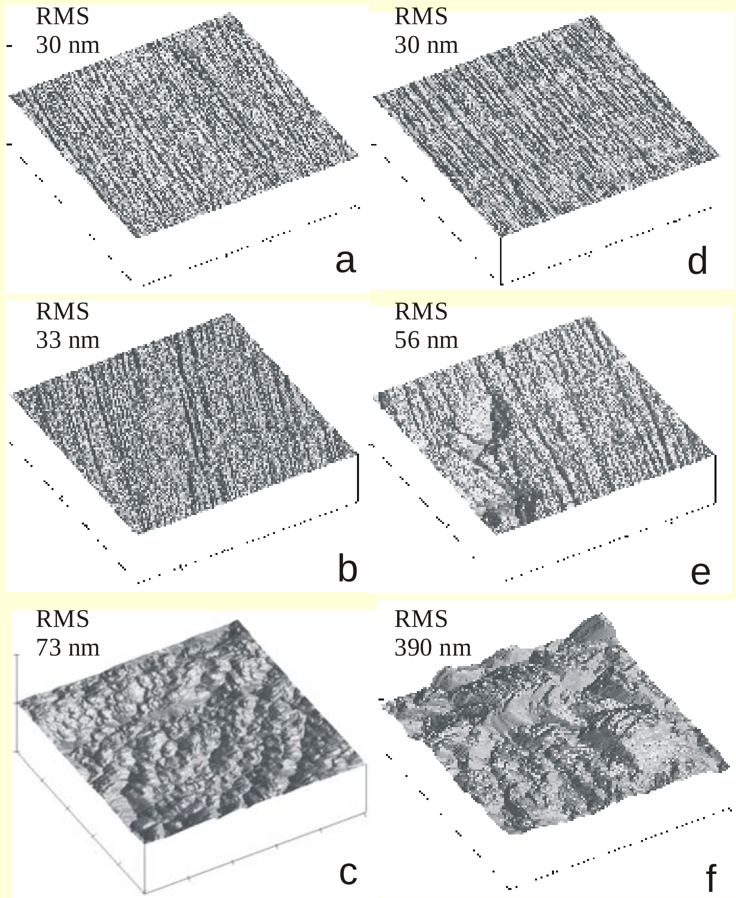
Love, Estroff, Kriebel, Nuzzo,Whitesides
Chemical Reviews, 2005, Vol. 105, No. 4 1121

Inhibition of Copper Corrosion by using dodecanethiol layers

Cu polished substrate

Thiol-covered Cu

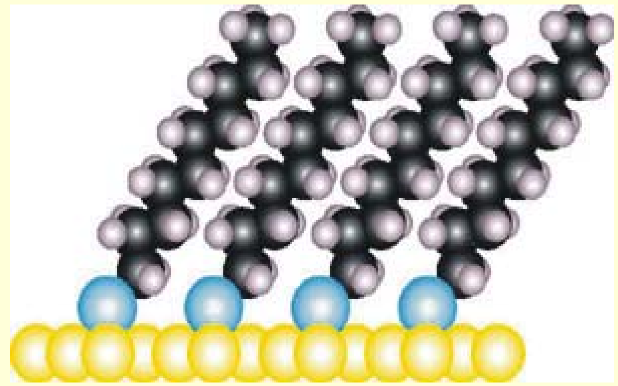
Thiol-free Cu



0.1 M NaCl
4 days immersion

1M Na Cl
4days immersion

Highly hidrophobic chains

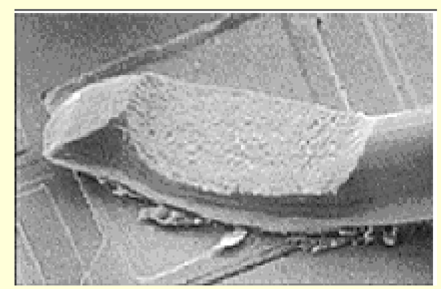


Blocking the transport of water and hydrated species to the metal surface

*A. Azzaroni, M. Cipollone, M.E. Vela, R.C. Salvarezza Langmuir, **17**, 2483(2001)*

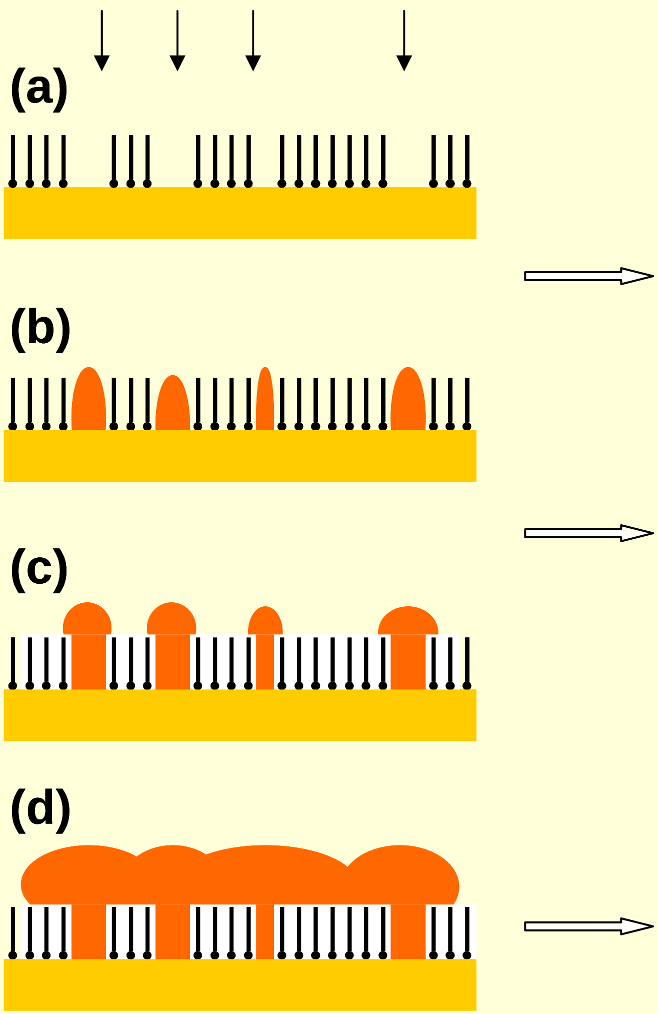
ORGANIC FILMS FOR PROTECTION OF COPPER AND BRONZE AGAINST ACID RAIN CORROSION
G. Brunoro, A. Frignani, A. Colledan, C. Chiavari
Corrosion Science, Vol. 45, pp. 2219-2231 (2003).

INHIBITION OF COPPER CORROSION BY SILANE COATINGS
F. Zucchi, V. Grassi, A. Frignani, G. Trabanelli
Corrosion Science, Vol. 46, pp. 2853-2865 (2004).

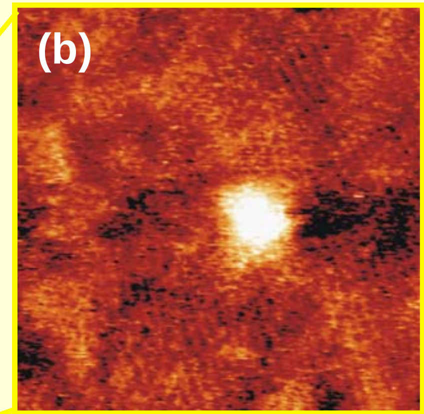


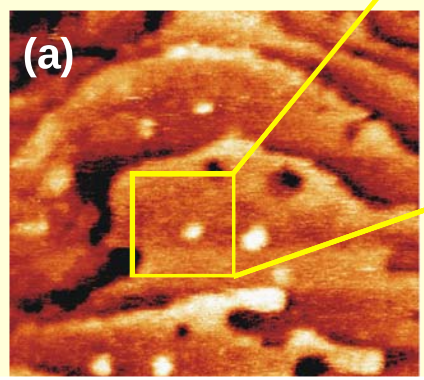
Corrosion Inhibition by Thiol-Derived SAMs for Enhanced Wire Bonding on Cu Surfaces
Caroline M. Whelan Michael Kinsella Hong Meng Ho, Karen Maex
Department of Electrical Engineering, Katholieke Universiteit Leuven, Belgium , JES January 8, 2004)

Preparation of metal supported nanoparticles by confined growth at molecular defects

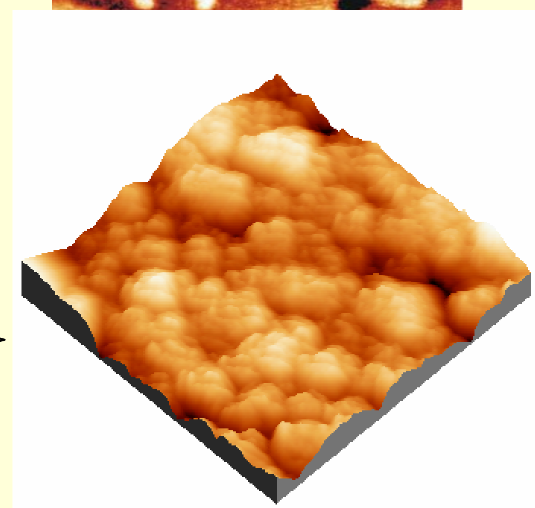


lateral: 5 nm
height : 0.3 nm



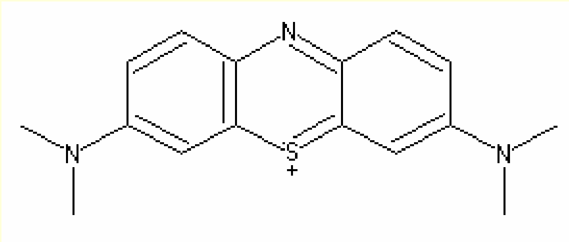


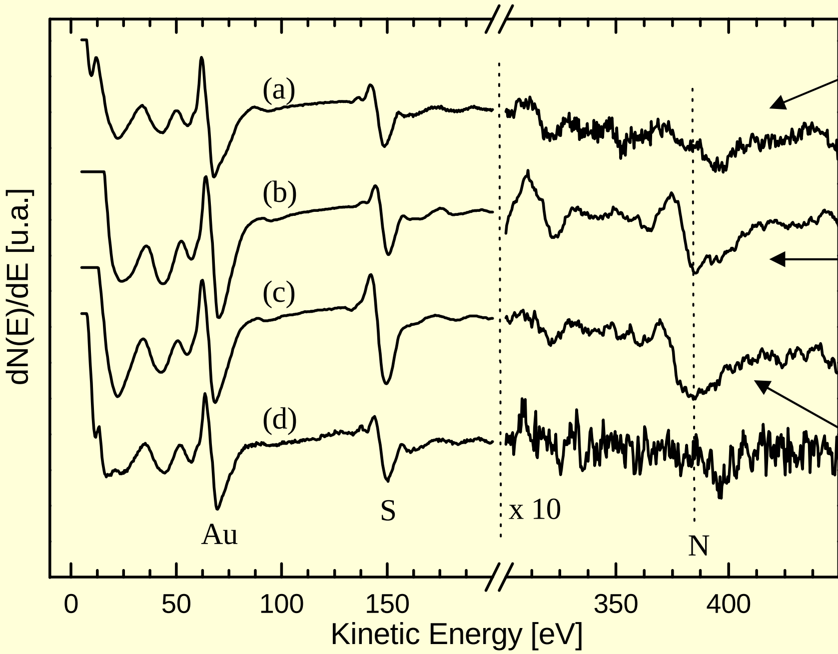
Cu deposited on dodecanethiol covered Au



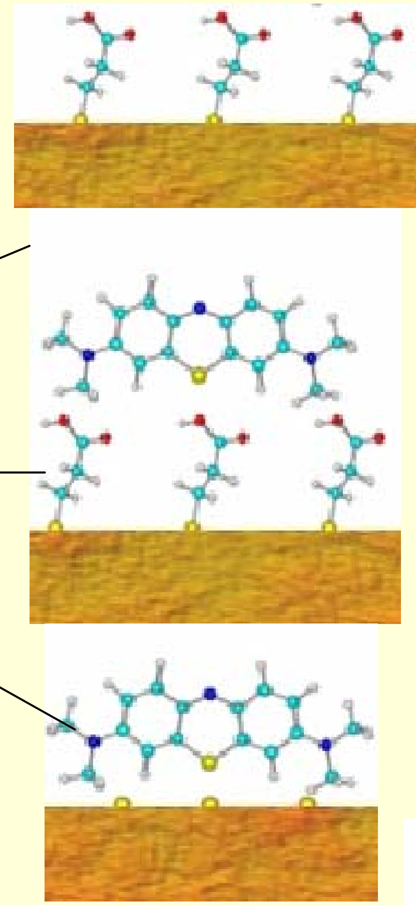
Poorly connected deposit –preparation of standing free films (Cu, Ni, Co)

Trapping molecules and ions: Methylene Blue on alkanethiolate SAMs

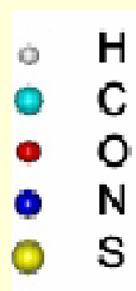


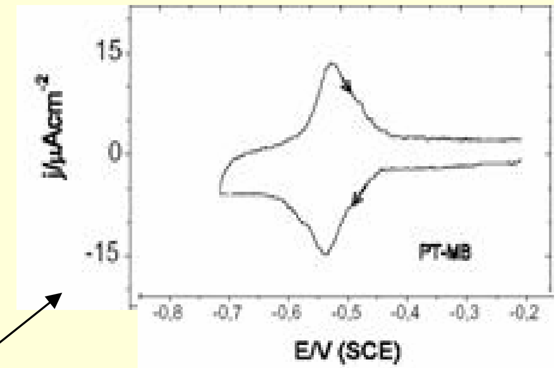


AES spectra

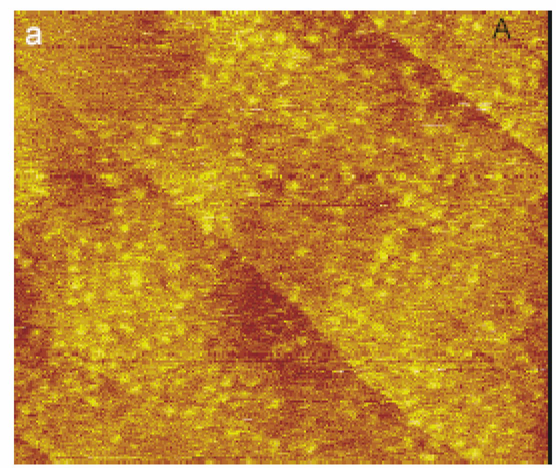


Au(111)



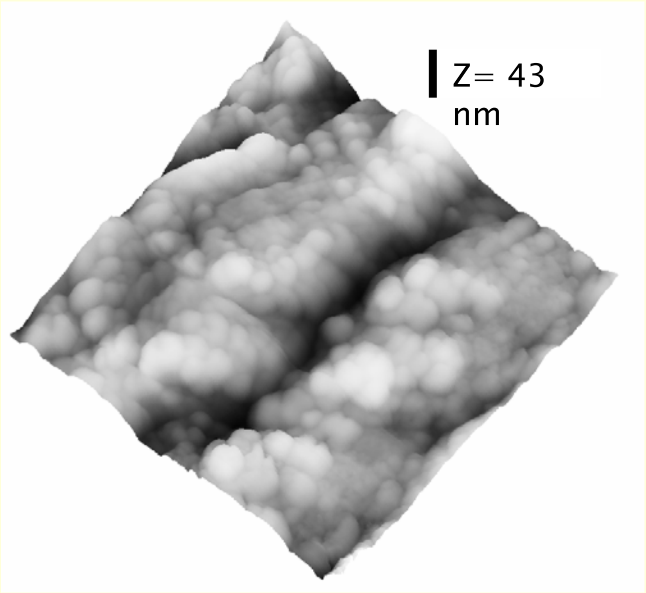


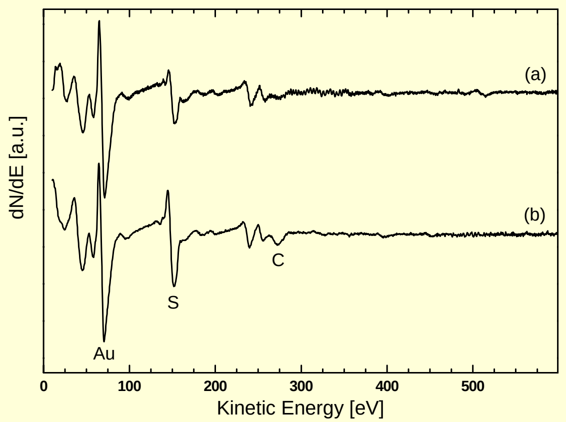
MB dimers?

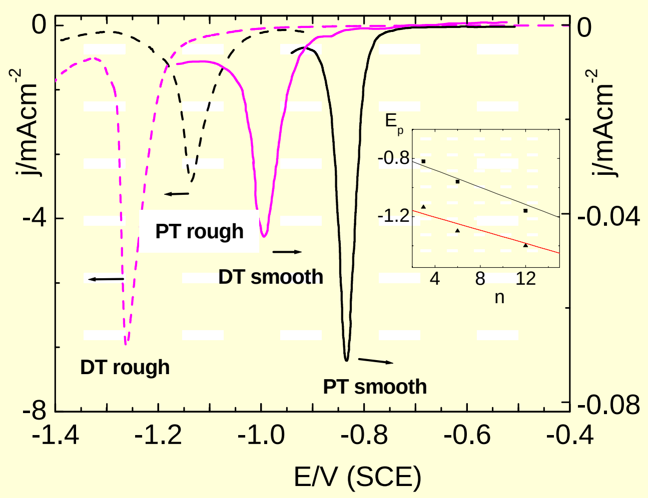


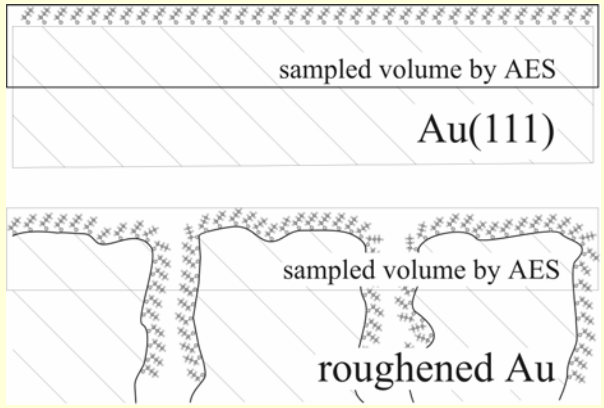
Benítez,Vericat, Tanco, Remes Lenicov, Castez, Vela, Salvarezza
*Langmuir, **20**, 5030-5037 (2004).*

Nanostructured gold surfaces (high-area)

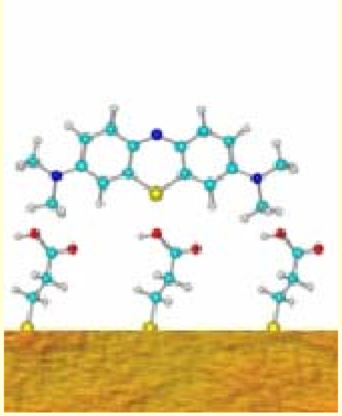




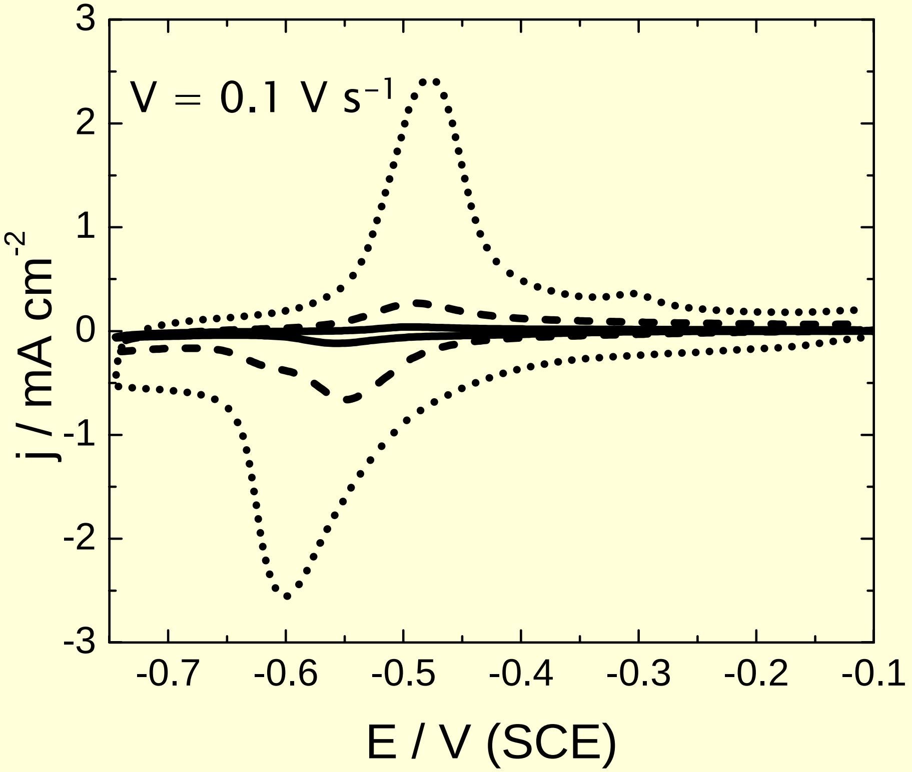




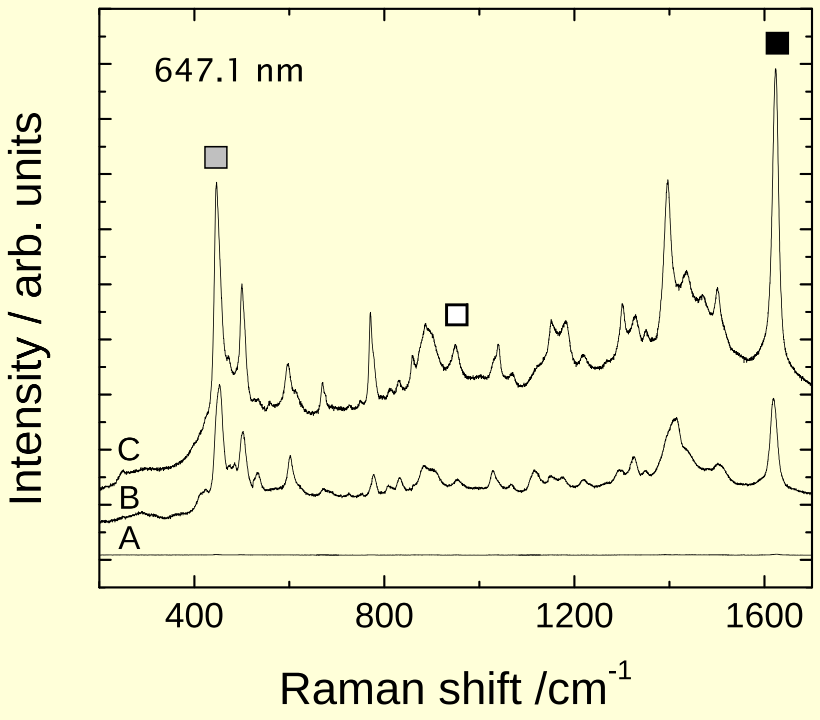
Nanoestructured gold surfaces



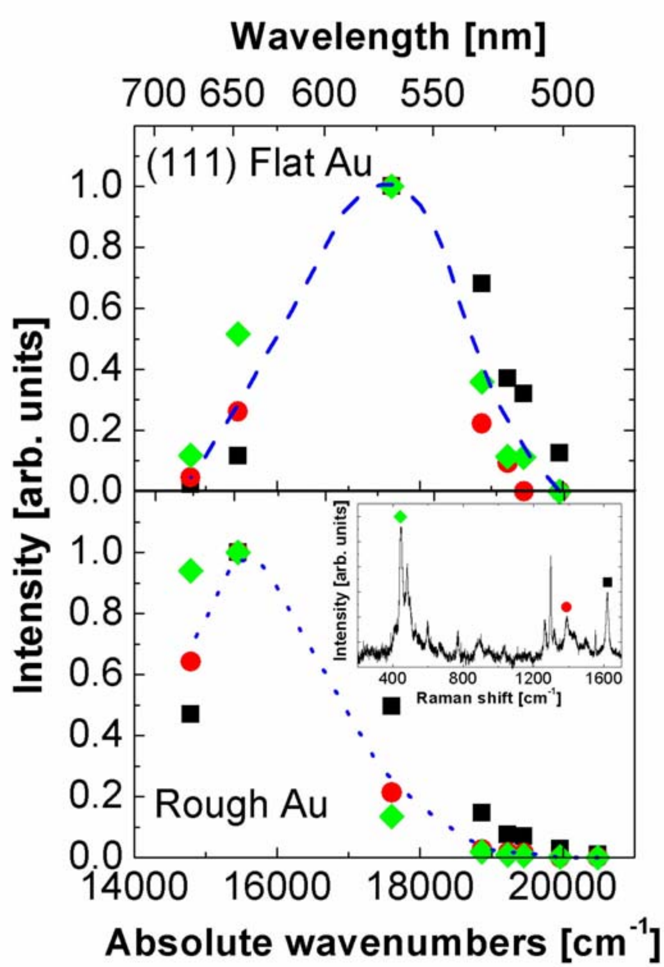
Methylene Blue
Redox behavior

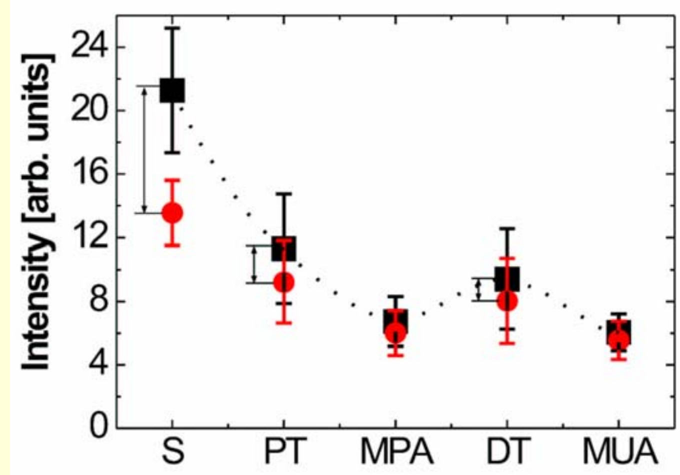


Methylene Blue
Raman

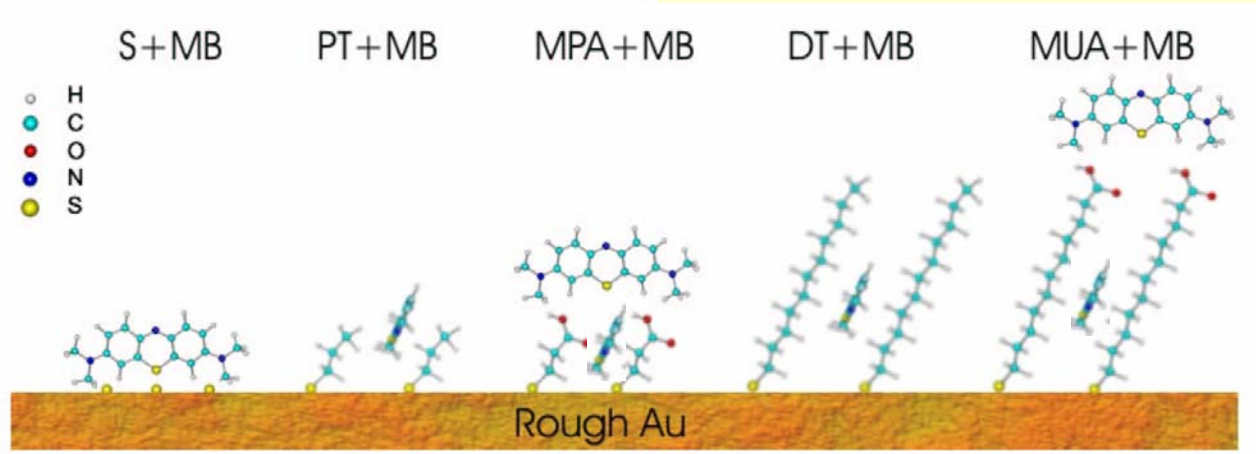


Electrochemical and optical sensors



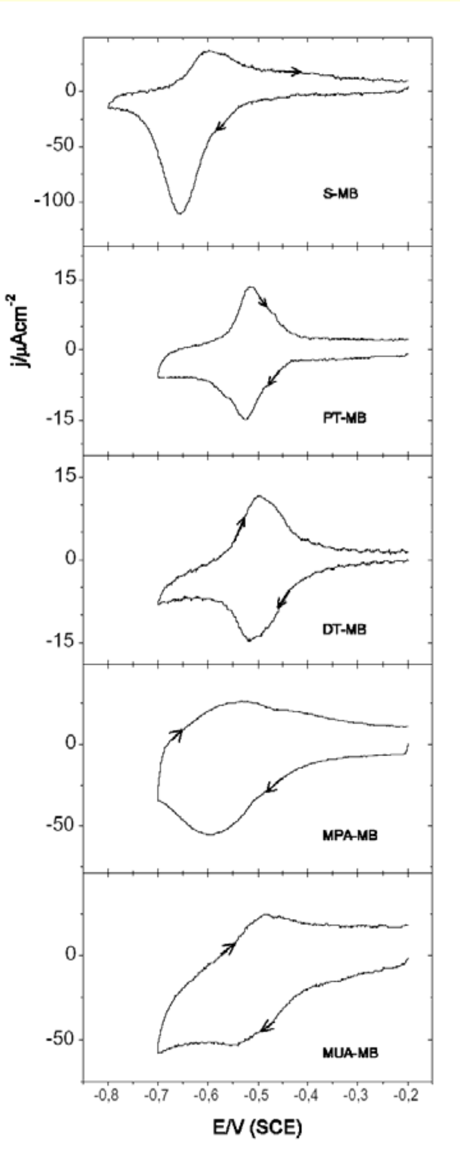


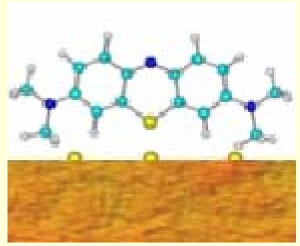
SERS pre-resonant yellow laser line 568 nm (circles). Fully SERS resonant red line 647 nm (squares).

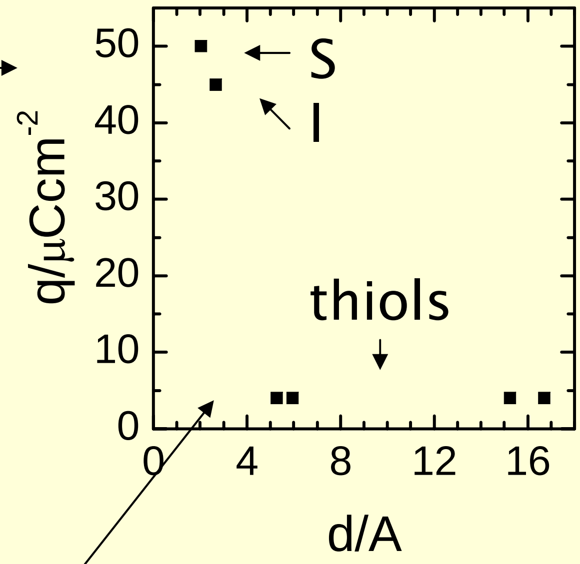


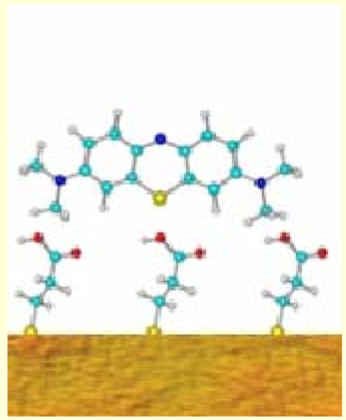
N. Tognalli, A. Fainstein C. Vericat, M Vela, R. C. Salvarezza, J. Phys. Chem. B **2006,** *110,* 354-360

Amount of electrochemically active MB vs spacer size

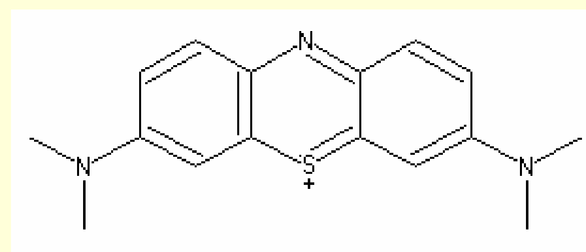




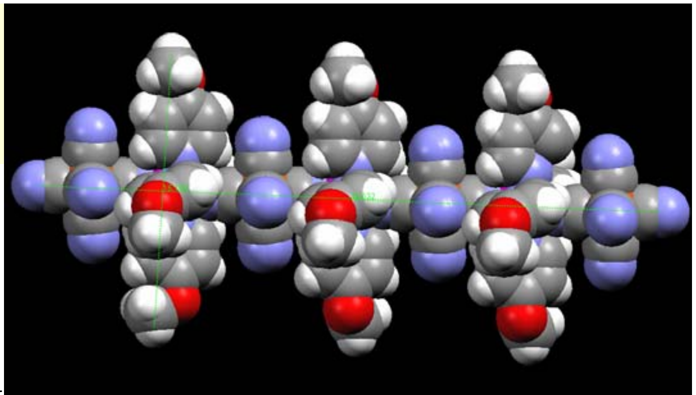


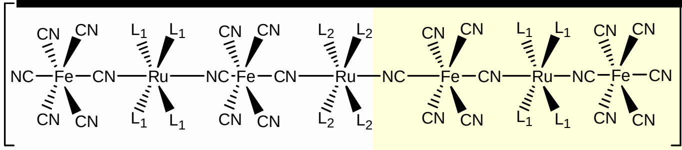


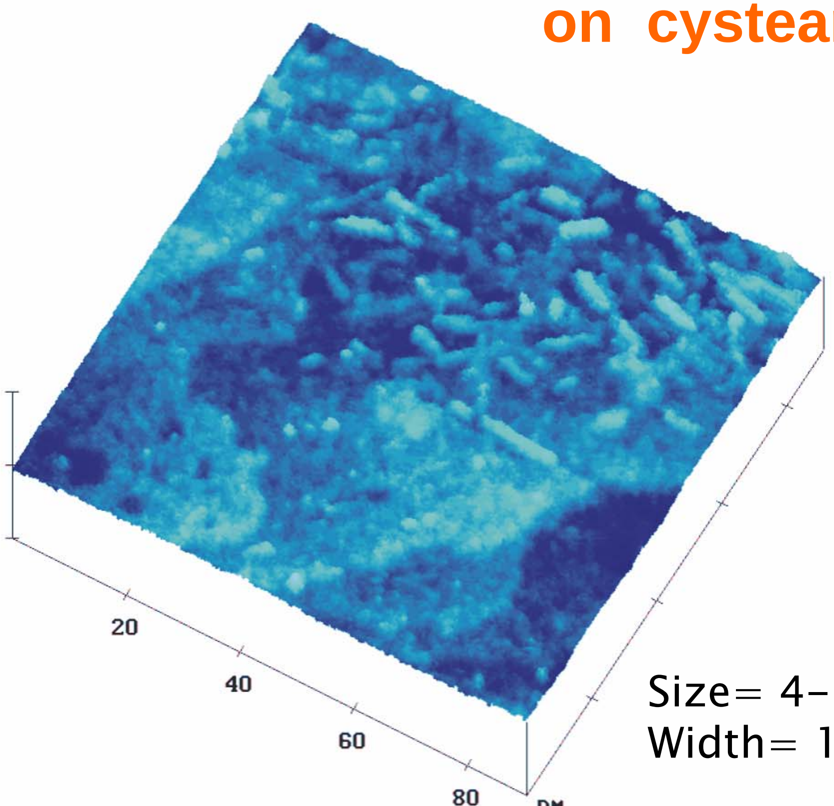
Electrochemically active MB for different thiols (spacers)

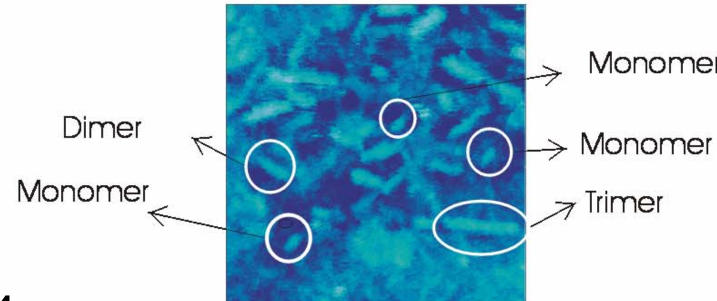


Molecular Wires: Negatively charged Fe-Ru complexes on cysteamine-Au(111)









Size= 4-14 nm
Width= 1.7-2 nm

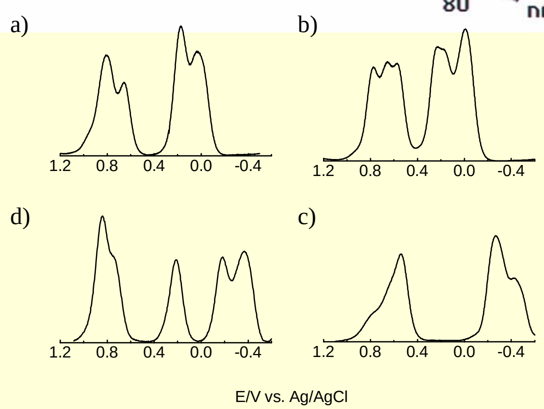
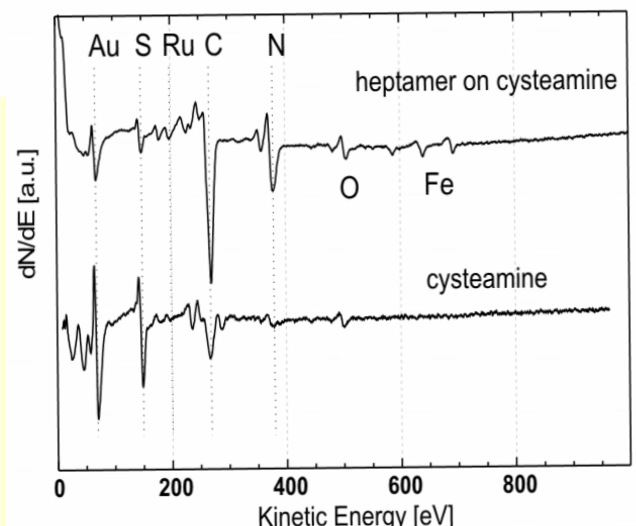


Figure 3- Square wave voltammetry for anions **1** (a) and **2** in water (b) and **2** (c) and **3** (d) in methanol.

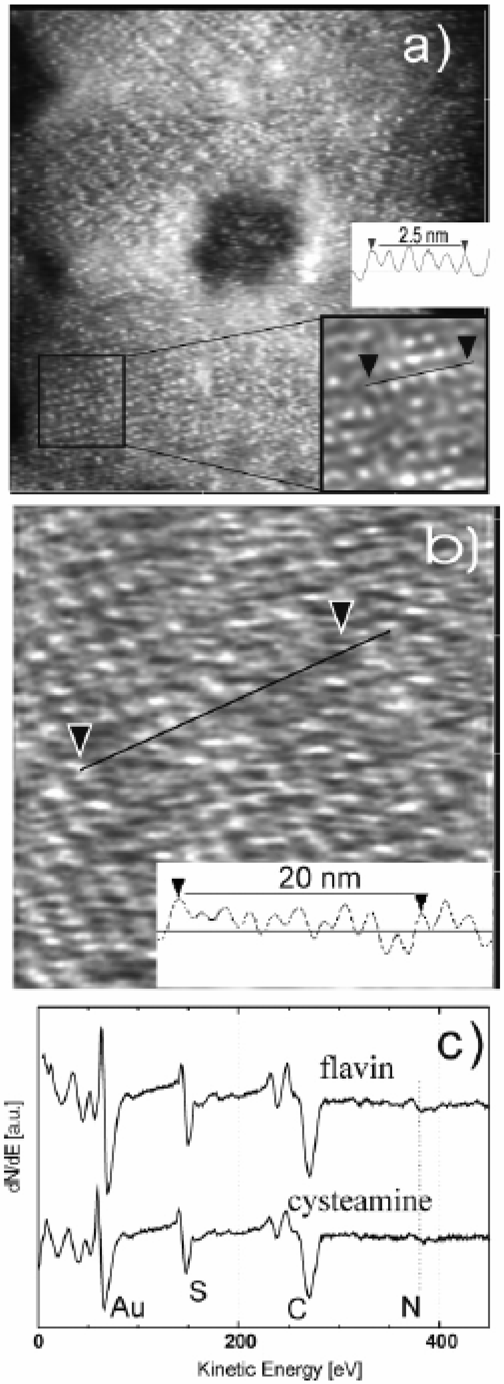
Voltammetry

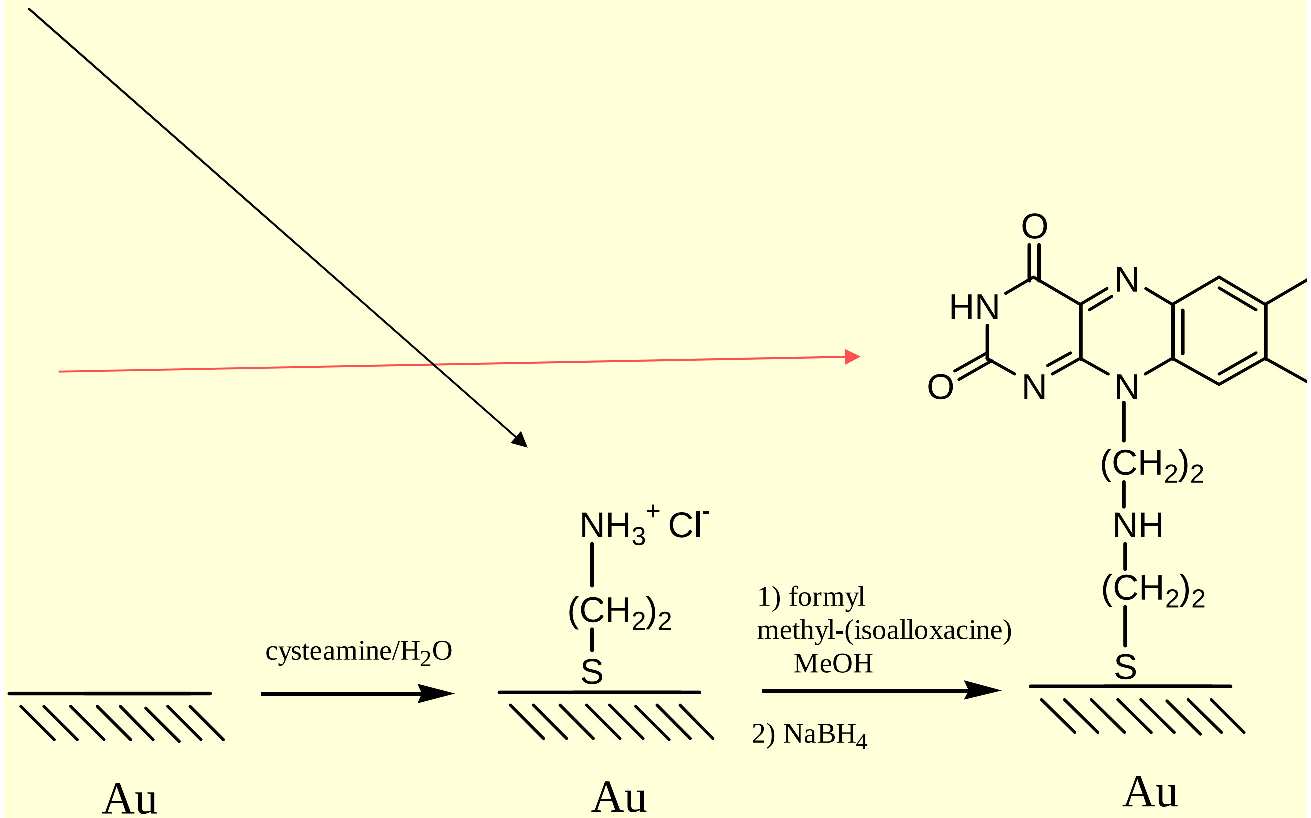
AES



Alborés, Slep, Baraldo, Benítez, Vela, Salvarezza submitted

Covalent binding to functionalized SAMs

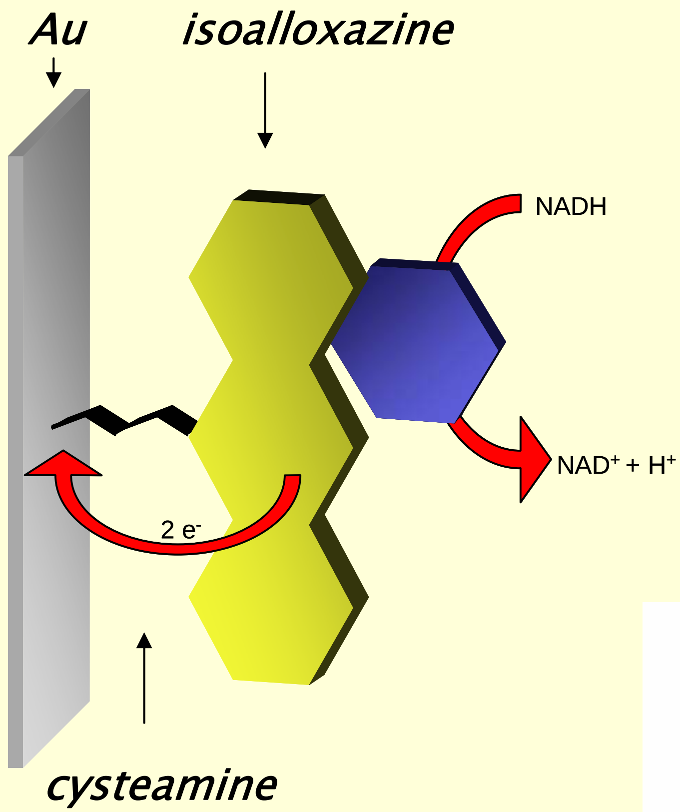


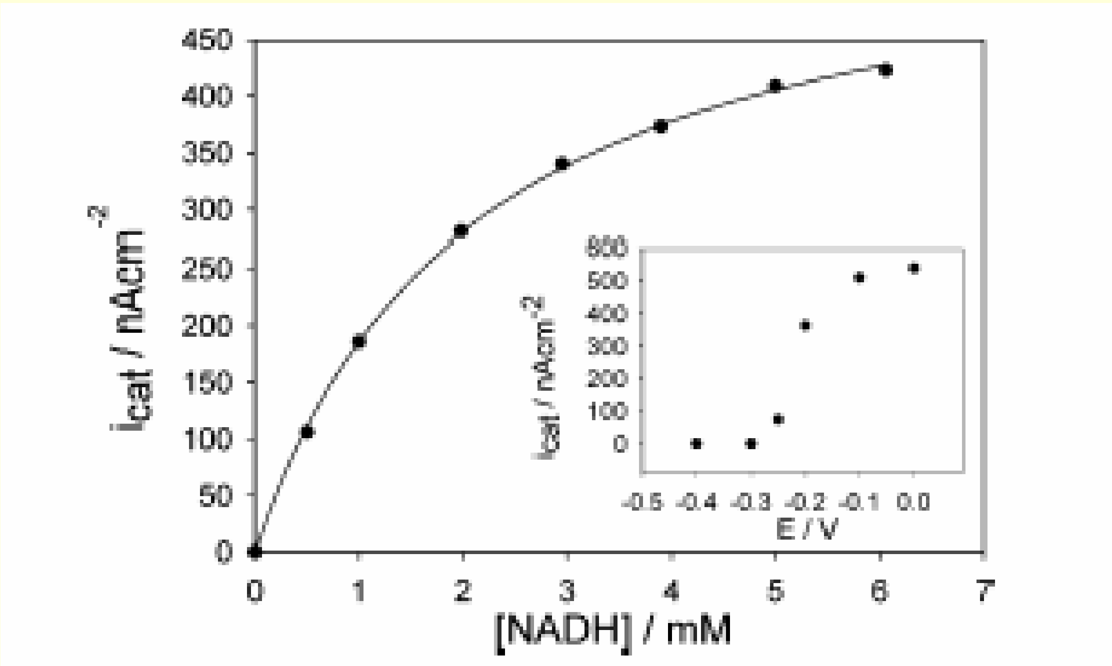


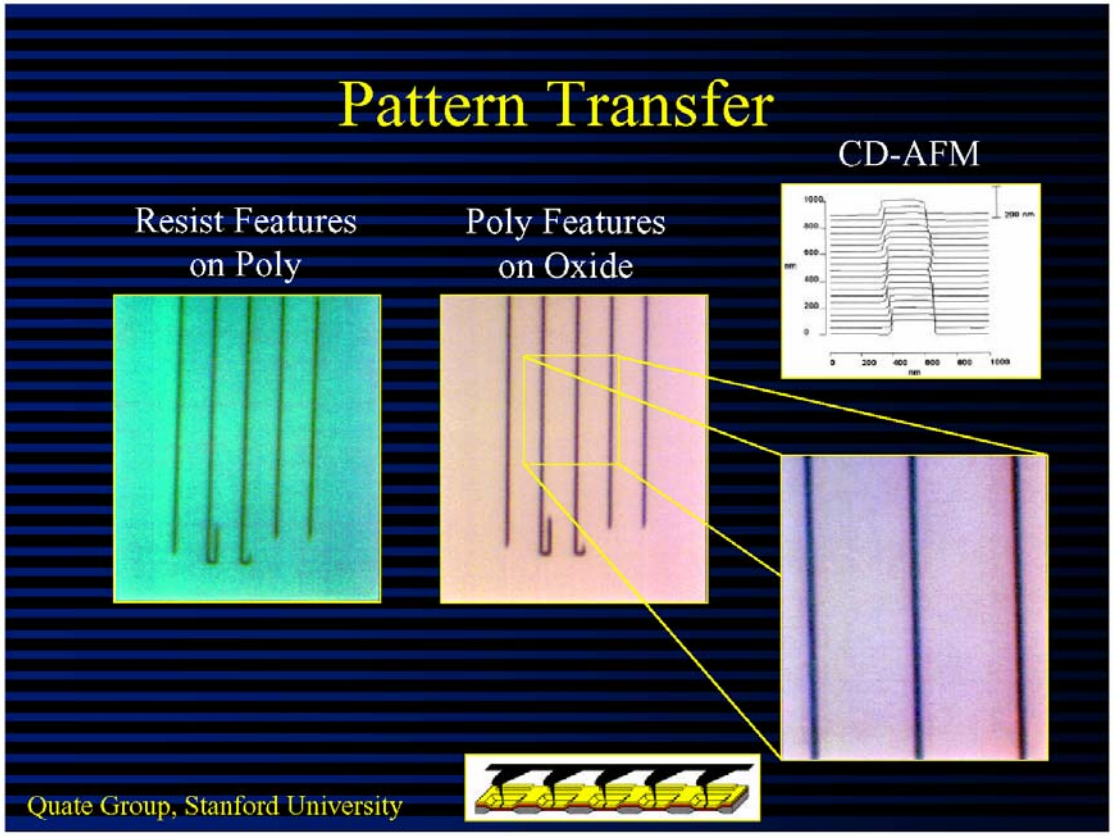
AES: SAM survives during the chemical reaction !!

E. J. Calvo, M. Rothacher†, C. Bonnazzola Wheeldon†, R. Salvarezza , M. E. Vela, G. Benitez, Langmuir 21, 7907-7911, (2005)

Biomimetics with self-assembled monolayer of catalytically active tethered isoalloxazine on Au







Chem. Rev. 2005, *105*, 1171–1196

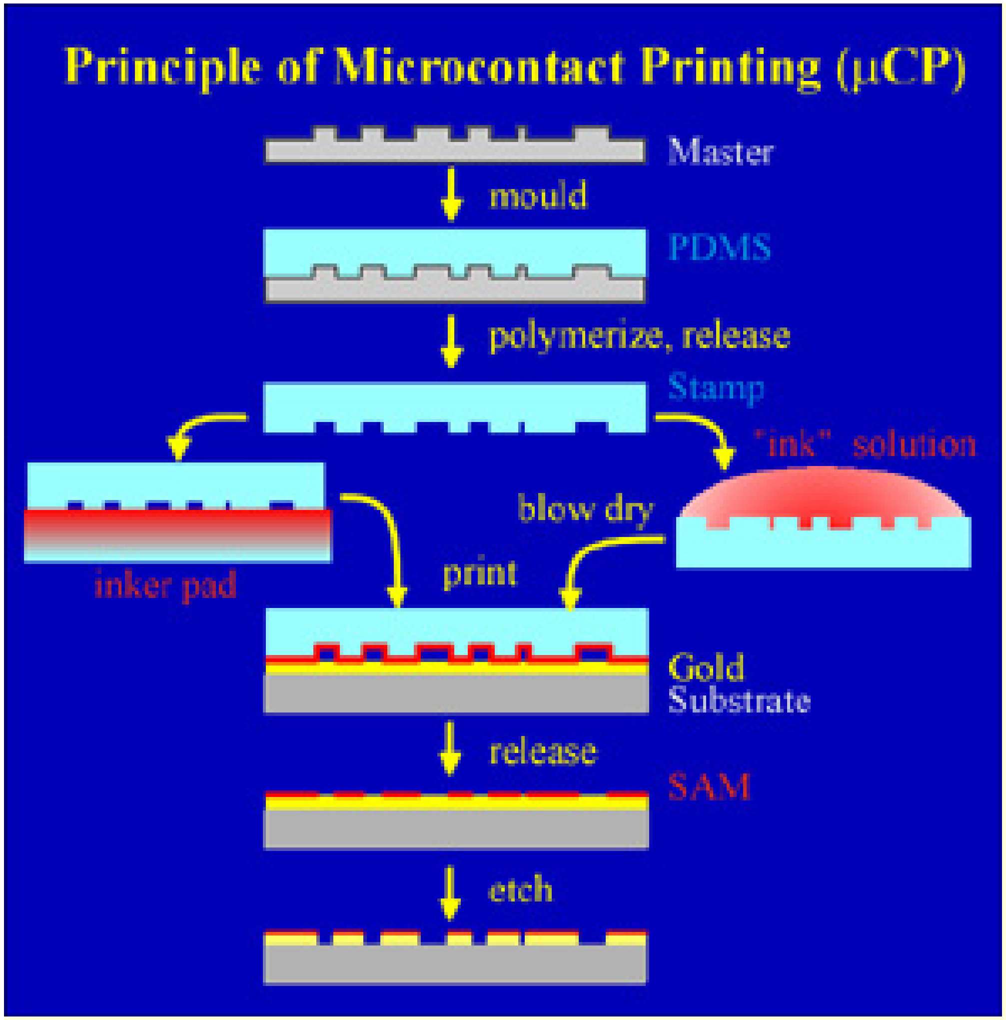
New Approaches to Nanofabrication: Molding, Printing, and Other Techniques

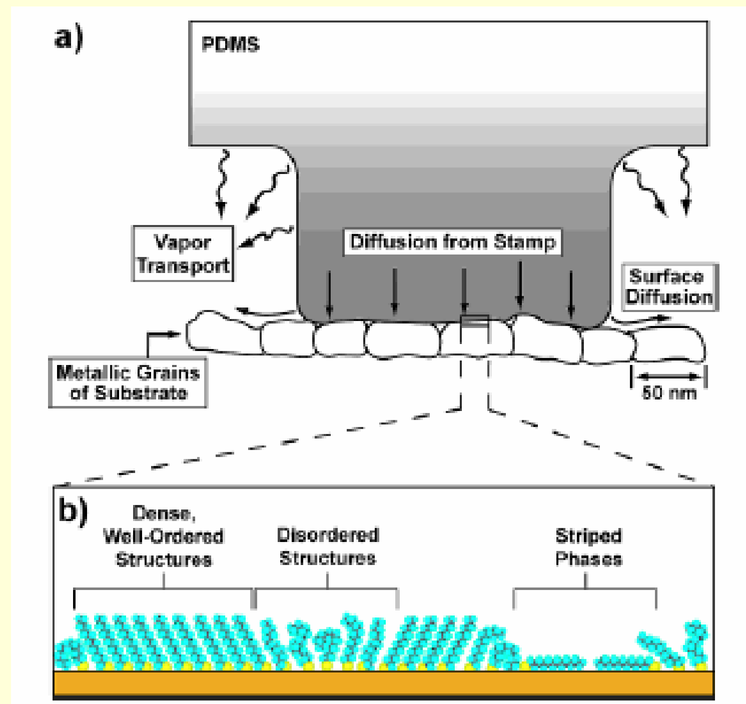
Byron D. Gates,† Qiaobing Xu,† Michael Stewart,‡ Declan Ryan,† C. Grant Willson,*,‡ and George M. Whitesides*,†

Table 1. Capabilities of Conventional and Unconventional Nanofabrication Techniques

technique	current capabilities (2004)		
	minimum feature[a]	resolution	pattern
photolithography[1,b]	37 nm	90 nm	parallel generation of arbitrary patterns
scanning beam lithography[88,c]	5 nm	20 nm	serial writing of arbitrary patterns
molding, embossing, and printing[116,123,168,d]	~5 nm	30 nm	parallel formation of arbitrary patterns
scanning probe lithography[28,52]	<1 nm	1 nm	serial positioning of atoms in arbitrary patterns
edge lithography[39,e]	8 nm	16 nm	parallel generation of noncrossing features
self-assembly[353–357,f]	>1 nm	>1 nm	parallel assembly of regular, repeating structures

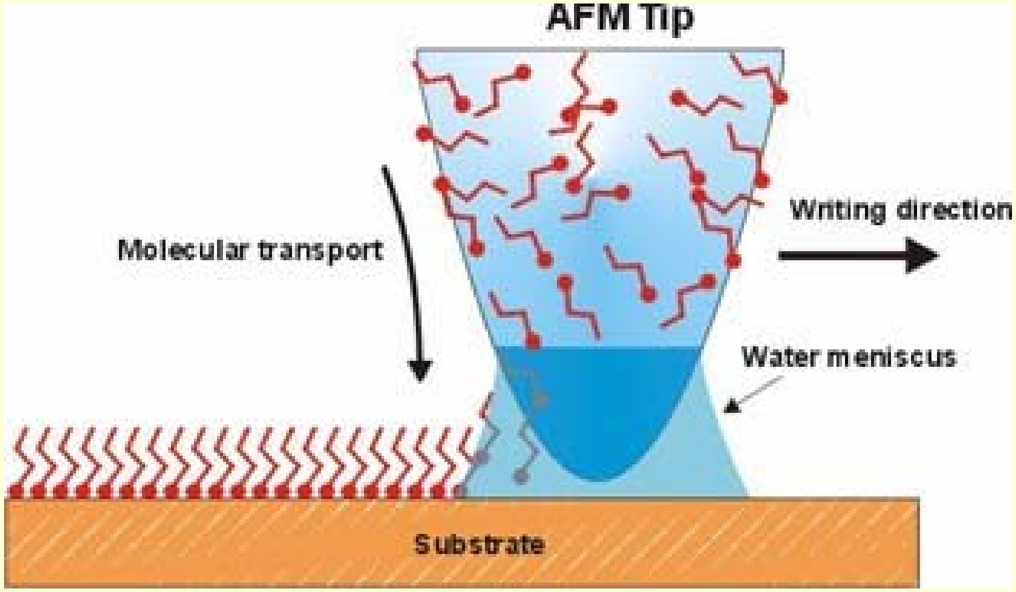
Pattern transfer: Microcontact Printing





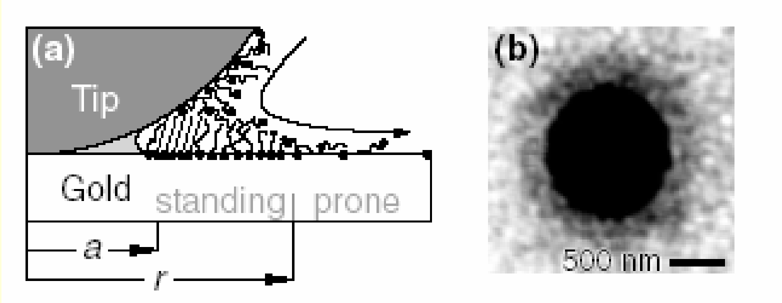
G. Whitesides et al, Chem. Rev 105, 1103 (2005);
Nanotechnology", G. Timp, Ed.; Springer Verlag: New York, (1999)

Dip-Pen Nanolithography



Dip-Pen Nanolithography: transport of molecules to the surface
Mirkin Group

Mass transport
surface diffusion
coefficient thiol on Au
$10^{-11} cm^2\ s^{-1}$
(dry conditions)



P. E. Sheehan, L. J. Whitman Phys. Rev. Lett, 88, 156104-1, 2992

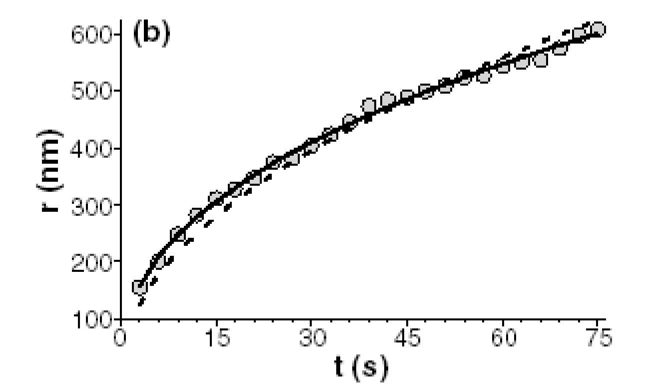
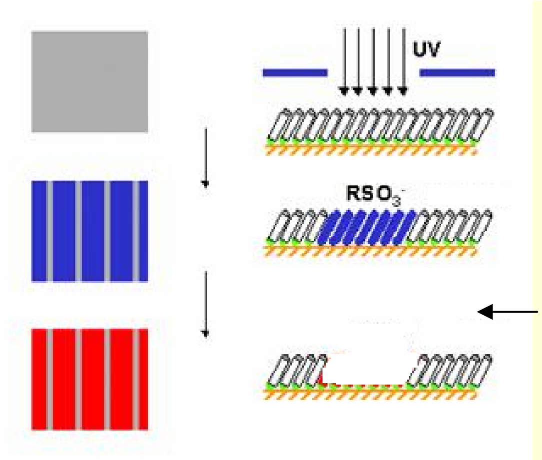
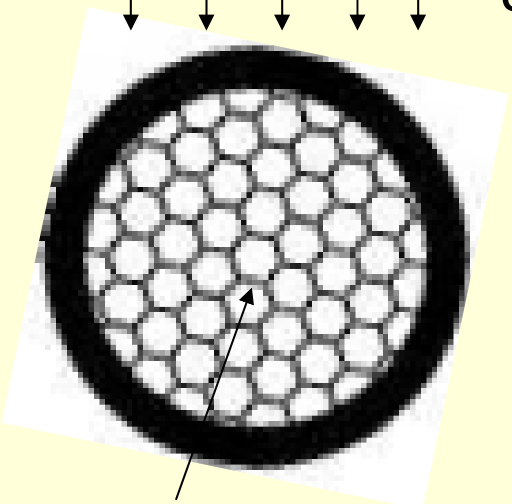


FIG. 1. (a) Friction image of ODT islands deposited on a gold surface by an ODT-coated AFM tip for sequentially longer tip-surface contact. The dark spots are areas of decreased friction caused by the adsorbed ODT. (b) The measured island radii as a function of contact time. The solid line is a fit to the radial diffusion model described in the text. The dashed line is a fit to an alternate model [8] requiring $t^{1/2}$ dependence.



water

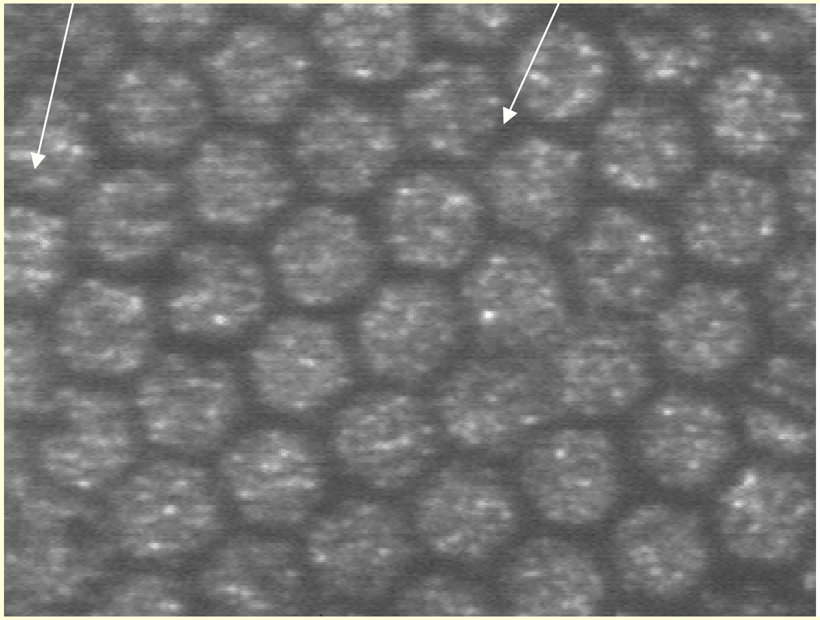


UV

Free-thiol Ag domains

Pd domains (microparticles)

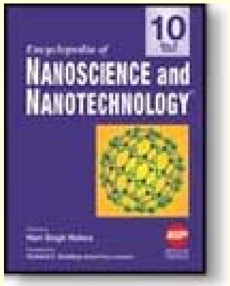
Ag-tiol



25 μm

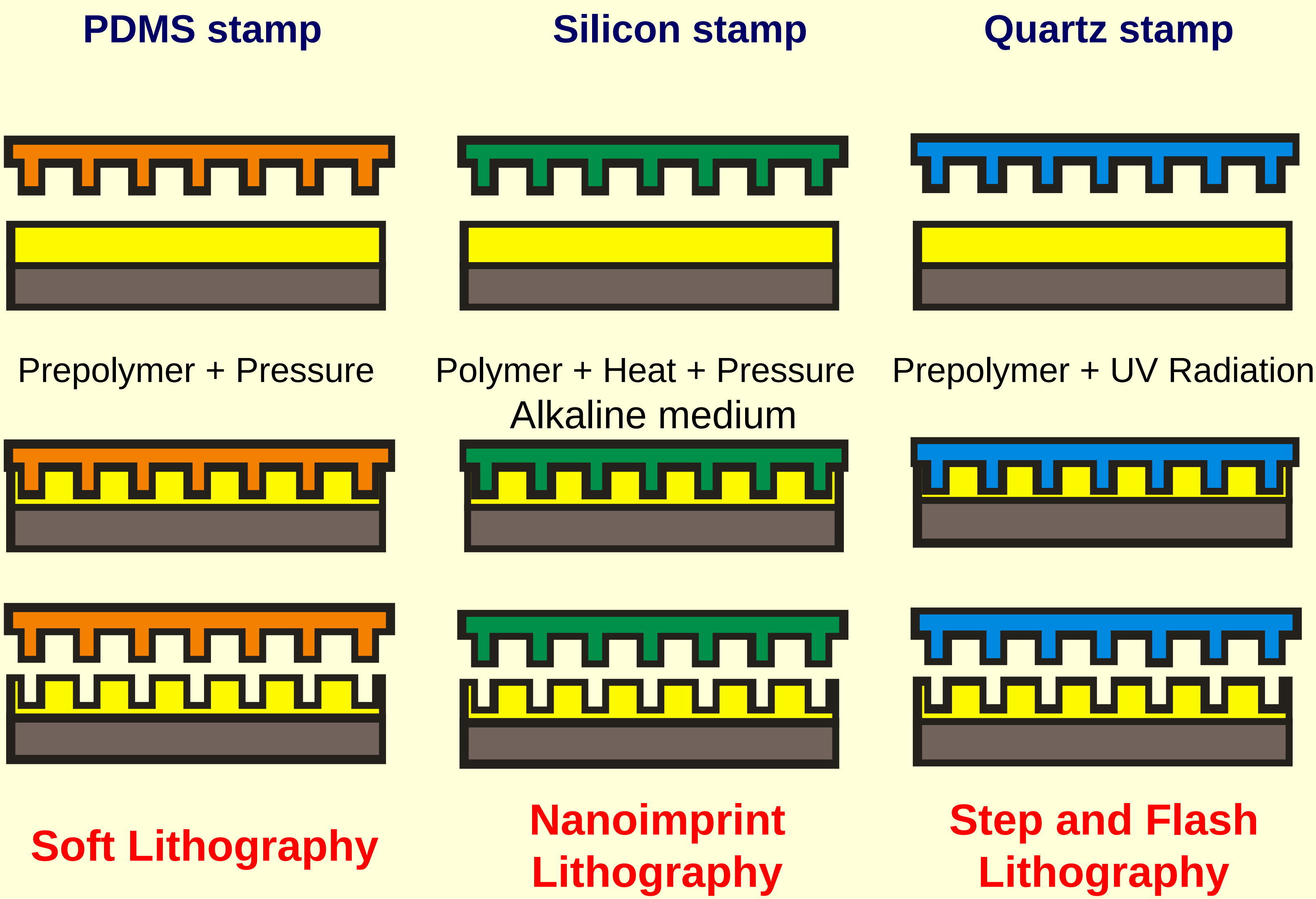
Solution containing Pd^{+2} ions

$$2\,Ag + Pd^{+2} = 2Ag^{+} + Pd$$



O. Azzaroni, P.L. Schilardi and R.C. Salvarezza,
"Encyclopedia of Nanoscience and Nanotechnology",
American Scientific Publishers, Volume 5, pp. 835-850(16)
California, 2004.

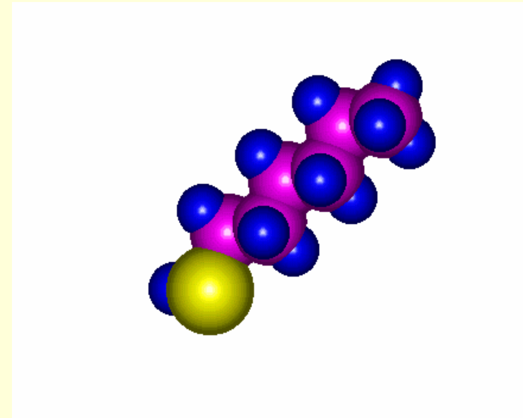
Soft Lithographic Techniques



Soft-lithography at nanoscale: mainly used for soft-materials (polymers with low adherence)

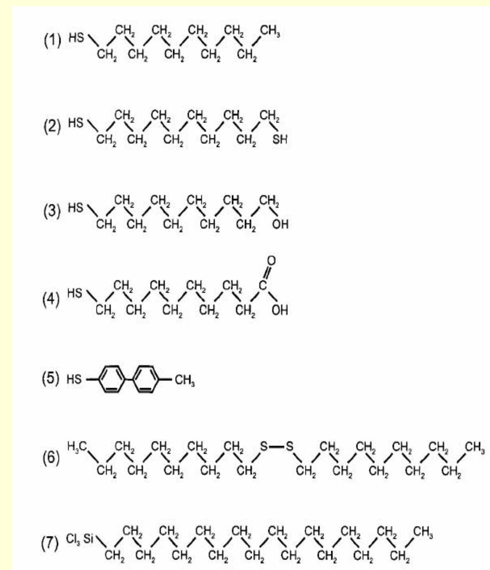
When the master/material system exhibits non-negligible adherence anti-sticking layers are needed

Anti-adherent layers: metals, oxides,sulfides,etc



Problems;

The roughness and grain size of the anti-adherent layer limit resolution, hardly applicable to the nanoscale

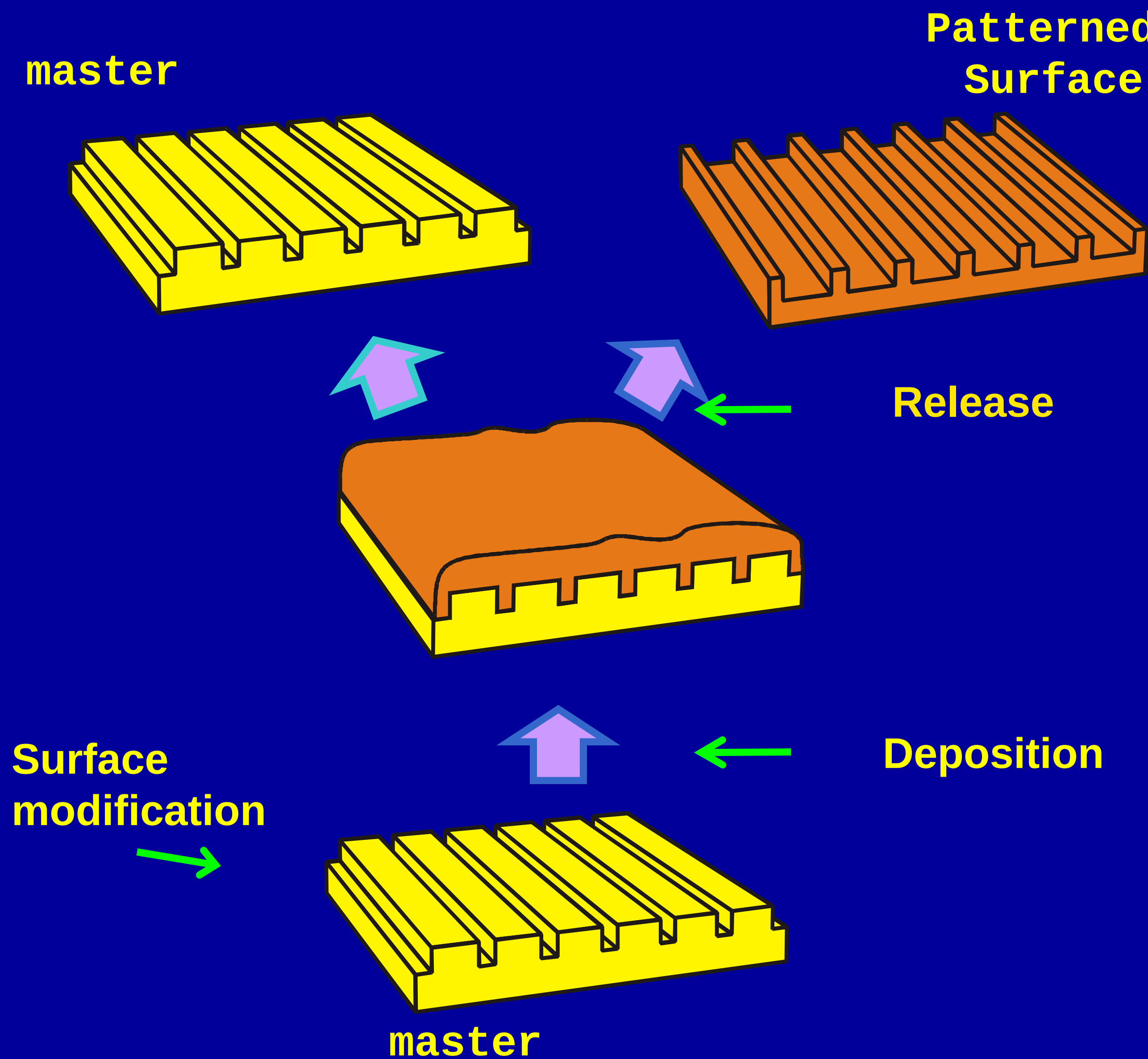


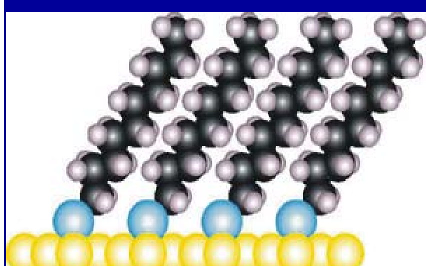
Solution:

Self-assembled molecular films

Methyl-terminated alkanethiols and silanes

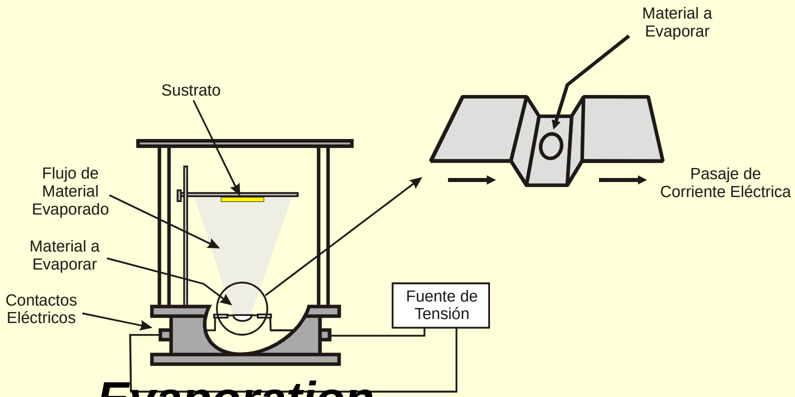
Patterning Hard Materials



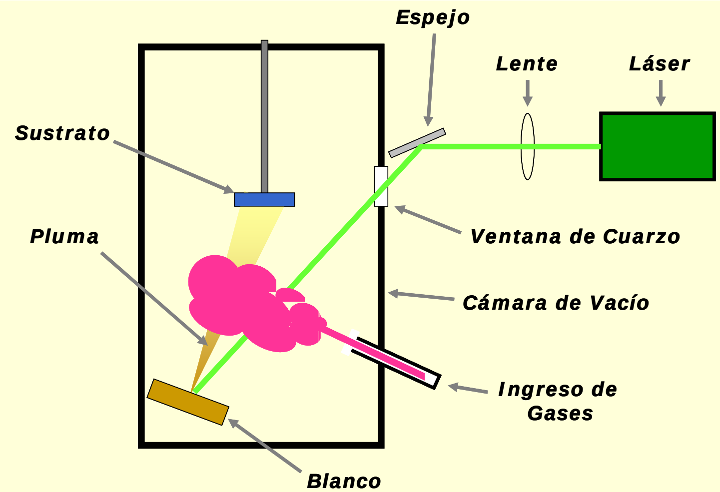


Anti-adherent layer :
Self assembled monolayers (SAMs)

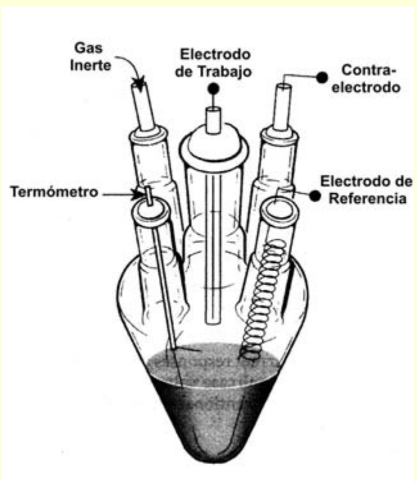
DEPOSITION ON SAMs

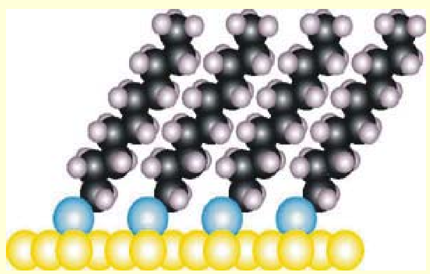


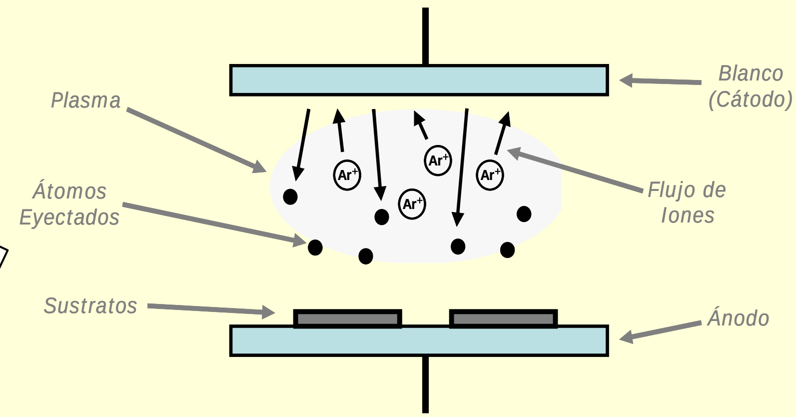
Evaporation (metals)



laser ablation Semiconductors (ZnO)







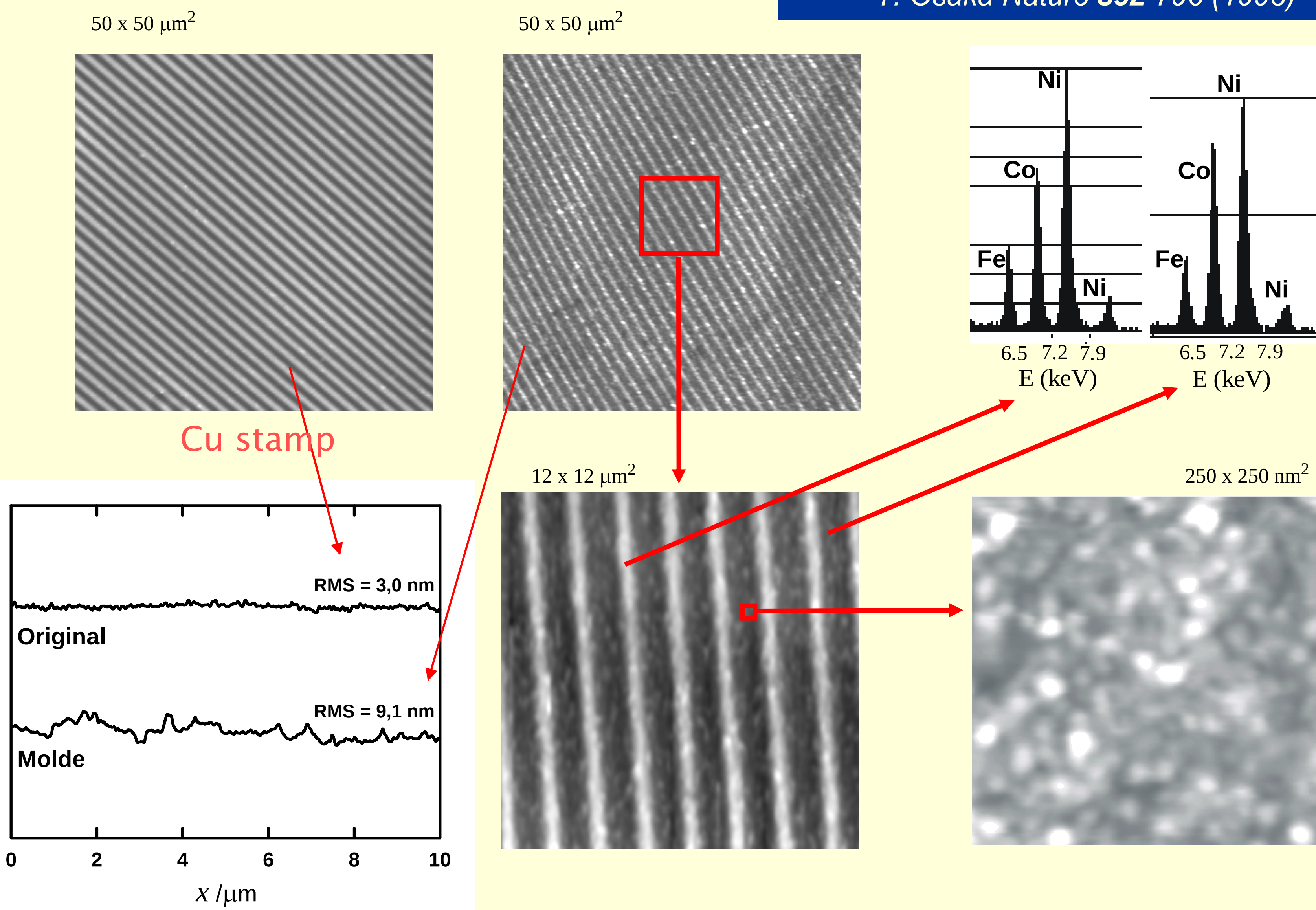
KEY POINT : SAM must survive under deposition conditions

Electrodeposition (metals,alloys ZnO, Cu_2O)

“reactive sputtering ” (ceramics, TiN, AlN)

Molding Electrodeposited Soft Magnetic Alloys $Fe_{11}Co_{38}Ni_{51}$

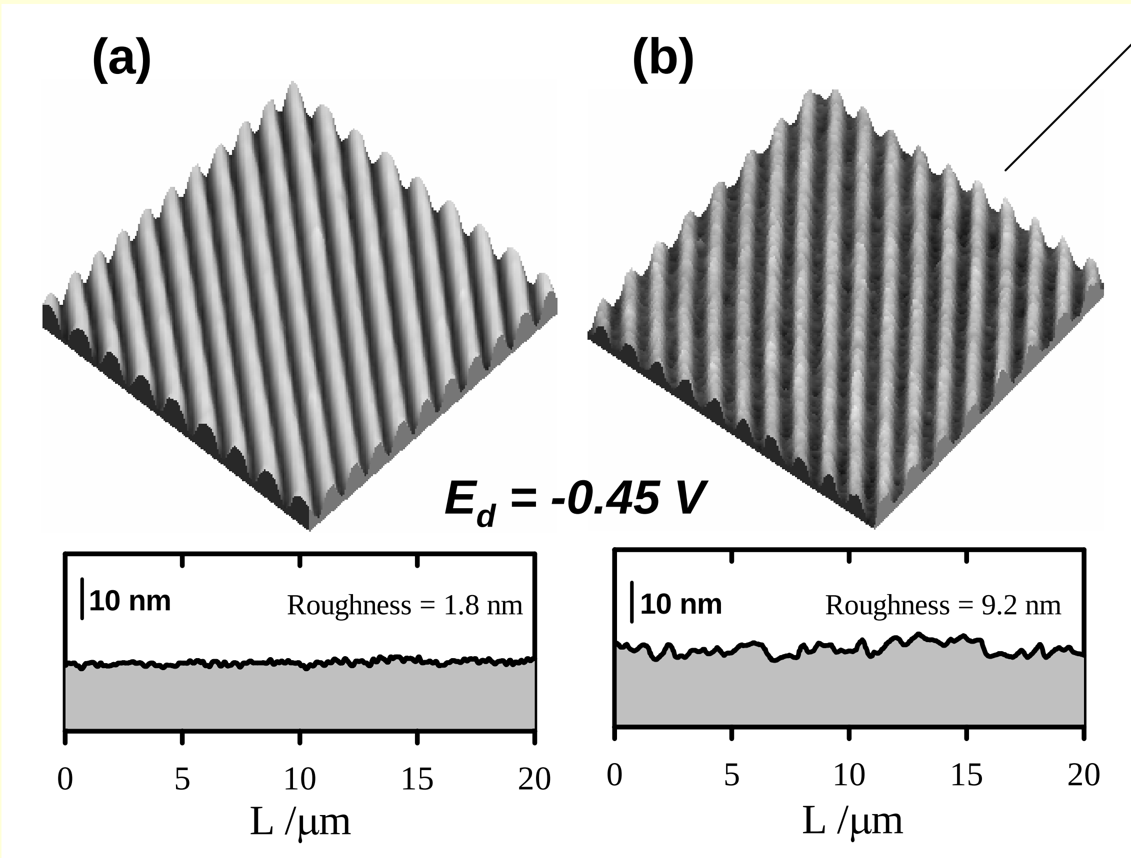
0.06 M $CoSO_4.7H_20$ +0.2 M $NiSO_4.6H_20$ + 0.015 M $FeSO_4.7H_20$+ 0.028 M NH_4Cl + 0.4 M H_3BO_3 + $2.6x10^{-4}$ M thiourea, pH = 2.8, j = 20 mA cm^{-2}
*T. Osaka Nature **392** 796 (1998)*

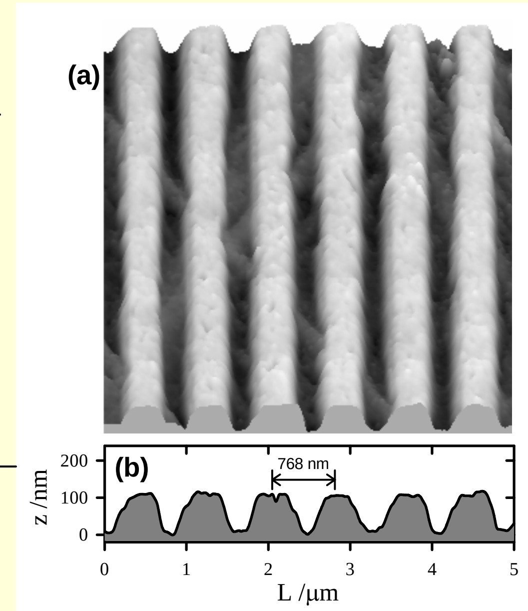


O. Azzaroni, P.L. Schilardi, R.C. Salvarezza, *Appl.Phys.Lett.* **80** ,1061 (2002)

Molding Electrodeposited Oxides

Cu master ***Cu_2O***

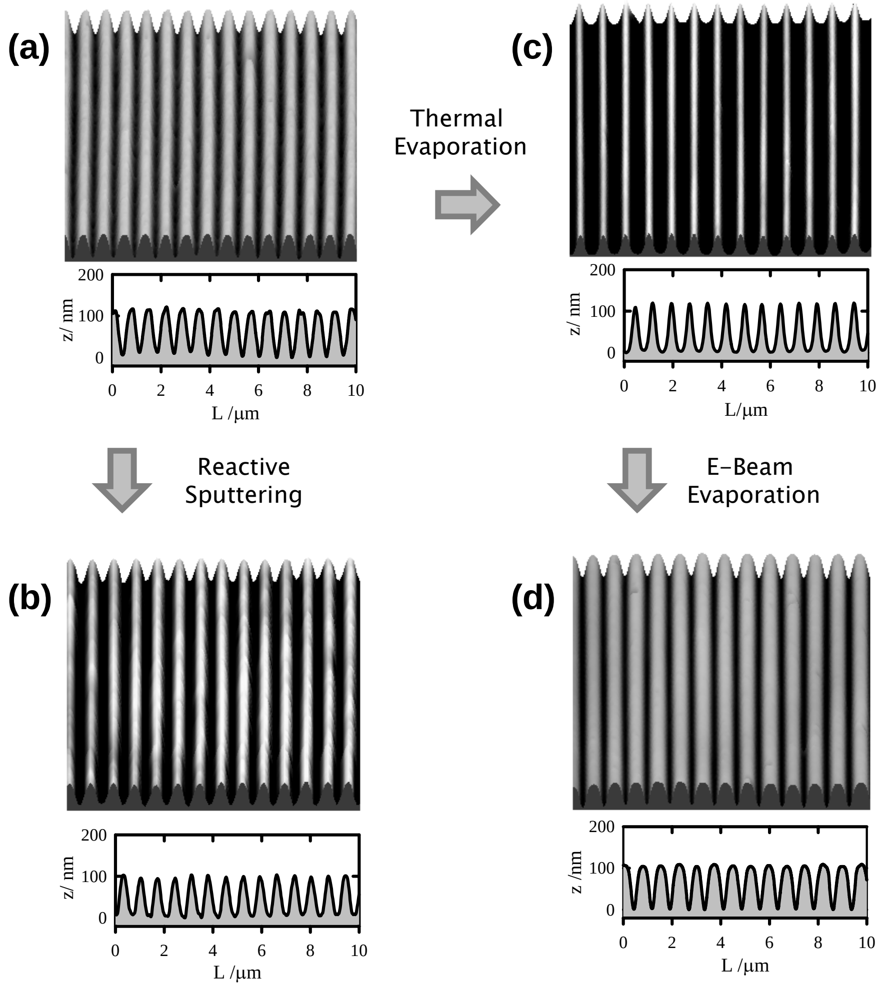




Salvarezza et al, Chem. Eur. J. 2006, 12, 38-49

0.4 M $CuSO_4.5H_2O$ + 3 M lactic acid pH = 9, T = 60°C
Switzer *et al. Scripta Materialia* 38,1731 (1998)

Cu **masters** **Au**

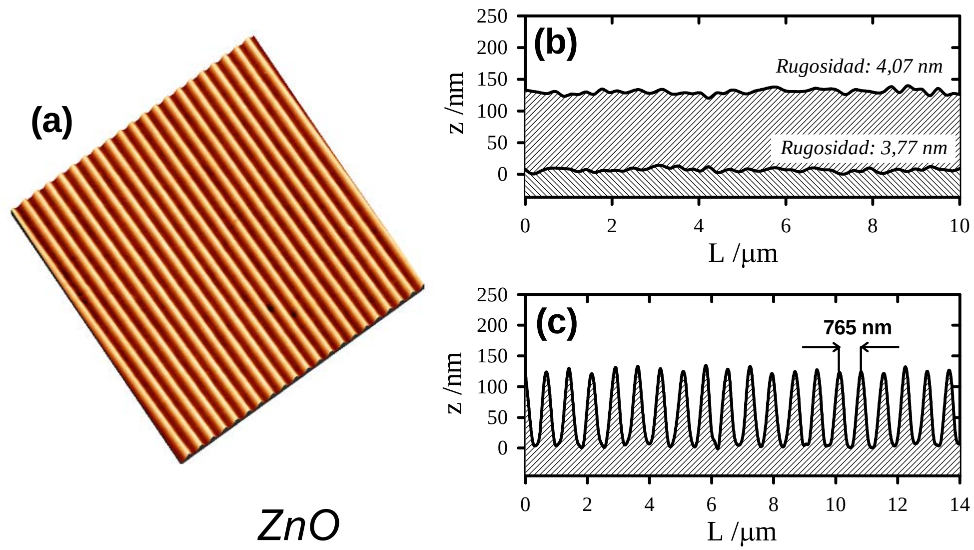


TiN **B_4C**

Micropatterning ceramic materials by reactive sputtering

Auger, Schilardi, Benítez, Gago, Fonticelli, Vazquez, Salvarezza O. Azzaroni , concept article, Small ***1,*** *300 (2005)*

Anti-adherent layer:dodecanethiol



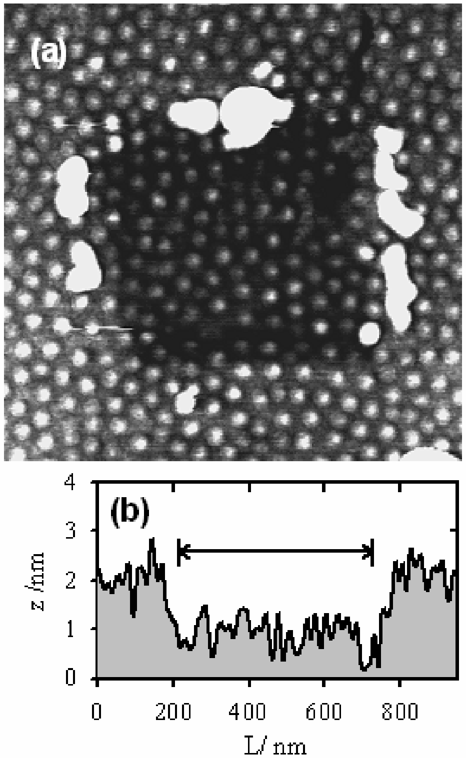
ZnO

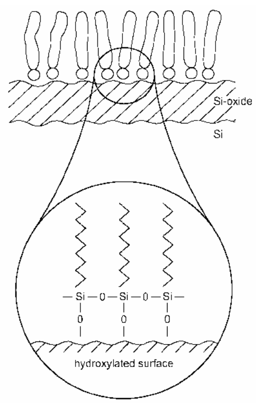
AFM images

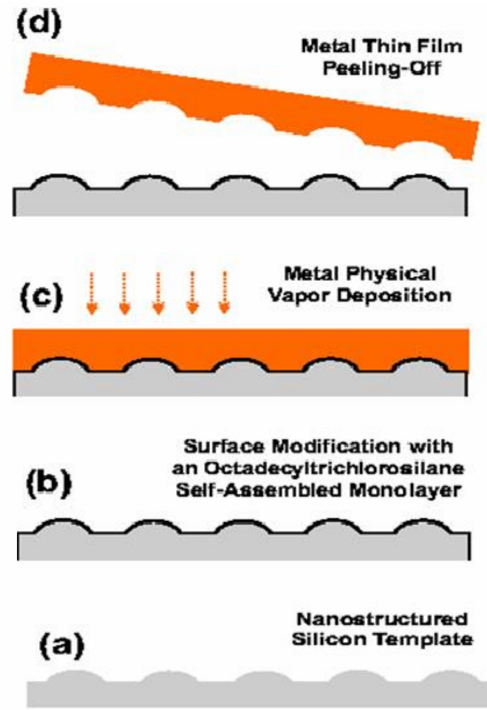
Micropatterning semiconductor materials by laser ablation

Azzaroni, Schilardi, Salvarezza, Herrero, Zaldo, Vázquez.
Applied Physics A 81, 109 (2005)

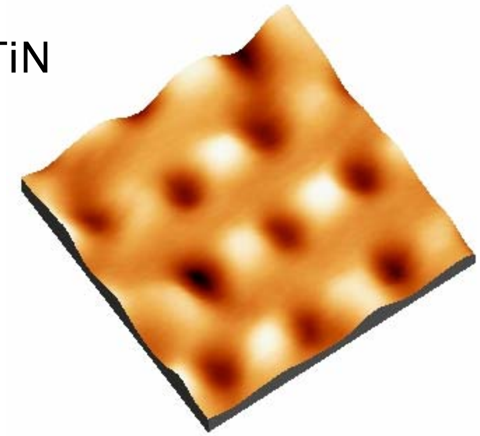
Nanopatterning metals and ceramics



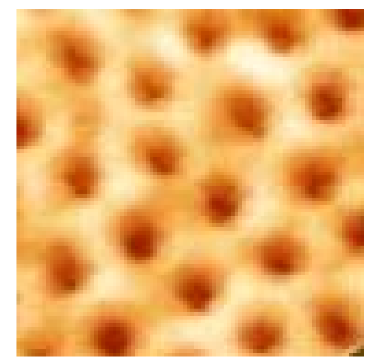


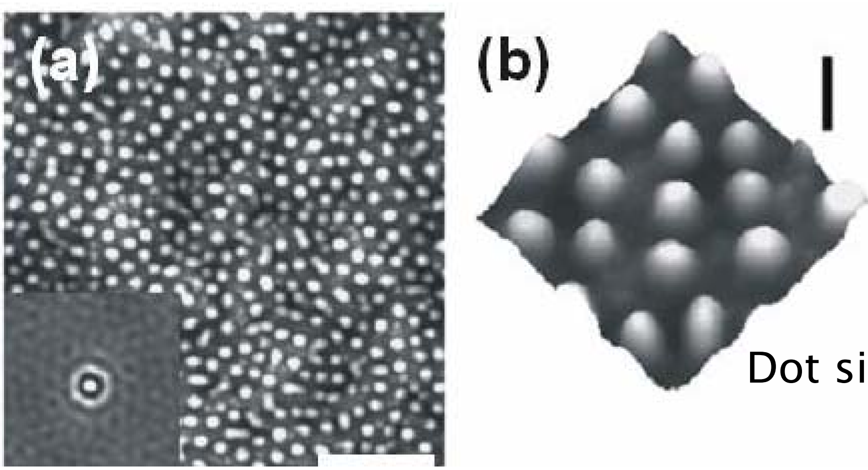


TiN



Au



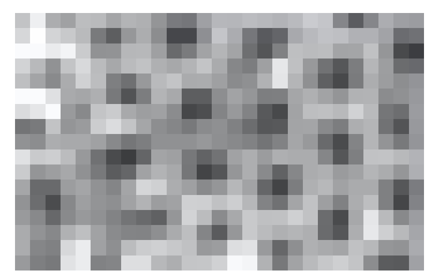


5nm

Si master

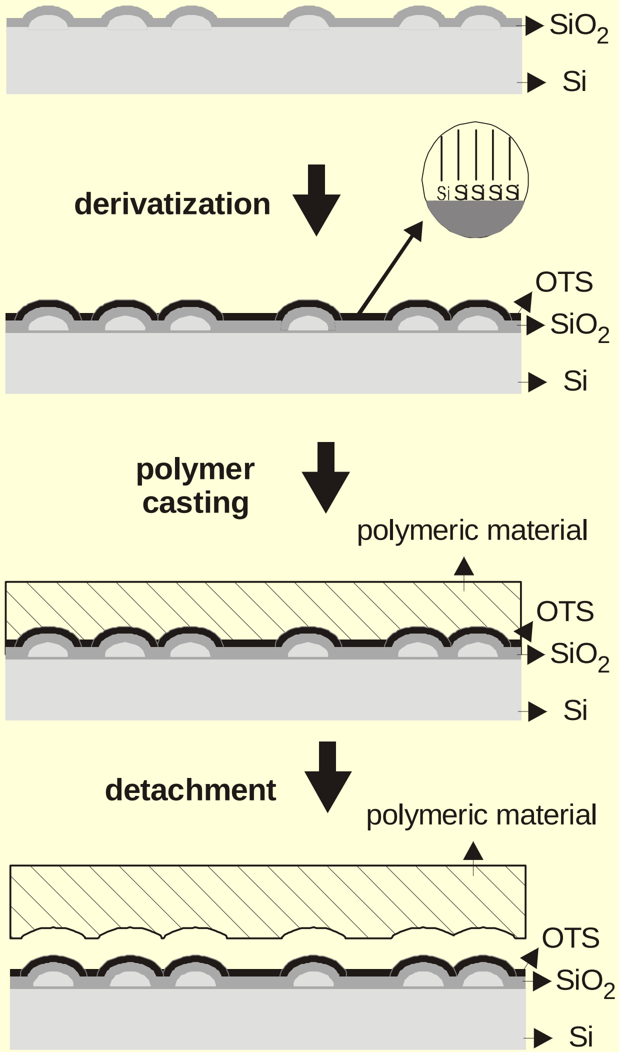
Dot size 40 nm

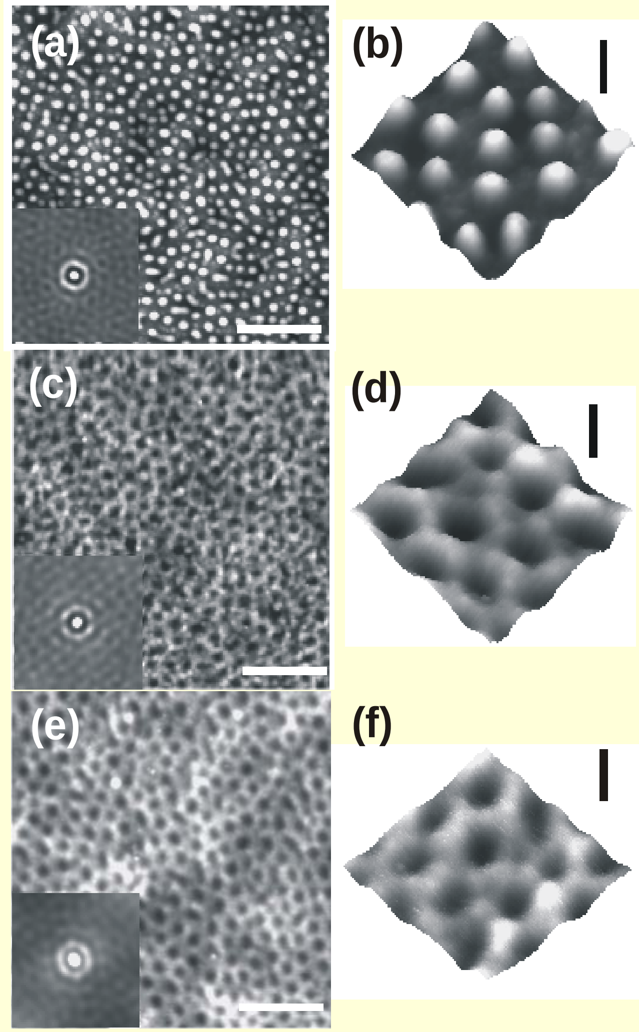
Al



O. Azzaroni, M. Fonticelli, P. Schilardi, G. Benitez, I. Caretti, R. Gago, L. Vazquez, R.C. Salvarezza Advanced Materials 16, 405 (2004)

Nanopatterning polymeric materials





Silicon-master
nanodots
Diameter = 40 nm
Height = 5 nm

Patterned Polystyrene

Patterned high-impact polystyrene

Anti-adherent layer:
Silanes (OTS)

O. Azzaroni, P.L. Schilardi, L.Vazquez and R.C. Salvarezza
Applied Physics Letters, ***82***, *453 (2003)*

SAMs are the most simple example of nanostructured systems. The molecules contain all the information needed to form two dimensional systems with specific chemical functionalities

The control de SAMs at the molecular lavel is crucial for their posible use in :

1) Molecular electronics
2) Metal protection
3) Anti-adherent layers for nano/micromolding
4) Building blocks for complex structures