CHM 696-11: Week 6

Instructor: Alexander Wei

Self-Assembled Monolayers
Supramolecular Surface Science

Reviews: Ulman, *Chem. Rev.* **1996**, *96*, 1533.
Flink et al, *Adv. Mater*. **2000**, *12*, 1315.
Love et al, *Chem. Rev*. **2005**, *105*, 1103.

Self-assembled monolayers (SAMs)

Two types of media for SAM formation:

1) At biphasic (air-solvent or solvent-solvent) interfaces

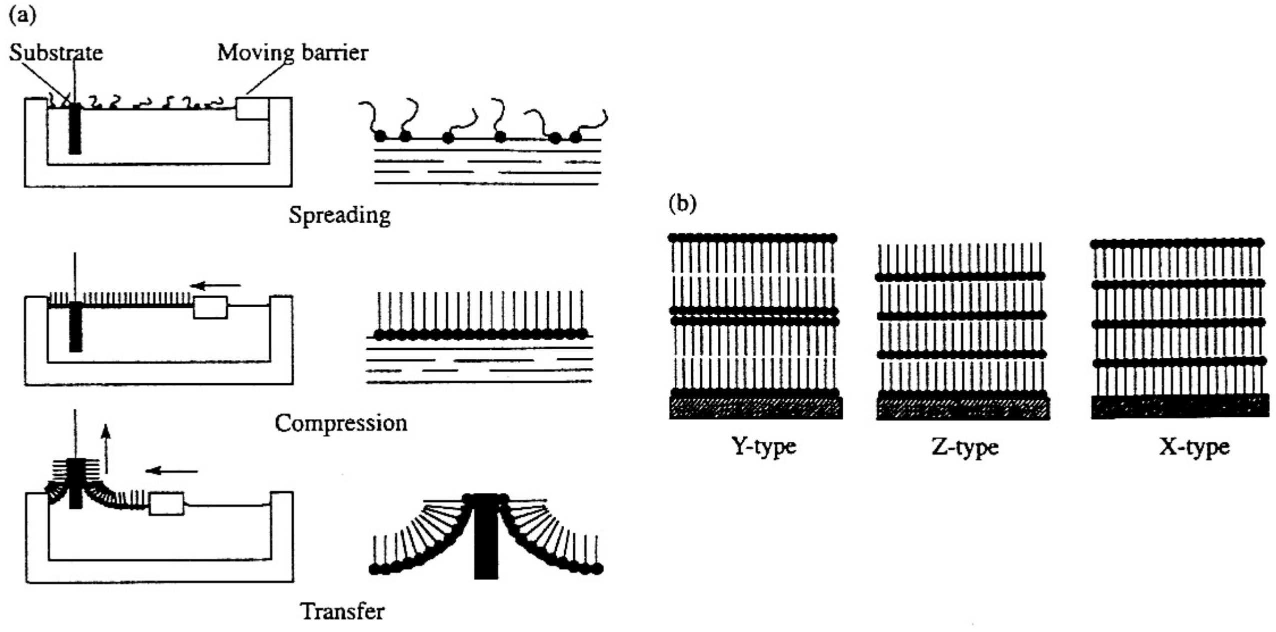
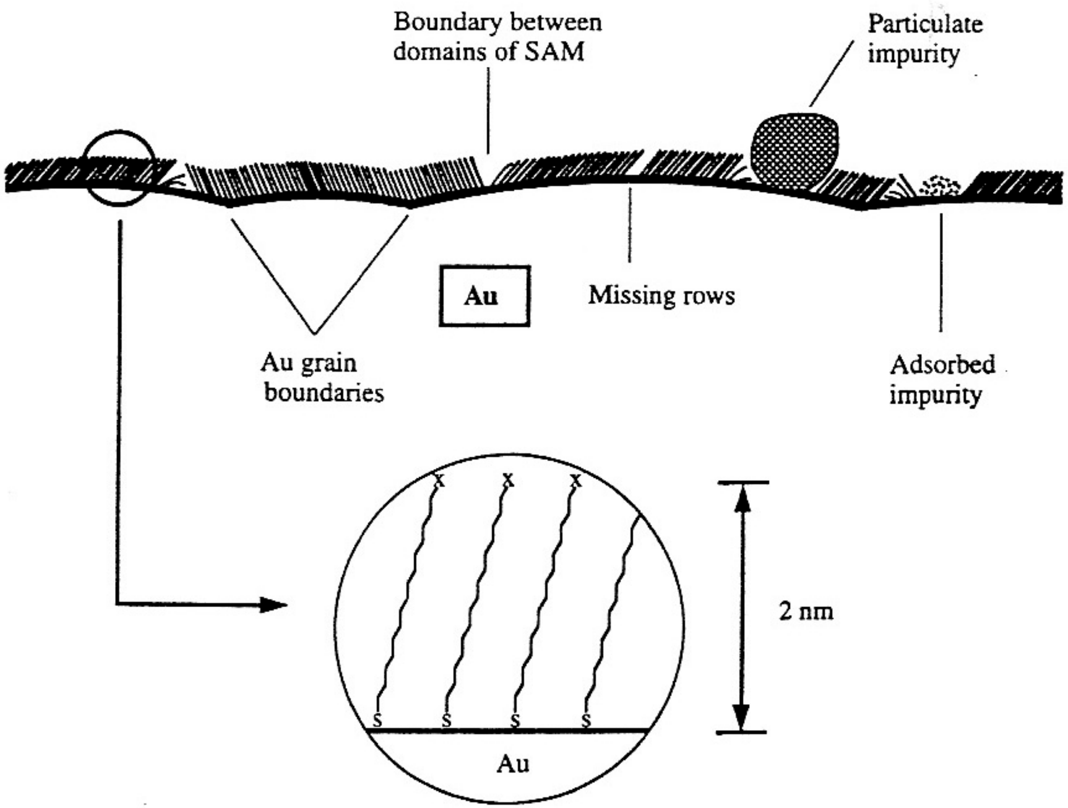


Figure 1 Preparation and structure of LB films. (a) A disordered, low-density amphiphile film at the air–water interface is compressed by means of a movable barrier. Movement of a polar substrate through the interface transfers the compressed monolayer, with hydrophilic groups facing the substrate. (b) Idealized structures of Y-, Z-, and X-type LB films.

Langmuir-Blodgett transfer: asssembling and depositing SAMs onto substrates

Self-assembled monolayers (SAMs)

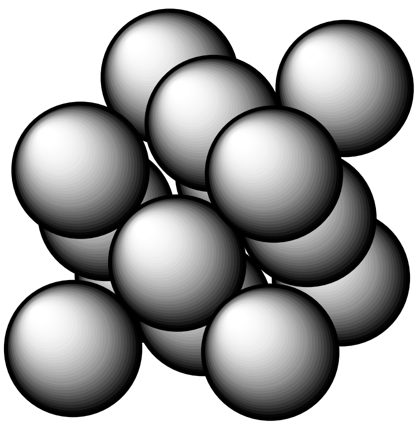
2) SAMs of chemisorptive ligands on solid substrates



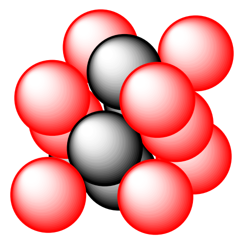
Many examples of chemisorptive SAMs: Alkanethiols on Au/Ag; carboxylates on metal-oxide surfaces, etc.

Substrates and surfaces: an introduction to crystalline lattice planes

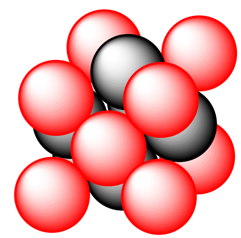
Face-centered cubic (fcc) structure: Predominant in metals (Au, Ag, Fe…)



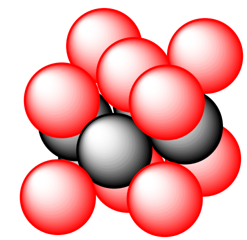
[100] lattice



[010] lattice

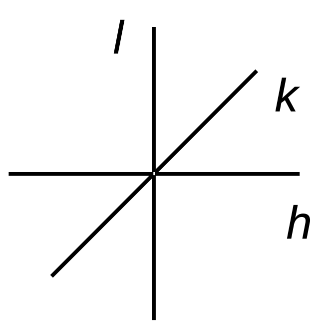


[001] lattice

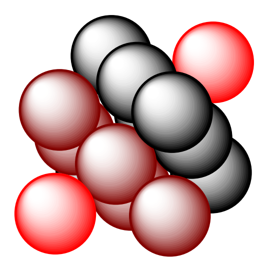


Miller index:

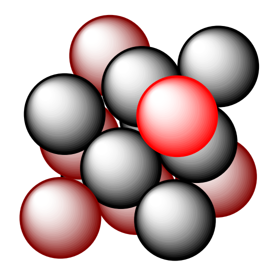
[*hkl*]



[111] lattice



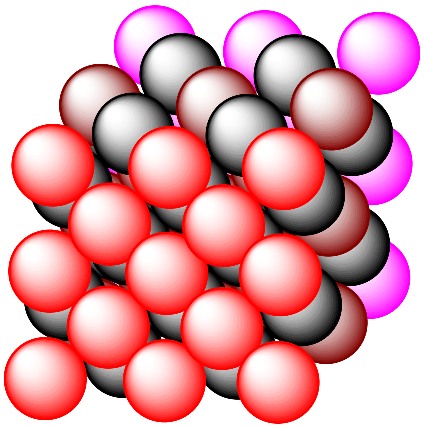
$[1\bar{1}1]$ lattice



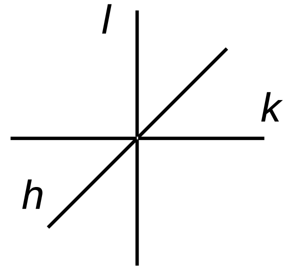
a.k.a. *ABC* stacking

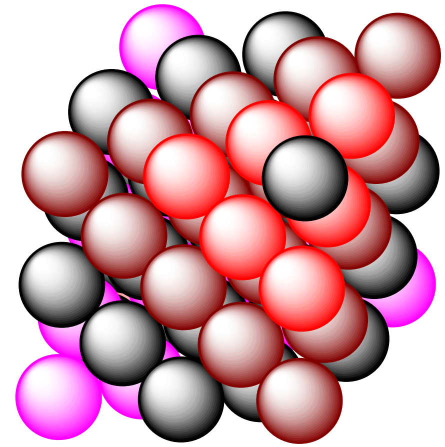
FCC lattice planes and slip planes

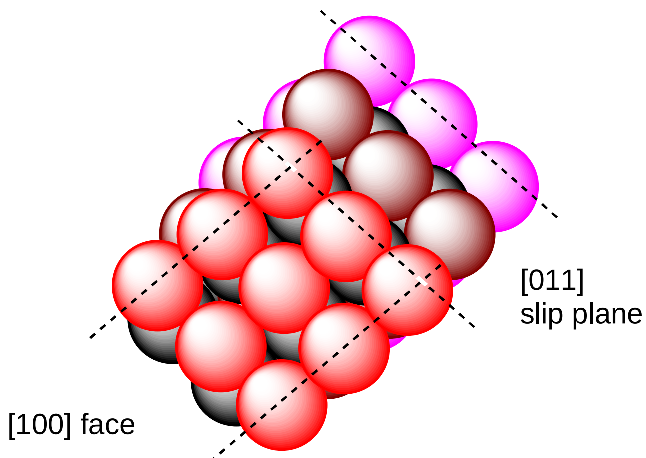
[100] plane: square lattice

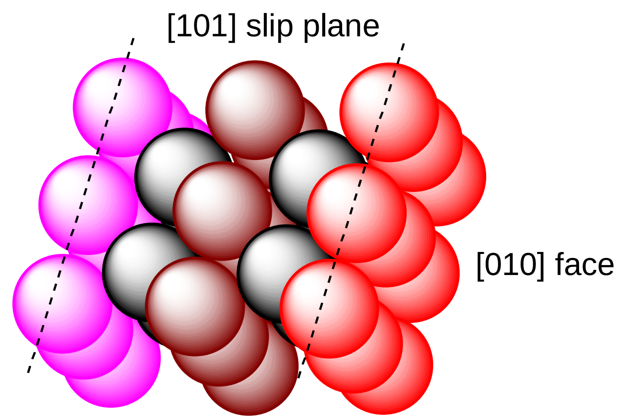


[111] plane: triangular or hexagonal lattice





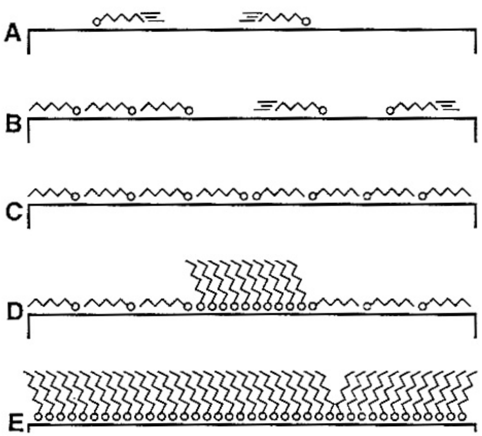




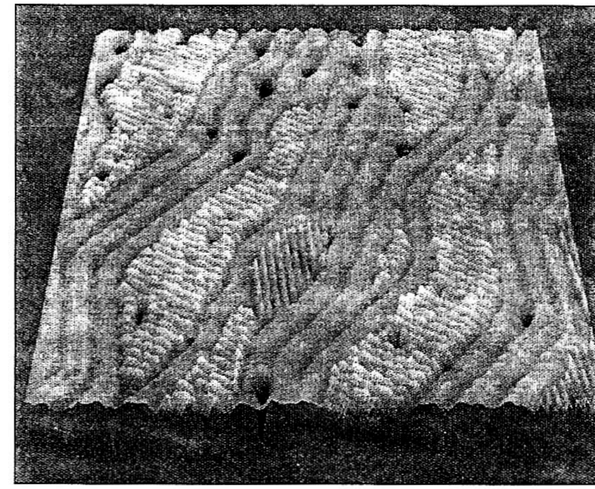
Self-assembly of alkanethiols on Au(111)

Construction of an alkanethiol SAM:

Poirier and Pylant, *Science* **1996**, *272*, 1123; 1145-48
Poirier, *Chem. Rev*. **1997**, *97*, 1117



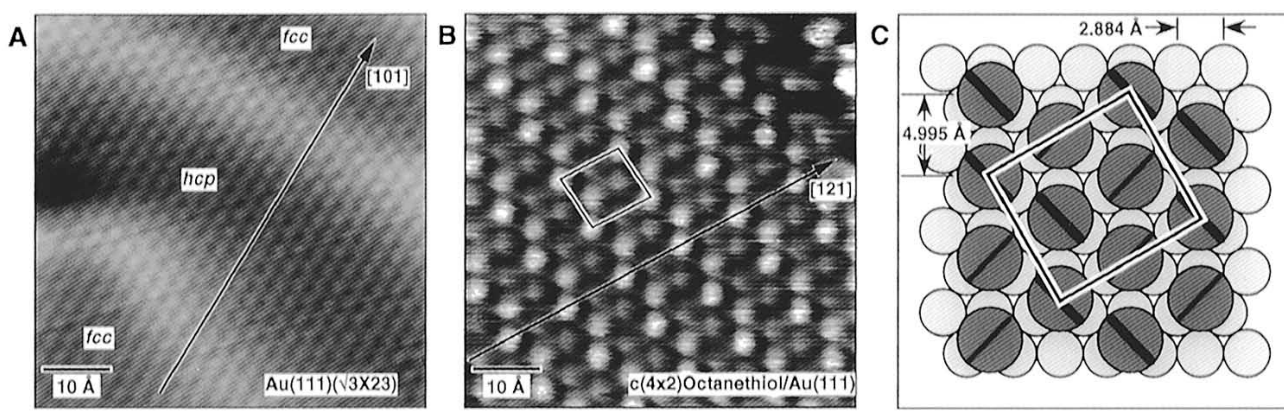
- Submonolayer phase: highly mobile ligands
- Formation of “striped” domains
- Surface saturation; striped domains dominant
- Phase transition to “upright” monolayers
- Maximum coverage by upright SAMs



Intermediate stage of alkanethiol self-assembly on Au(111) surface as characterized by constant-current STM. Zigzag features are bare, reconstructed Au surface. Striped features are islands of alkanethiol molecules, arranged in rows, and with surface-aligned molecular axes. Dark depressions, such as in bottom center, are islands of Au atom vacancies.

Epitaxial relationship between Au(111) and alkanethiol SAM:
$\sqrt{3} \times \sqrt{3}$ R 30º

DuBois and Nuzzo, *Annu. Rev. Phys. Chem*. **1992**, *43*, 437.



Au(111) substrate | C8 thiol SAM | ‘Herringbone’ packing

Structural Characterization of SAMs on Au

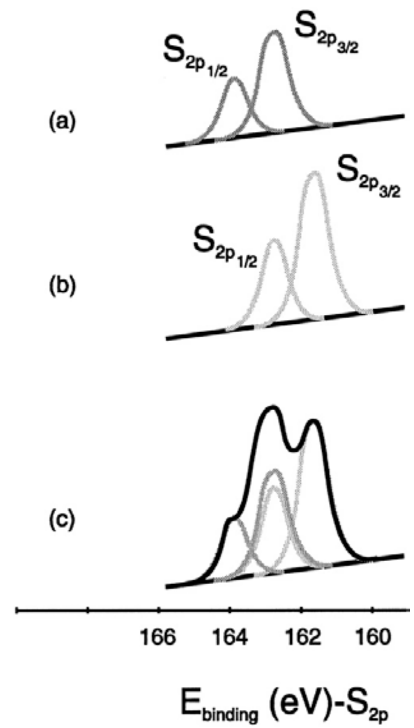
X-ray photoelectron spectroscopy (XPS): surface atom content, bonding

Surface IR spectroscopy (RAIRS, PM-IRAS): functional groups, conformation

Surface-enhanced Raman scattering (SERS) (nanostructured substrates)

Ellipsometry: estimation of SAM thickness

Near-edge X-ray adsorption fine structure spectroscopy (NEXAFS): determination of molecular tilt angle



XPS “doublet” of S, unbound (free thiol)

S bound to Au (thiolate)

Deconvoluted spectrum of free and bound S, in a 2:3 ratio

Buelen et al, *Langmuir* **1998**, *14*, 6424.

Alkanethiol SAMs on Au:

X-$(CH_2)_n$-SH: Spontaneous 2D ordering for *n* > 8

Variations in SAM structure:

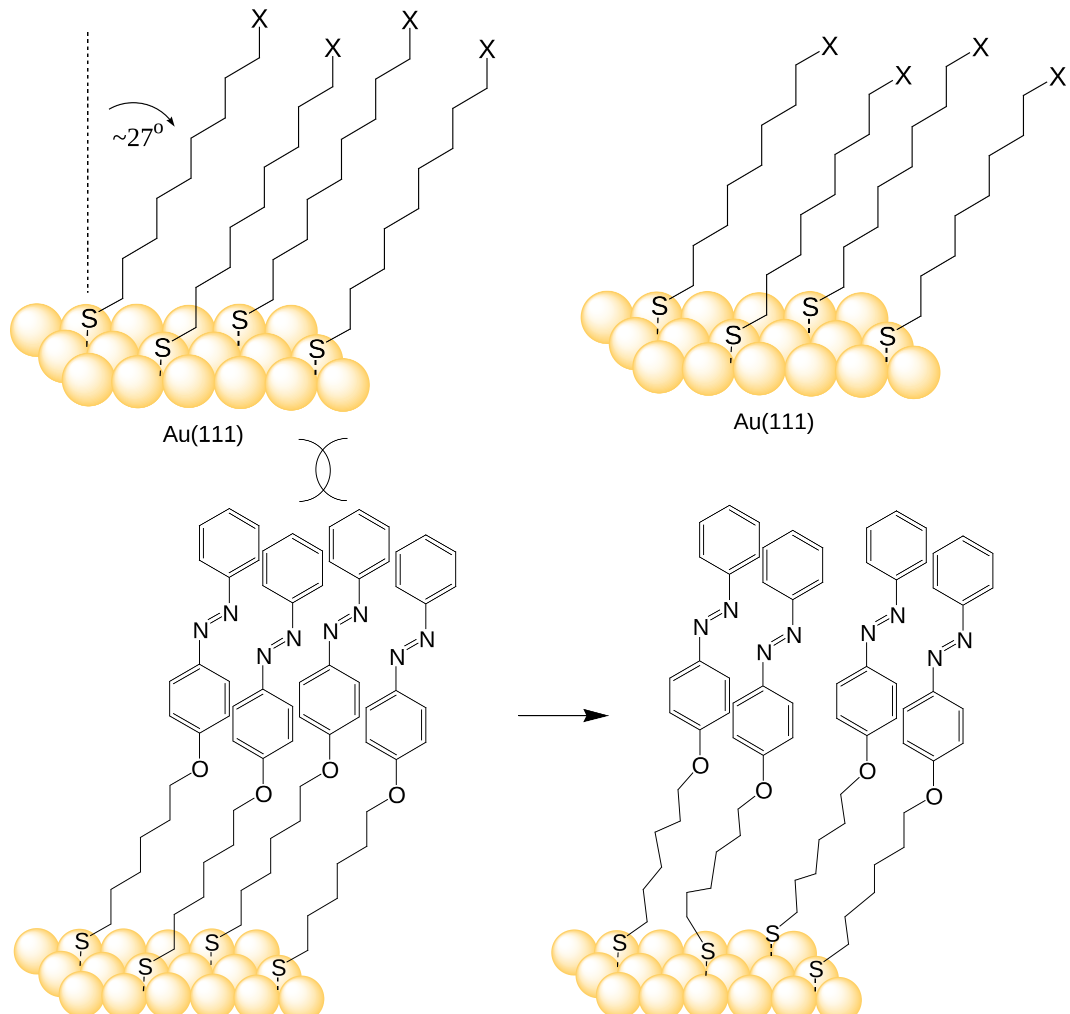
1) Odd-even effects

Differences observable by surface IR:
Laibinis et al, *JACS* **1991**, *113*, 7152.

2) Steric effects

Headgroup packing geometry can create incommensurate lattice w.r.t. Au(111)

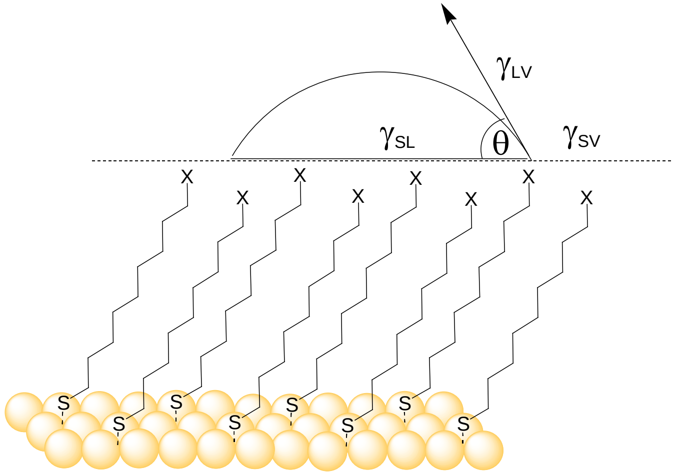
Delamarche et al, *Adv. Mater.* **1996**, *8*, 719.



Surface properties of alkanethiol SAMs on Au

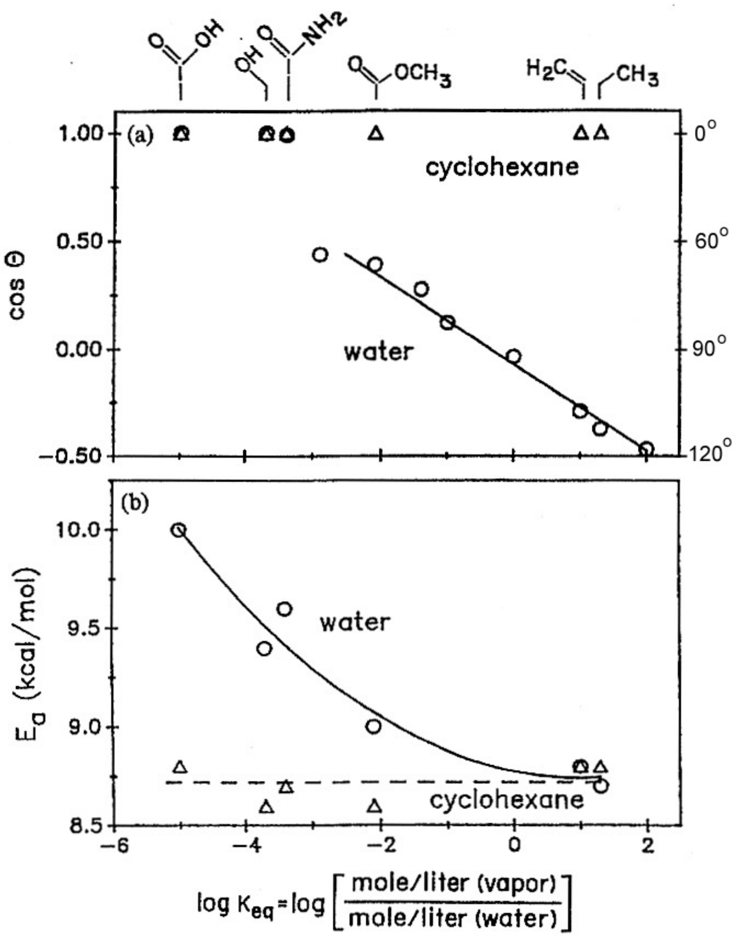
Wettability: contact angle measurements

(but droplet shape strongly influenced by contact line)



γ_{SV} = interfacial surface energy (solid-vapor)

$\gamma_{SV} - \gamma_{SL} = \gamma_{LV}\cos\theta$ (Young-Dupre equation)

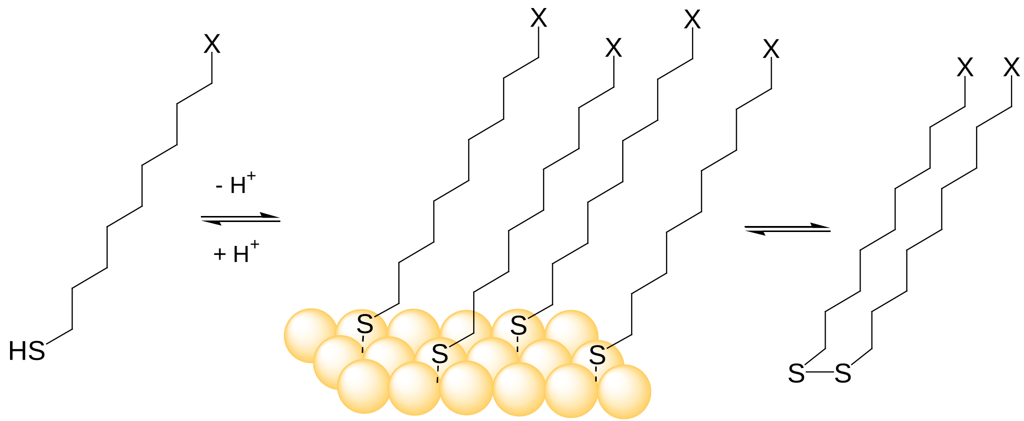


Contact angle and desorption energy (E_a) vs. log(Partition coeff.)

DuBois and Nuzzo,
Annu. Rev. Phys. Chem. **1992**, *43*, 437.

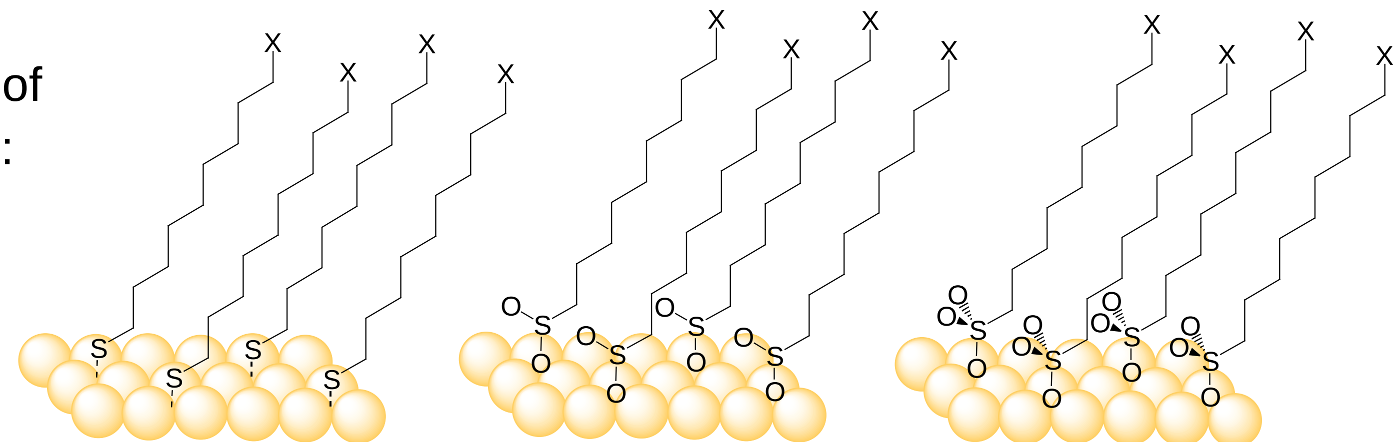
Stability of Alkanethiol SAMs on Au

Reversible adsorption:



Au(111)

(Photo)oxidation of sulfur headgroup:



RS^-: thiolate
strongly chemisorptive
(slow exchange rates)

RSO_2^-: sulfinate
mildly adsorptive; labile
(moderate to fast exchange)

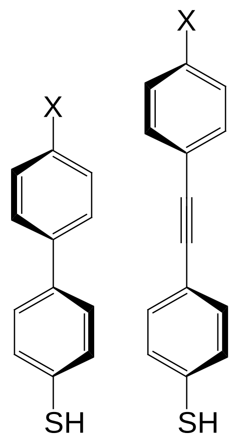
RSO_3^-: sulfonate
weak adsorption; unstable

Garrell et al, *JACS* **1995**, *117*, 11563.

Other examples of SAM-forming molecules

Phenylethynyl- and biphenylthiols

Ulman, *Acc. Chem. Res.* **2001**, *34*, 855.



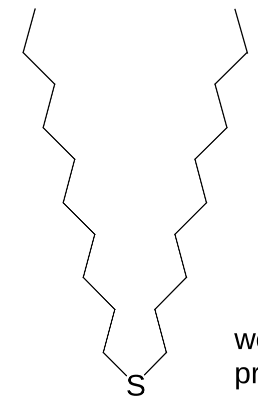
tilt angle < 5^o

edge-to-face packing

Sulfides

Beulen et al, *Langmuir* **1996**, *12*, 6170.

Shelly et al, *Langmuir* **2002**, *18*, 1791.



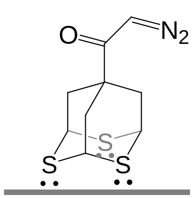
weakly adsorptive; prone to oxidation

Increasing ligand chemisorption: examples

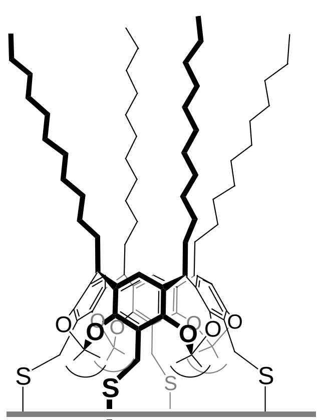
Multivalent ligands

Balasubramanian et al, *Langmuir* **2002**, *18*, 3676.

Hu et al, *Langmuir* **2004**, *20*, 4933.



Au(111)

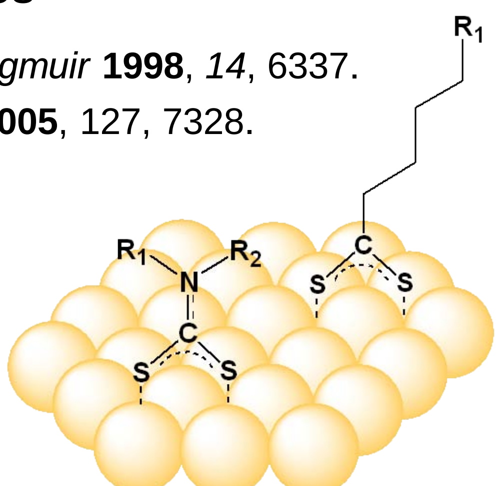


Au(100)

Carbodithioates

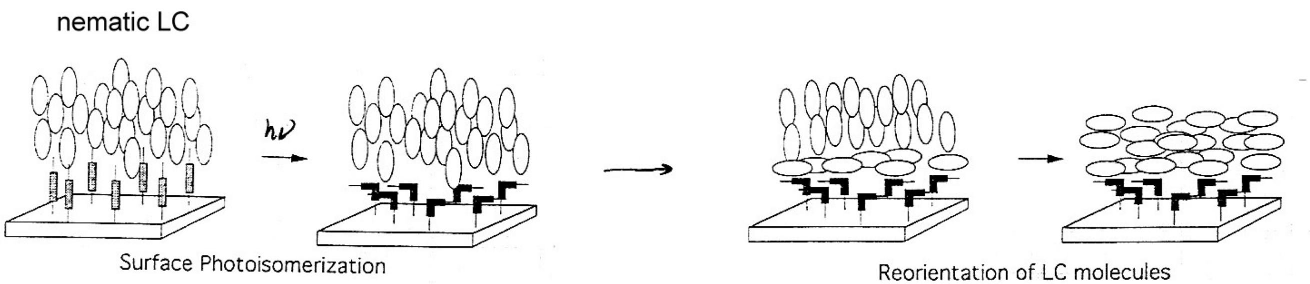
Colorado et al, *Langmuir* **1998**, *14*, 6337.

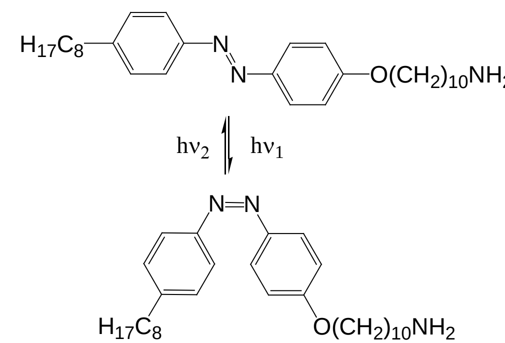
Zhao et al, *JACS* **2005**, 127, 7328.



Functionalized SAMs

Example of a photoactive SAM with azobenzene groups:





SiO_2 (glass) surface

Ueda et al, *Israel J. Chem.* **1996**, *36*, 371.

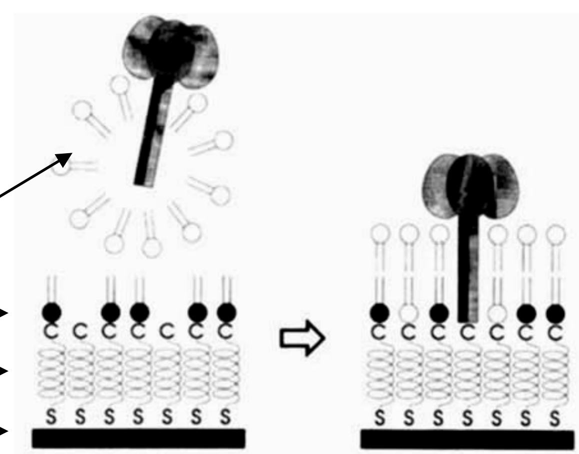
Example of artificial membrane bilayer on Au:

Membrane-bound ATPase (proton pump)

Covalently attached phospholipids

Thiol-terminated oligo-alanine

Au(111)



Naumann et al, *Angew. Chem.* **1995**, *34*, 2056.

SAMs and sensor technologies

Common sensor modalities:

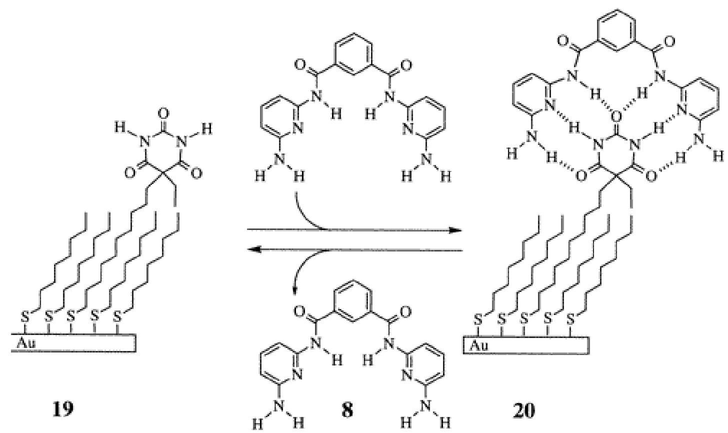
1) Electrochemical: potentiometry, voltammetry (ion sensing); impedance spectroscopy (changes in capacitance)

2) Optical: surface plasmon resonance (SPR) (changes in local refractive index); fluorescence-based detection (<u>can be quenched by Au substrate</u>)

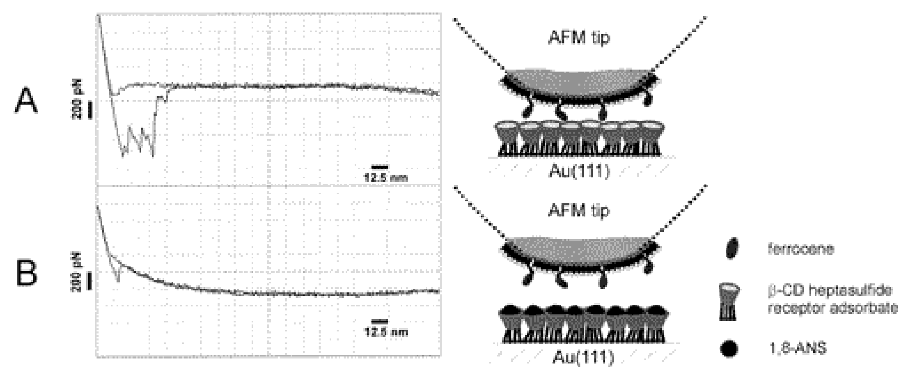
3) Spectroscopic: surface IR, SERS

4) Piezoelectric (mass sensing) : Quartz crystal microbalance (QCM)

5) AFM: Chemical Force Microscopy (direct measurement of noncovalent interactions)



Motesharei and Myles, *JACS* **1998**, *120*, 7328.



Schonherr et al, *JACS* **2000**, *122*, 4963.

SAMs and sensor technologies

Quartz Crystal Microbalance (QCM): Detection of adsorbed gases

Ex. cavitand tetrasulfides on Au(111)

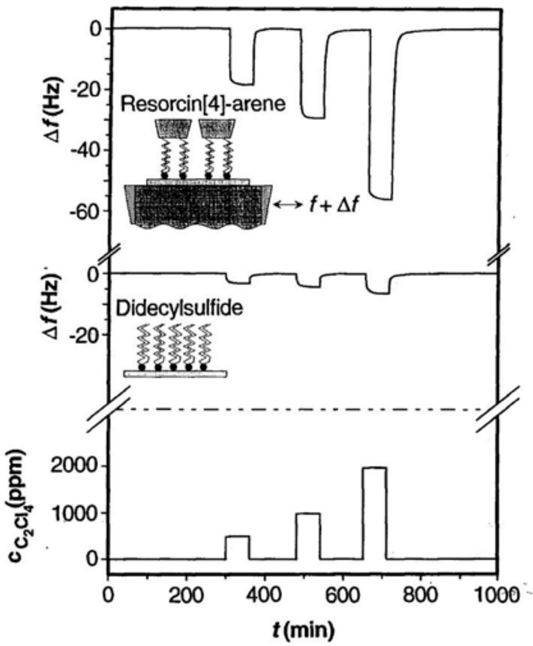
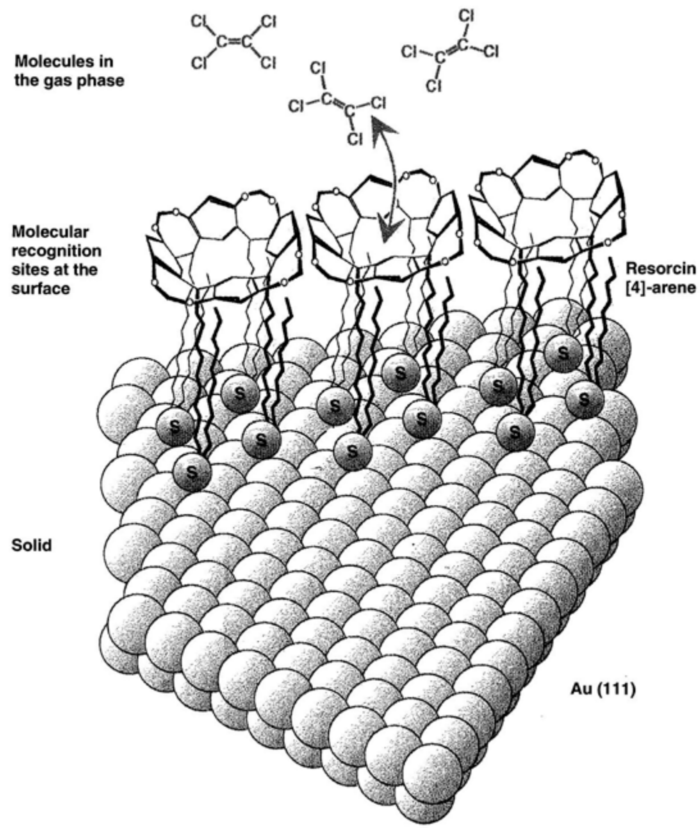
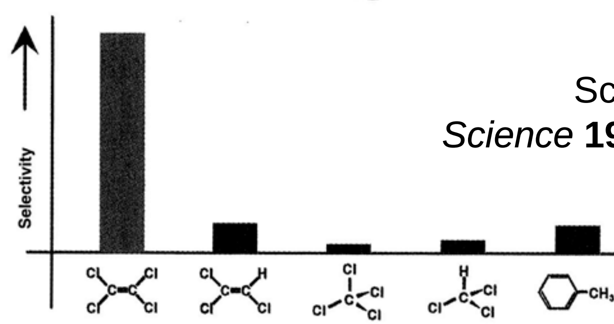


Fig. 4. Changes of frequencies Δ*f* as a function of time *t* during exposure of monolayers of resorcin[4]arene and didecylsulfide to different concentrations $c_{C_2Cl_4}$ in synthetic air at $T = 303$ K. For simplification, the noise of the signal, ± (2 to 3) Hz (which mainly results from small fluctuations of the temperature, which affect the oscillation frequency of the quartz), is omitted here.





Schierbaum et al.
Science **1994**, *265*, 1413.