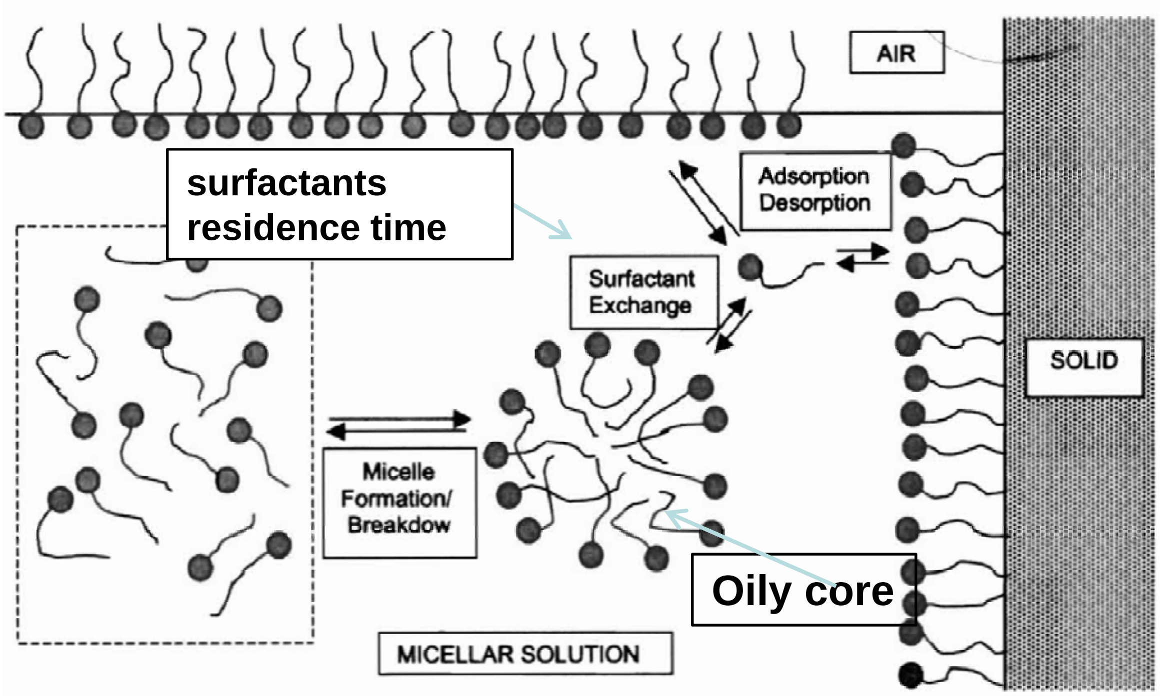
Self-Assembly

Lecture 4

Surfactants Self-Assembly

Surfactant self-assembly



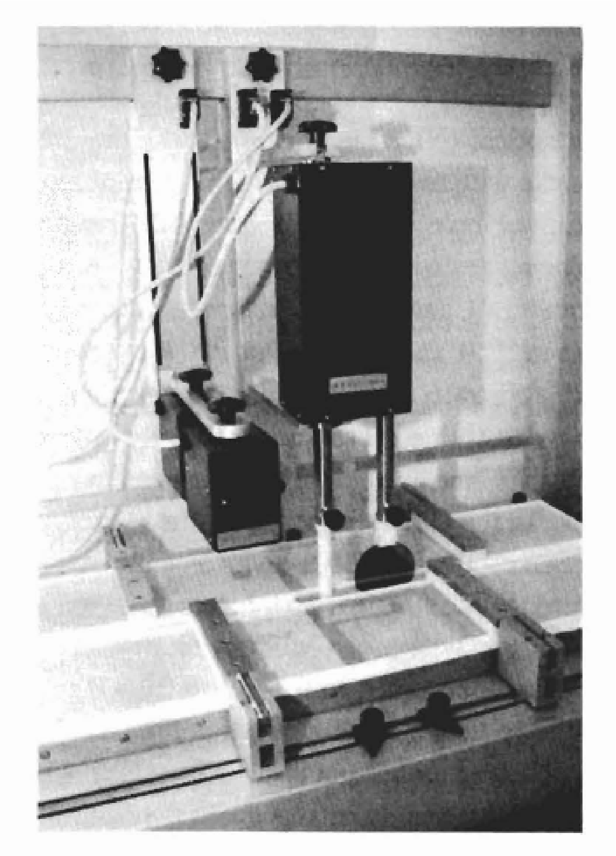
- At low concentrations surfactants form adsorbed layers of air/solution and solid/solution interfaces
- At ***critical micellization concentration*** (cmc) the surfactant starts self-assembling into micelles
  - driven by hydrophobic interaction
  - spontaneous and reversible cooperative transition

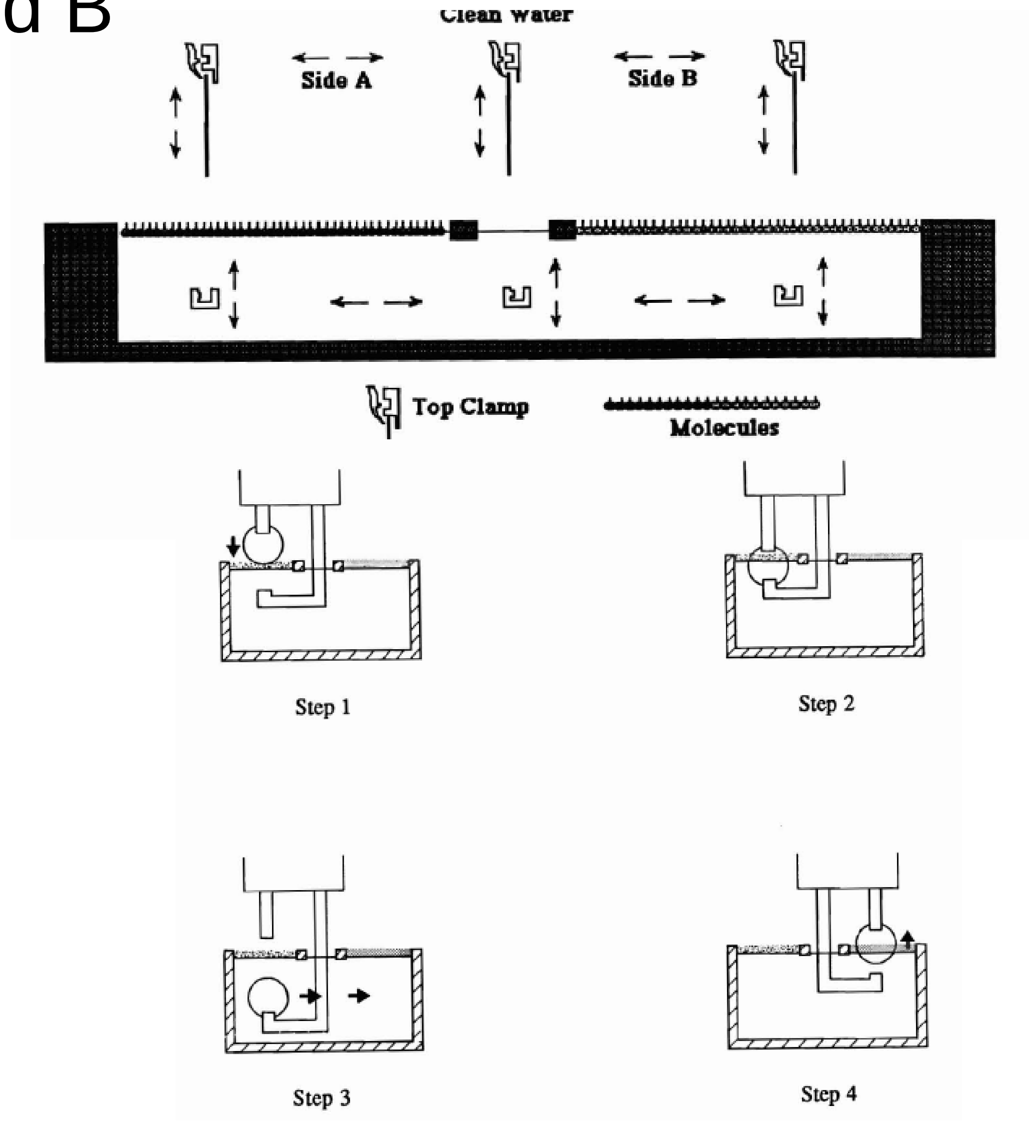
LB Trough

- The trough is usually made of single piece solid Teflon
- Thorough cleaning of the bath (H2SO4,HNO3/HCl etc.), only inorganic cleaning is allowed.
- No organic vaour in the lab
- Filtered subphase based on DI water
- Hydrophilic substrates: Si, glass, quartz, mica, Al, Cr, Sn and their oxides, Au and Ag. Hydrophobic substrate: silanized Si (e.g. with OTS)

LB Trough

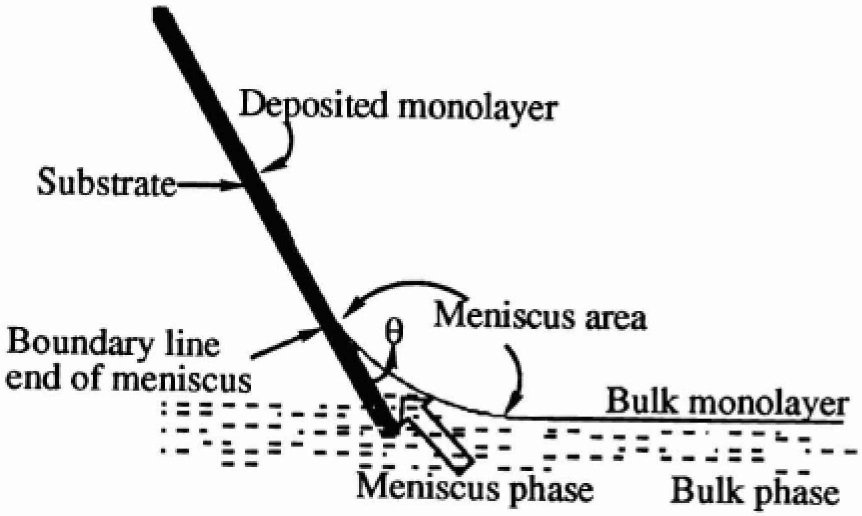
- Double-bath (KSV5000) allows transfer of two different layers A and B

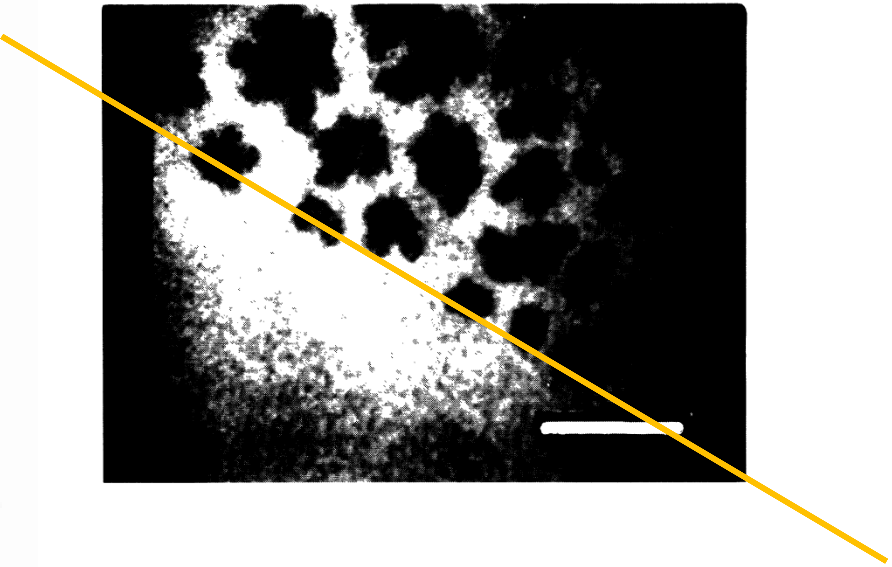




LB transfer

- The monolayer state in the meniscus area is different from the bulk subphase
- one-to-one transfer between the water and the substrate cannot be assumed





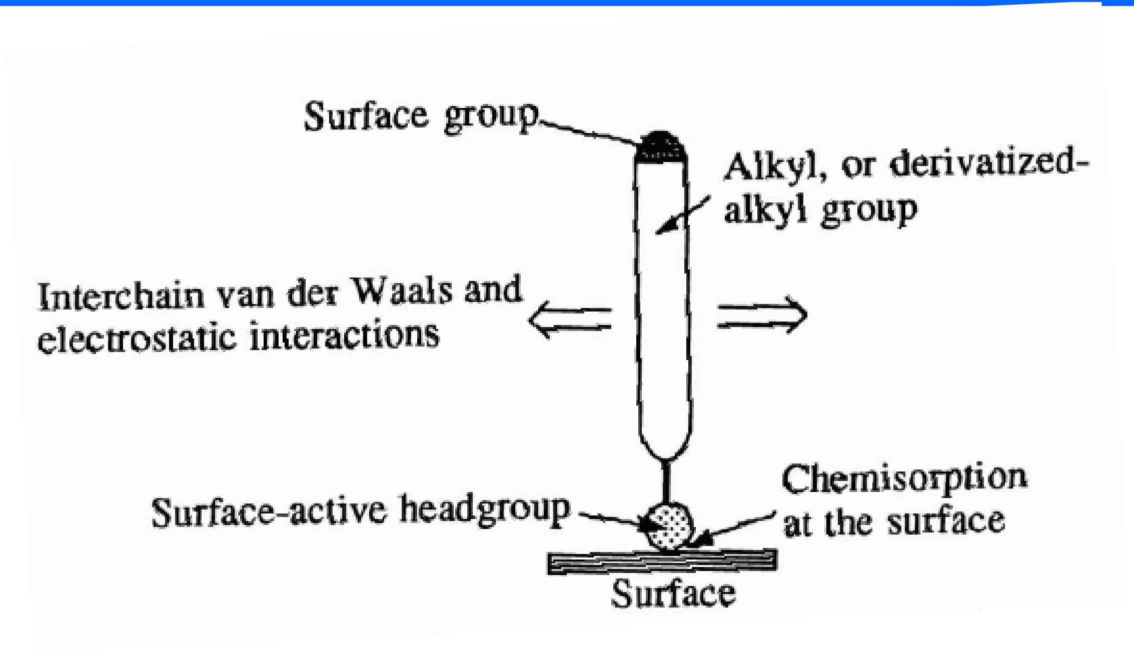
LB transfer

- Shaefer technique (horizontal lifting): good for deposition of very rigid films (2D-solid)
- In many cases, as lifting disrupts the meniscus, the monolayer from water-air interface is sucked in forming Y-type transfer
- Advantages:
  - horizontal deposition rate is not reduced due to viscosity
  - non-centrosymmetric X-films can be formed
  - organic superlattices can be constructed

Self-Assembled monolayers

- **Molecular assemblies** that formed **spontaneously** by immersion of appropriate substrates into a solution of an active surfactant
- Major SA forming molecules:
  - organosilicons on hydroxylated surfaces (SiO_2, Al_2O_3, glass etc.)
  - alkanethiols on Au, Ag, Cu
  - dialkyl sulfides on Au
  - dialkyl disulfides on Au
  - alcohols and amines on Pt
  - carboxylic acids on Al_2O_3 and Ag

Self-Assembled Monolayers



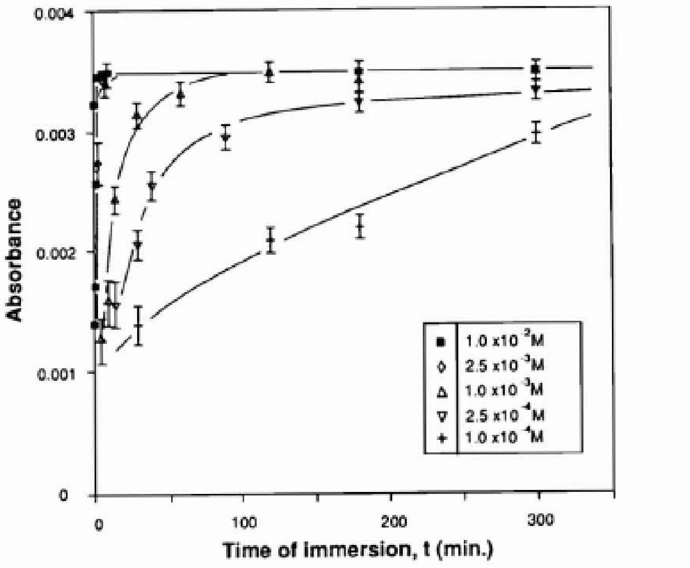
- Typical energies involved:
  - – head substrate interaction ~10kcal/mol (e.g. thiolates on Au ~40-45 kcal/mol)
  - – van der Waals forces between alkyl chains ~1kcal/mol
  - – electrostatic interaction between the surface groups

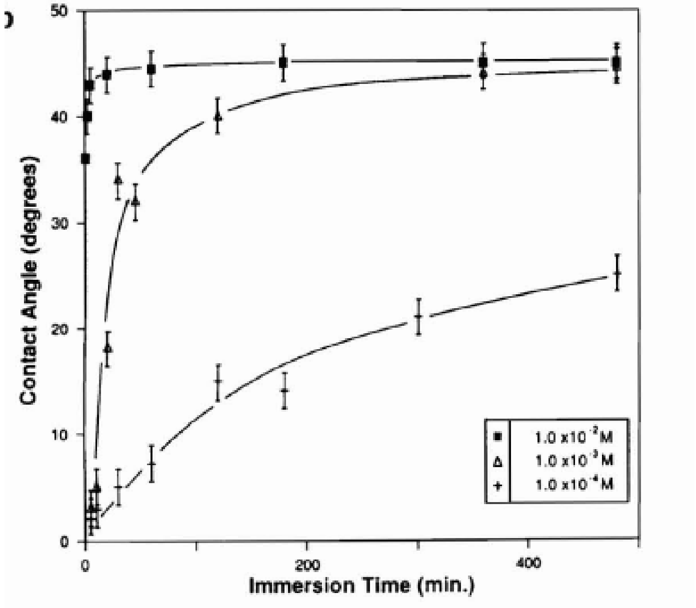
Kinetics of SAM

- Stearic acid ($C_{17}H_{35}COOH$) on Al_2O_3 and glass
  - time required to form a monolayer decreases with the concentration
  - substrate dependent: assembly on Al2O3 is faster than on glass
- can be described by Langmuir equation (i.e. limited by adsorption kinetics)

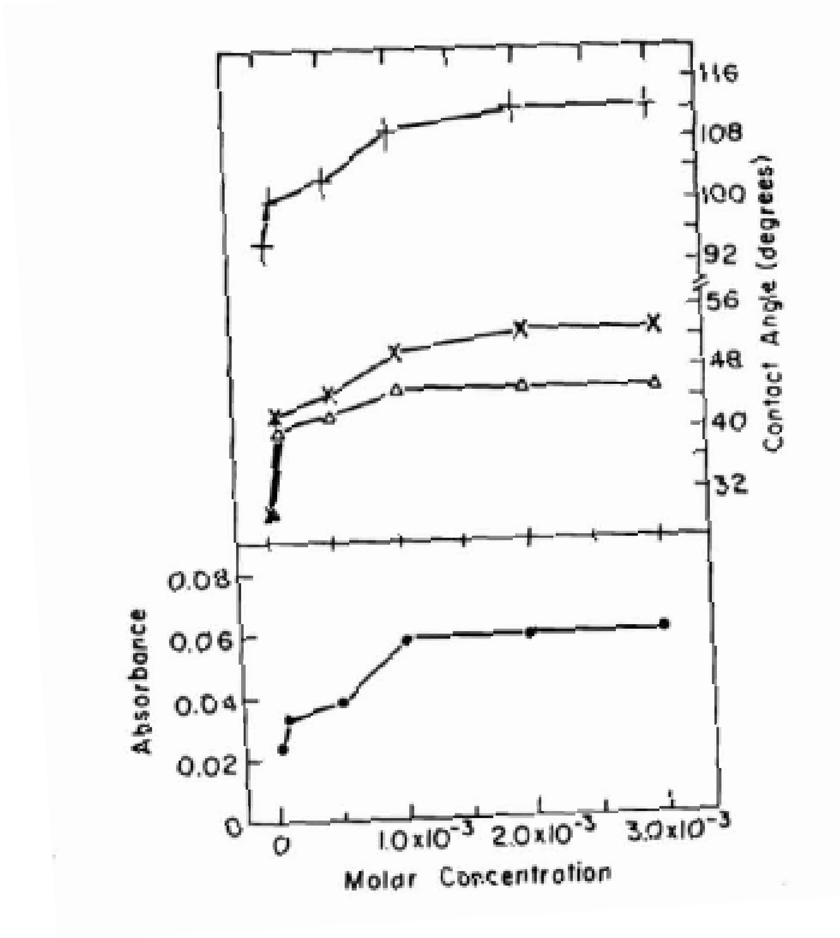
$$\frac{d\theta}{dt} = \frac{k_a}{N_0} c(1-\theta) - \frac{k_d}{N_0}\theta \Rightarrow \theta_{eq} = \frac{k_a c}{k_a c + k_d} = \frac{c}{c+K}$$

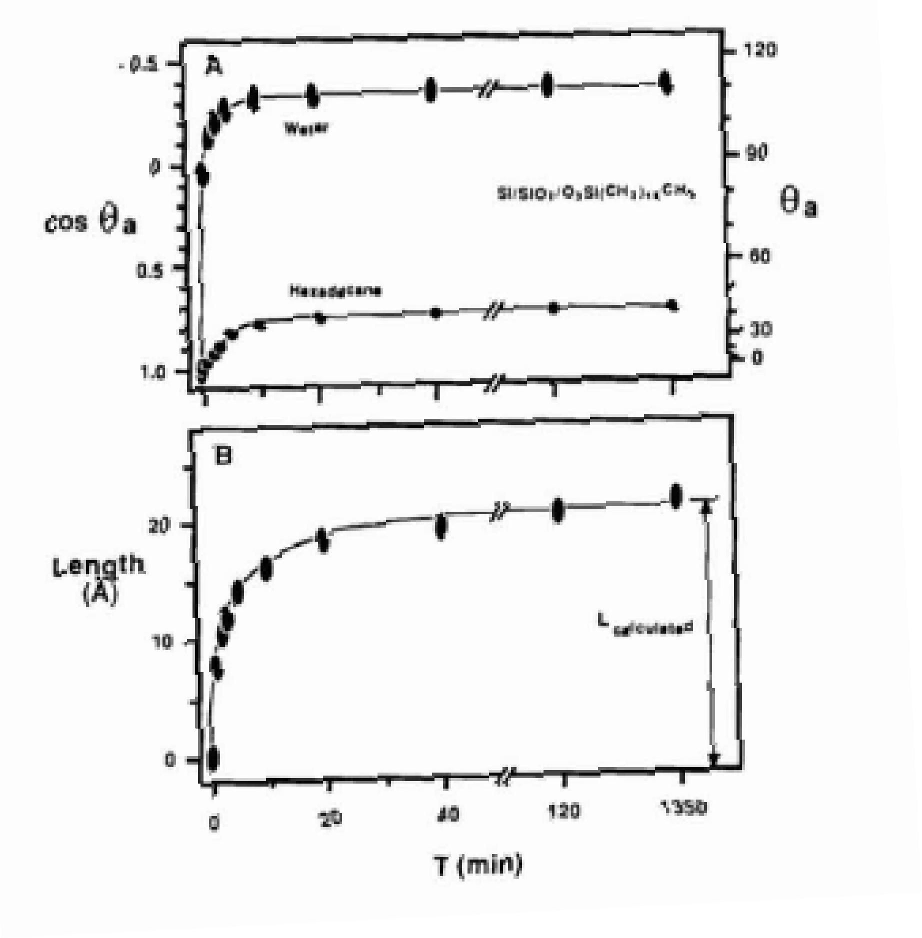
$$K = \frac{k_d}{k_a} \propto \exp\left(\Delta G_a / RT\right) \Rightarrow \Delta G_a(Al_2O_3) \approx -9.2 kcal/mol$$





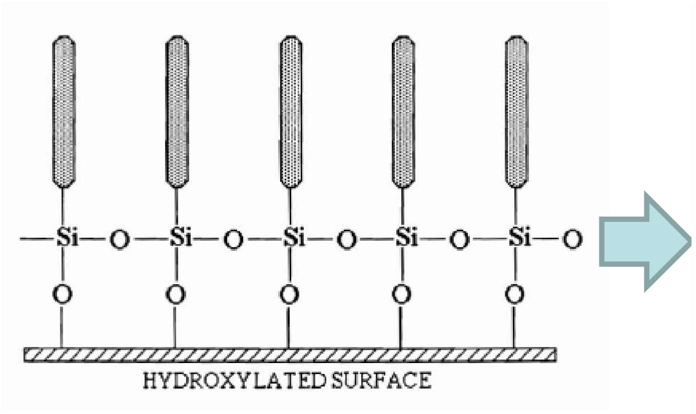
Kinetics of SAM

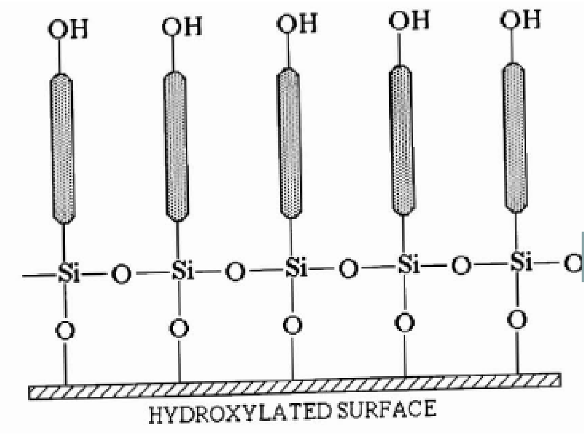


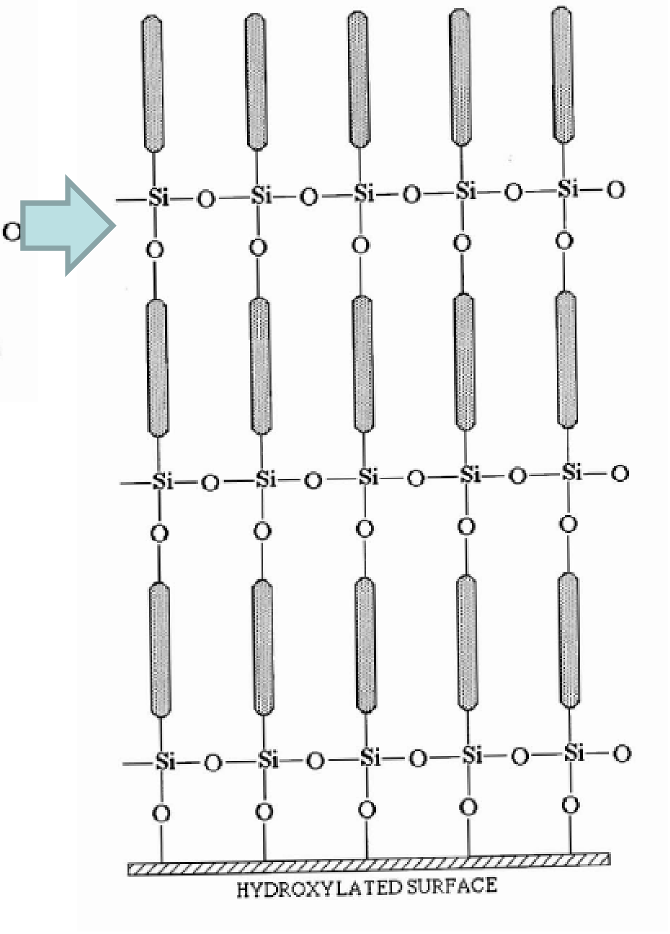


- Octyltrichlorosilane (OTS) on Si
- Tetradecyltrichlorosilane (TTS) on Si

SA multilayer





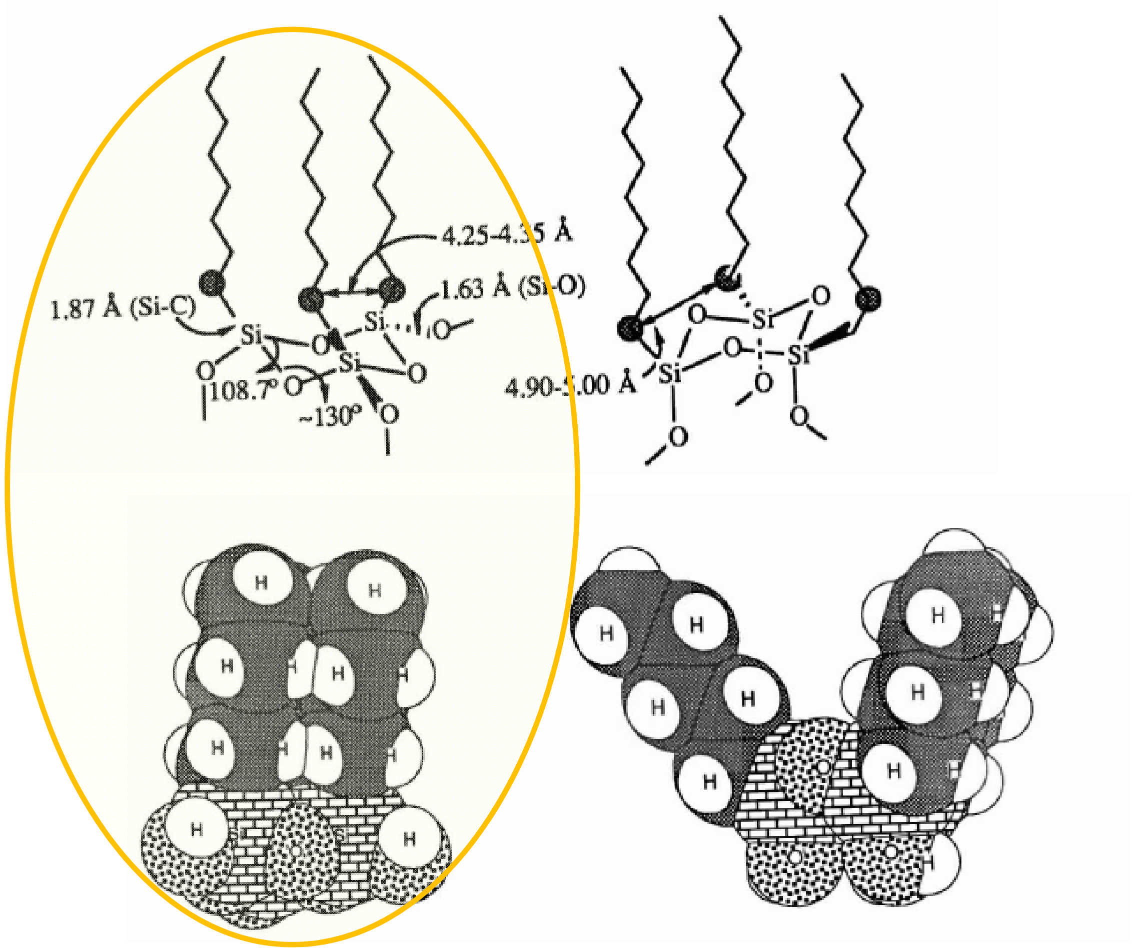


- If a monolayer on surface can be modified to bear hydroxyl groups (e.g. reduction of surface ester group) a multilayer can be created

Structure of Siloxane SAM

- oligomers of siloxane adsorb faster from a solution than monomers
- two major trimer configurations are possible

corresponds to experimentally observed 15º tilt

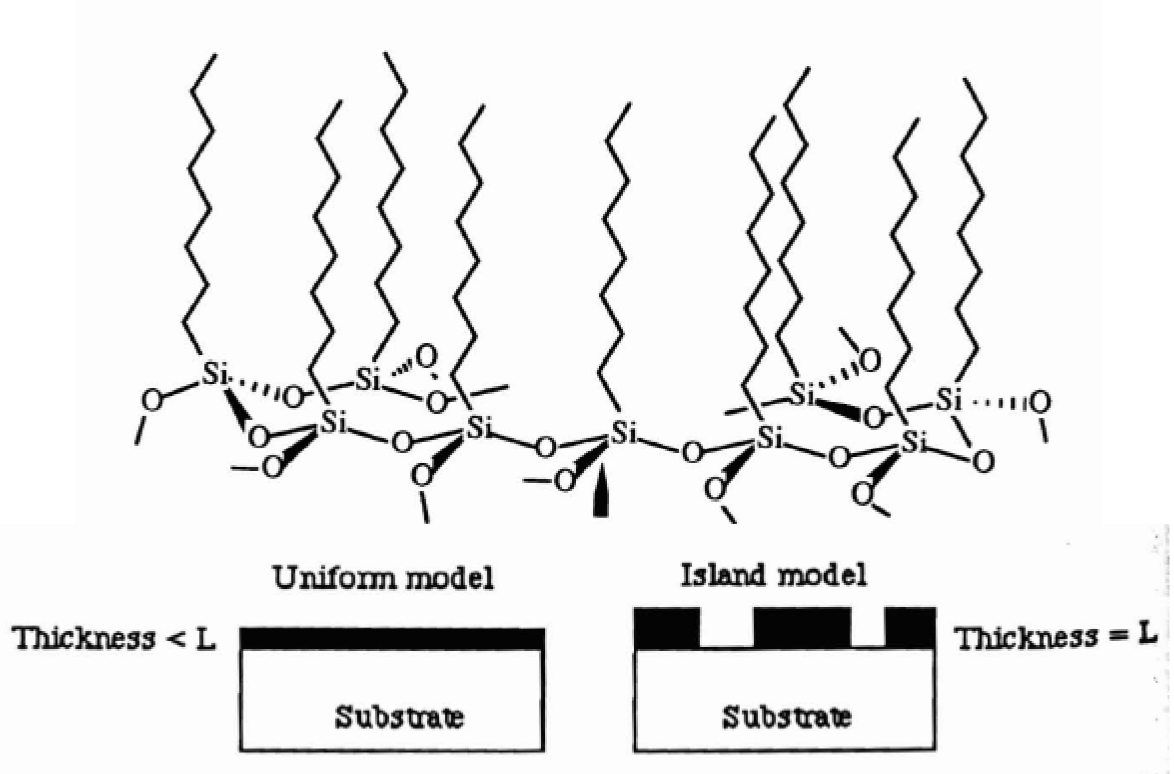


axial

equatorial

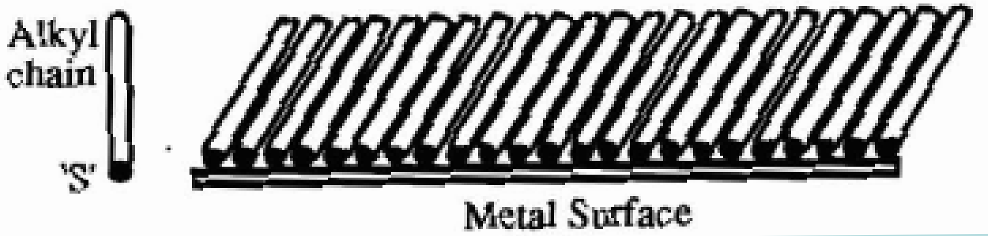
Structure of Siloxane SAM

- alkylsilanes SAMs are inherererently **more disordered** and **less closely packed** that alkanethiols due to more limited freedom to move and re-arrange
- measured thickness of OTS on Si ~25Å, tilt 14º.

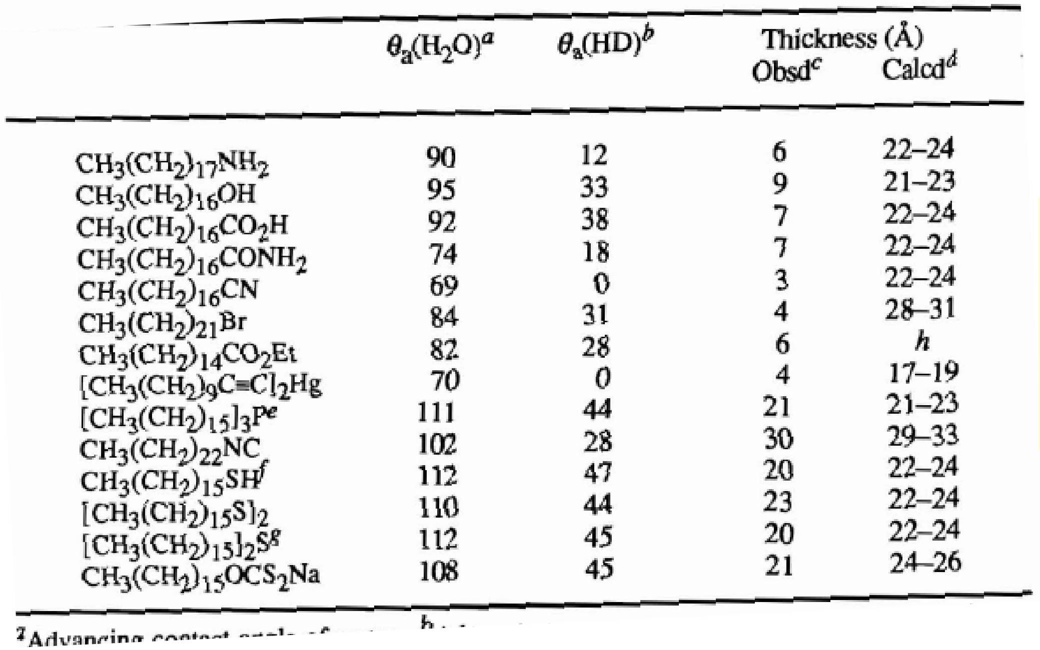


Alkanethiol SAMs

- usually produced by immersion of a substrate into mM solution.
- immersion time is typically ~1h for alkanethiols, several days for disulfides and sulfides



Adsorption of alkanes with various terminal groups on gold



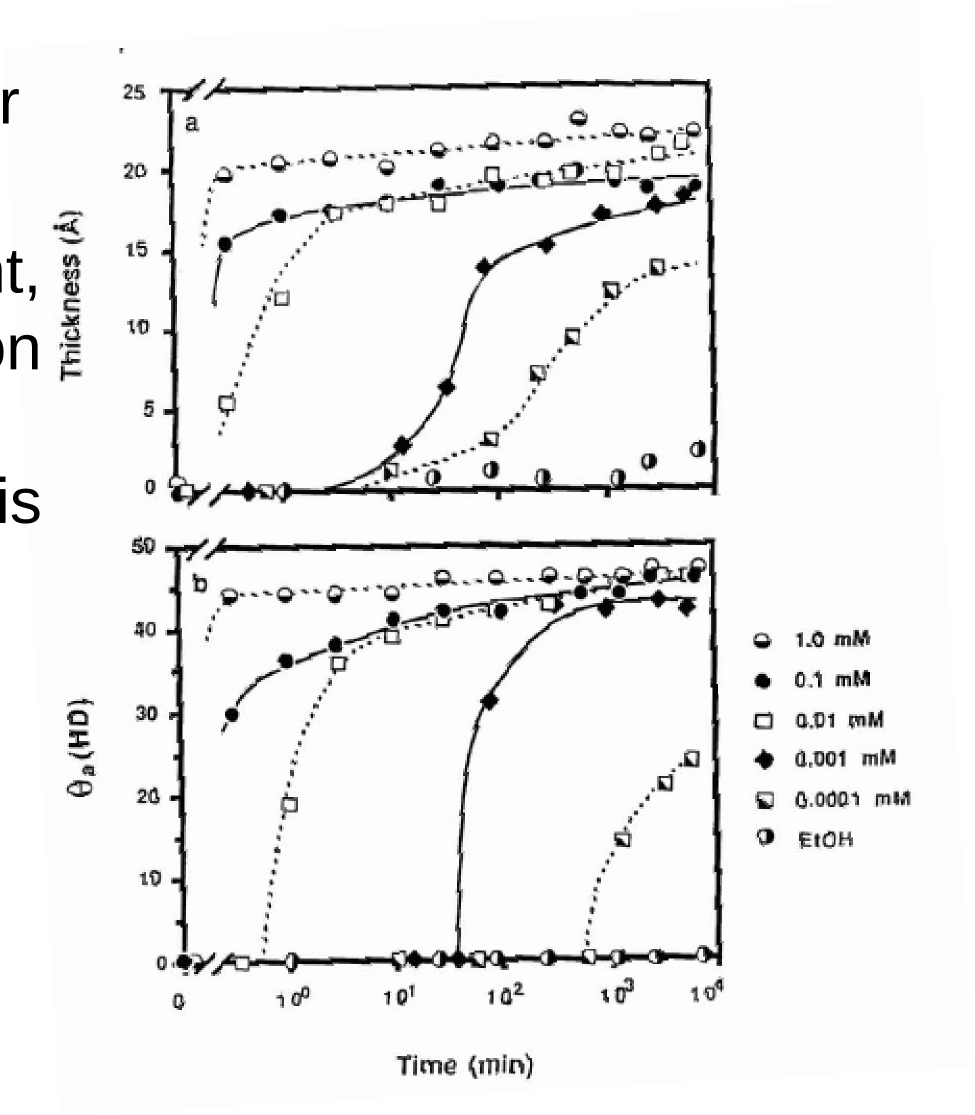
	$\theta_a(H_2O)^a$	$\theta_a(HD)^b$	Thickness (Å) Obsd[c]	Thickness (Å) Calcd[d]
$CH_3(CH_2)_{17}NH_2$	90	12	6	22–24
$CH_3(CH_2)_{16}OH$	95	33	9	21–23
$CH_3(CH_2)_{16}CO_2H$	92	38	7	22–24
$CH_3(CH_2)_{16}CONH_2$	74	18	7	22–24
$CH_3(CH_2)_{16}CN$	69	0	3	22–24
$CH_3(CH_2)_{21}Br$	84	31	4	28–31
$CH_3(CH_2)_{14}CO_2Et$	82	28	6	*h*
$[CH_3(CH_2)_9C{\equiv}C]_2Hg$	70	0	4	17–19
$[CH_3(CH_2)_{15}]_3P^e$	111	44	21	21–23
$CH_3(CH_2)_{22}NC$	102	28	30	29–33
$CH_3(CH_2)_{15}SH^f$	112	47	20	22–24
$[CH_3(CH_2)_{15}S]_2$	110	44	23	22–24
$[CH_3(CH_2)_{15}]_2S^g$	112	45	20	22–24
$CH_3(CH_2)_{15}OCS_2Na$	108	45	21	24–26

[a] Advancing

Only S and P form dense monolayers on gold

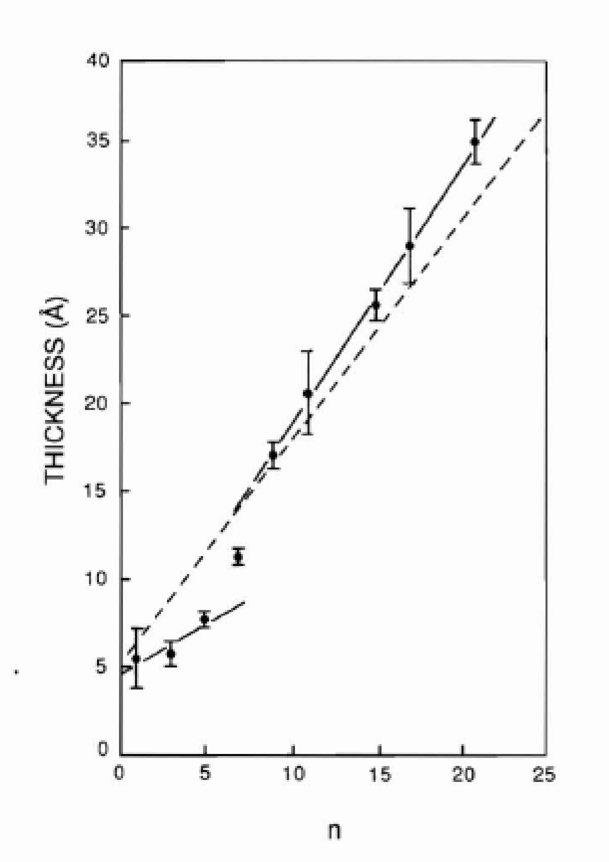
Kinetics of SAM formation on gold

- kinetics is faster for longer chains due to stronger van der Waals interaction
- in case of phenyl rings present, the kinetic still depends only on the length of alkane chain, phenyl position closer to thiol is preferred
- two kinetics are observed: adsorption (fast) and re-arrangement (slow)

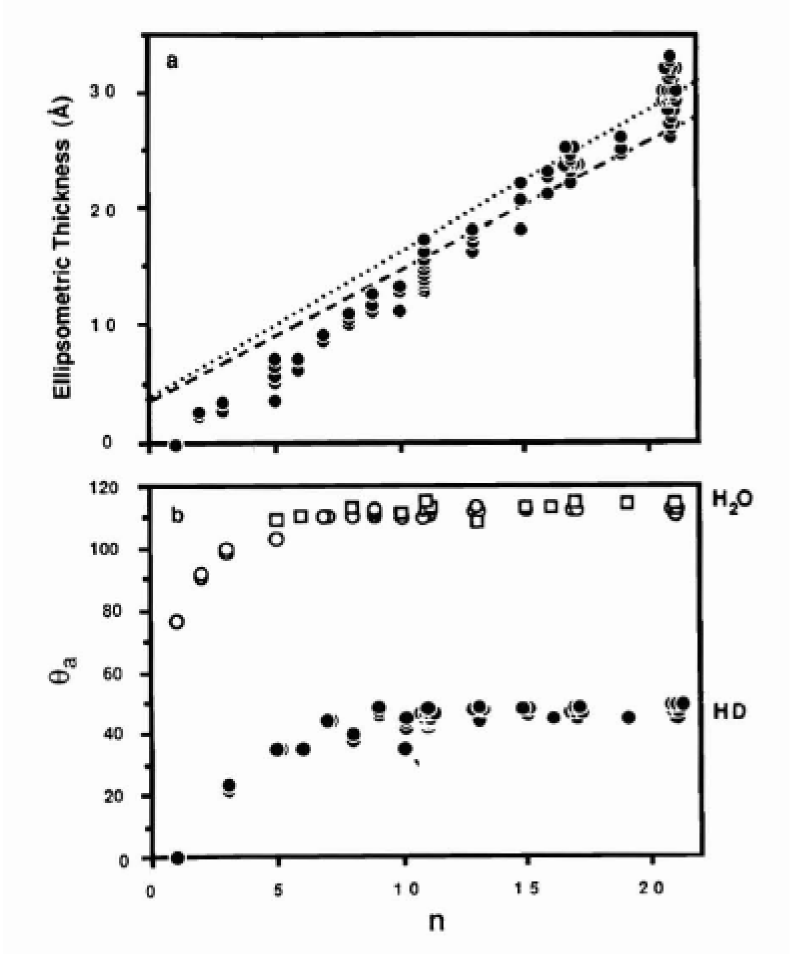


Structure of alkanethiol SAMs

- most probably, the alkanethiols shorter than n=9 form liquid-like structure



thickness vs. # of carbons



ellipsometric thickness and adv.angle vs. # of carbons

Structure of alkanethiol SAMs

- Chemisorption mechanism on Au
  - dialkylsulfides

$$RS-SR+Au^{0}\longrightarrow 2RS-Au^{+}+Au^{0}$$

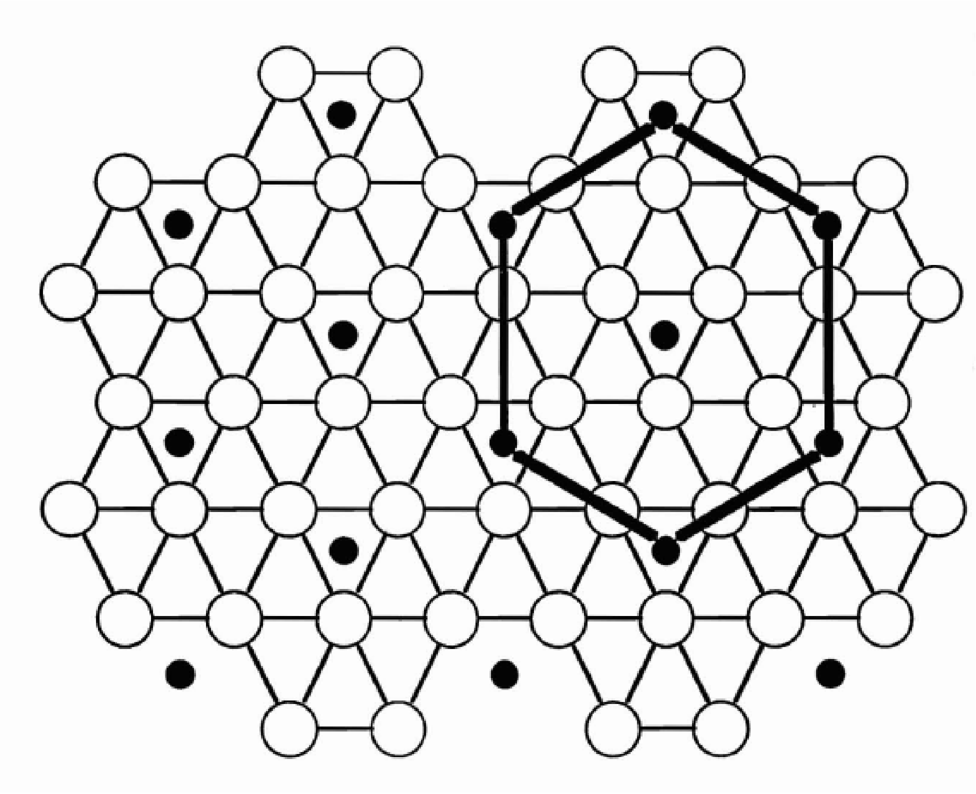
  - thiols (not established yet)

$$RS-H+Au^{0}\longrightarrow RS^{-}-Au^{+}+\frac{1}{2}H_{2}+Au^{0}$$

$$RS-H+Au^{0}+oxidant\longrightarrow RS^{-}-Au^{+}+\frac{1}{2}H_{2}0+Au^{0}$$

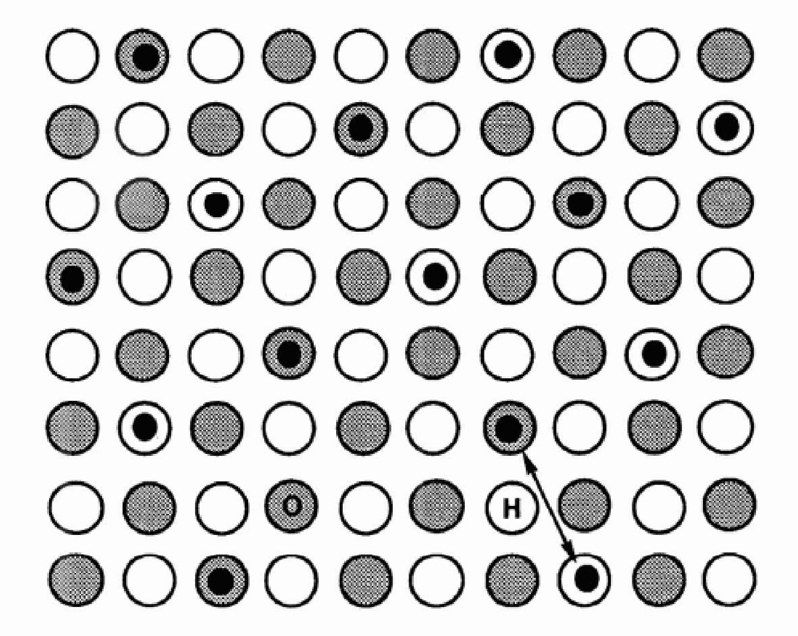
Structure of alkanethiol SAMs

- on Au(111) bonding has both σ and π character
- S...S distance 4.99Å, area 21.4 Å^2.
- hexagonal symmetry



Au (111)

- S...S distance 4.56Å, area 21.4 Å^2.
- based-centered square symmetry



Au (100)

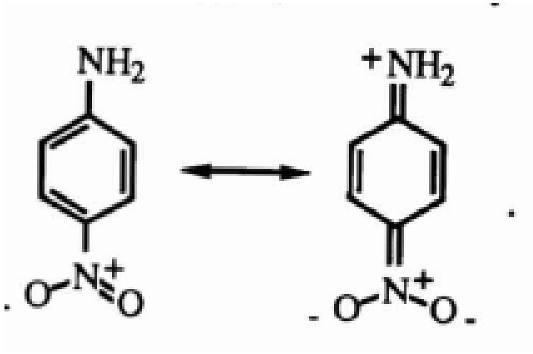
Applications

- **Nonlinear optics** – interaction of light with matter that produces new light field different in wavelength or phase

$$\vec{p} = \alpha \cdot \vec{E} + \beta \cdot \vec{E}^2 + \gamma \cdot \vec{E}^3 + \ldots$$

2nd rank tensor

3rd rank tensor

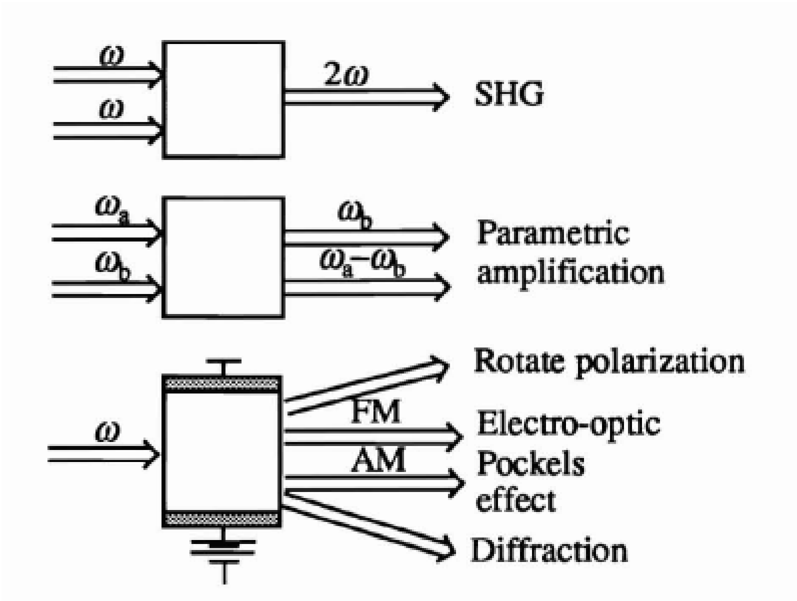


- absence of centre of symmetry is required for second-order polarizability
- molecules with conjugated bonds possess large α and γ.

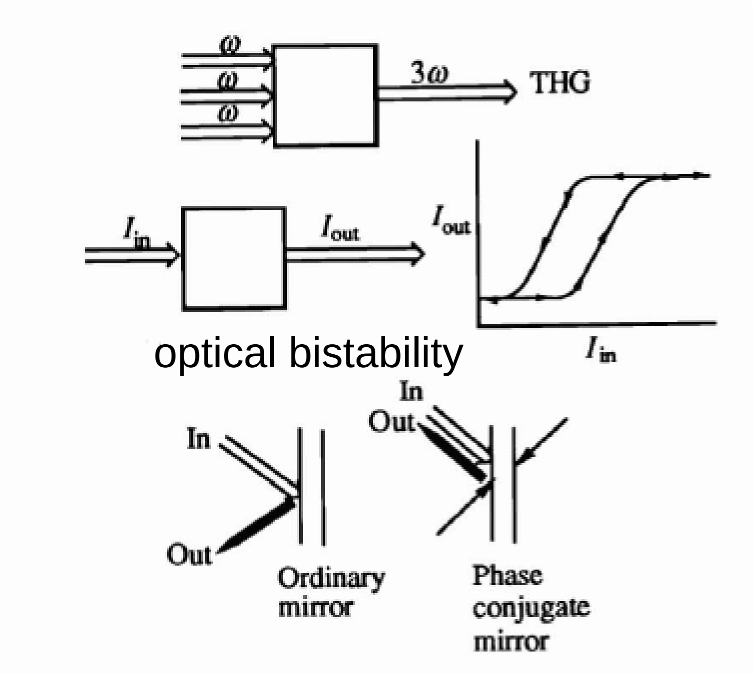
Applications

- consequences of non-linear susceptibility:

$\chi^{(2)}$:



$\chi^{(3)}$:



optical bistability

Applications

- Dielectric layers