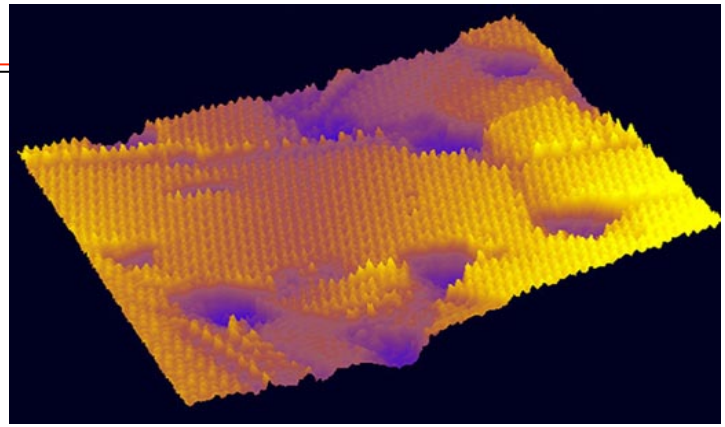
Self-Assembled Monolayers (SAMs)

A. Ulman *Chem. Rev.* **1996**, *96*, 1533-1554.

J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo, G. M. Whitesides
Chem. Rev. **2005**, *105*, 1103-1169.

nanostructures are “all surface”

$$V \propto l^3$$
$$S \propto l^2$$



STM Image of a SAM

- atoms or molecules at the surface of a material experience a different environment from those in the bulk and thus have different free energies, electronic states, reactivities, mobilities, and structures.
- the physical properties of nanostructures depend to a much greater extent on their surface and interfacial environment than do bulk material.

2D-SAMs

Table 1. Combinations of Headgroups and Substrates Used in Forming SAMs on Metals, Oxides, and Semiconductors

Ligand	Substrates	Morphology of Substrate: Thin Films or Bulk Material	Morphology of Substrate: Nanoparticles or Other Nanostructures
ROH	Fe_2O_3		35
	Si-H	36	
	Si	37	
RCOO-/RCOOH	α-Al_2O_3	38,39	
	Fe_2O_3		40
	Ni		41,42
	Ti/TiO_2	43	
RCOO-OOCR	Si(111):H	44	
	Si(100):H		
Ene-diol	Fe_2O_3		45
RNH_2	FeS_2	46	
	Mica	47	
	Stainless Steel 316L	48	
	$YBa_2Cu_3O_{7-\delta}$	49	
	CdSe		50
RC≡N	Ag	51	
	Au		
R-N≡N$^+$(BF_4^-)	GaAs(100)	52	
	Pd	52	
	Si(111):H	52	
RSH	Ag	26	53,54
	$Ag_{50}Ni_{50}$	55	
	AgS		56
	Au	26	57
	AuAg		58
	AuCu		58
	Au_xPd_{1-x}		58
	CdTe		59
	CdSe		60
	CdS		61,62
	Cu	26	58
	FePt		63-66
	GaAs	67	
	Ge	68	
	Hg	69-71	
	HgTe		72
	InP	73	
	Ir		74
	Ni	75	
	PbS		76-78
	Pd	30	74,79
	PdAg		58
	Pt	32	80
	Ru		81
	Stainless Steel 316L	48	
	$YBa_2Cu_3O_{7-\delta}$	82	
	Zn	83	
	ZnSe	84	
	ZnS		85
RSAc	Au	86	
	Au		87
RSR'	Au	88	
RSSR'	Ag	89	90
	Au	20	90-92
	CdS		61
	Pd	30	
	Au	93	
RCSSH	Au	94	
	CdSe		95
$RS_2O_3^-Na^+$	Au	96	98
	Cu	97	
RSeH	Ag	99	
	Au	100,101	
	CdS		60
	CdSe		102
RSeSeR'	Au	101	
R_3P	Au		103
	FeS_2	46	
	CdS		104
	CdSe		104
	CdTe		104
$R_3P{=}O$	Co		105,106
	CdS		104
	CdSe		104
	CdTe		104
RPO_3^{2-}/$RP(O)(OH)_2$	Al	107	
	Al-OH	108	
	$Ca_{10}(PO_4,CO_3)_6(OH)_2$	109	
	GaAs	110	
	GaN	110	
	Indium tin oxide (ITO)	111	
	Mica	112	
	TiO_2	113,114	
	ZrO_2	114,115	
	CdSe		116-118
	CdTe		118,119
RPO_4^{2-}	Al_2O_3	120	
	Nb_2O_5	120	
	Ta_2O_5	121	
	TiO_2	120,122	
RN≡C	Pt	123	124
$RHC{=}CH_2$	Si	37	
RC≡CH	Si(111):H	125	
$RSiX_3$ X = H, CL, OCH_2CH_3	HfO_2	126	
	ITO	127	
	PtO	128	
	TiO_2	113,126,129	
	ZrO_2	126,129	

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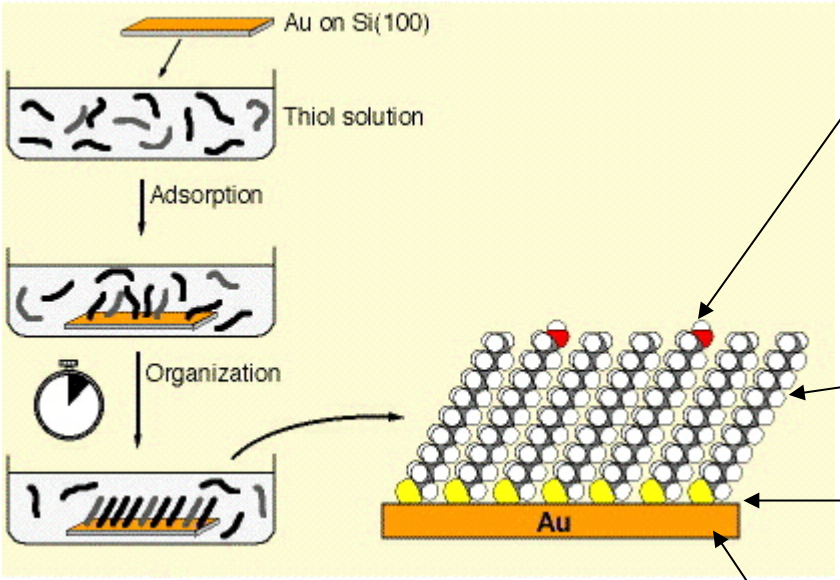
2D-SAMs

Self-assembled monolayers are formed by simply immersing a substrate into a solution of the surface-active material. The driving force for the spontaneous formation of 2D assembly includes chemical bond formation of molecules with the surface and intermolecular interactions.



air-monolayer interface group
group-specific interactions
(H-bonding, dipolar)

intermolecular interactions
alkyl groups

chemisorption at the surface,
surface-active head group

metal substrate

piranha solution: 3:1 concentrated H_2SO_4: 30% H_2O_2

acqua regia solution: 3:1 $HCl:HNO_3$

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2D-SAMs

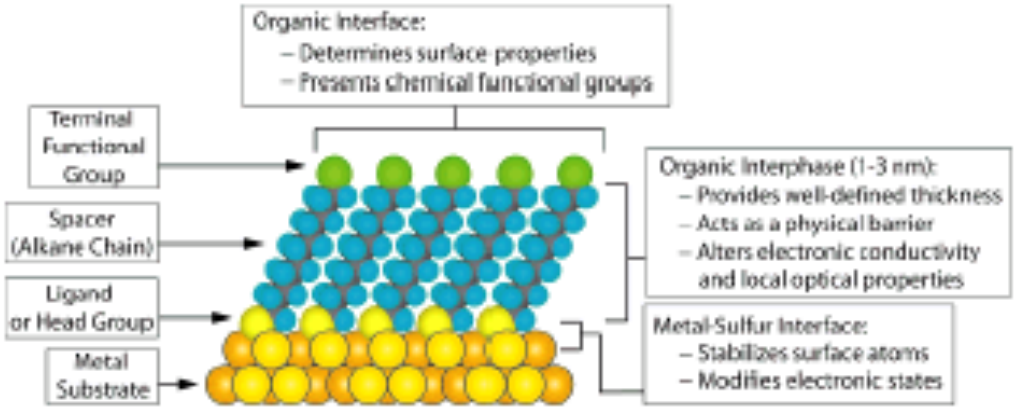

Figure 1. Schematic diagram of an ideal, single-crystalline SAM of alkanethiolates supported on a gold surface with a (111) texture. The anatomy and characteristics of the SAM are highlighted.

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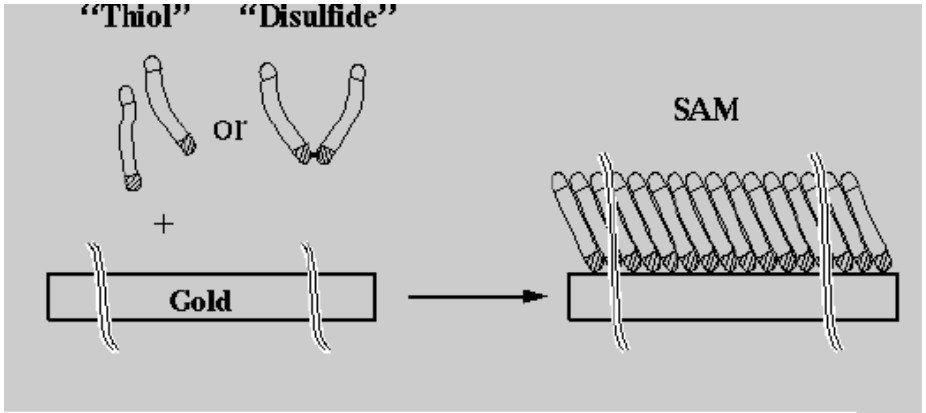
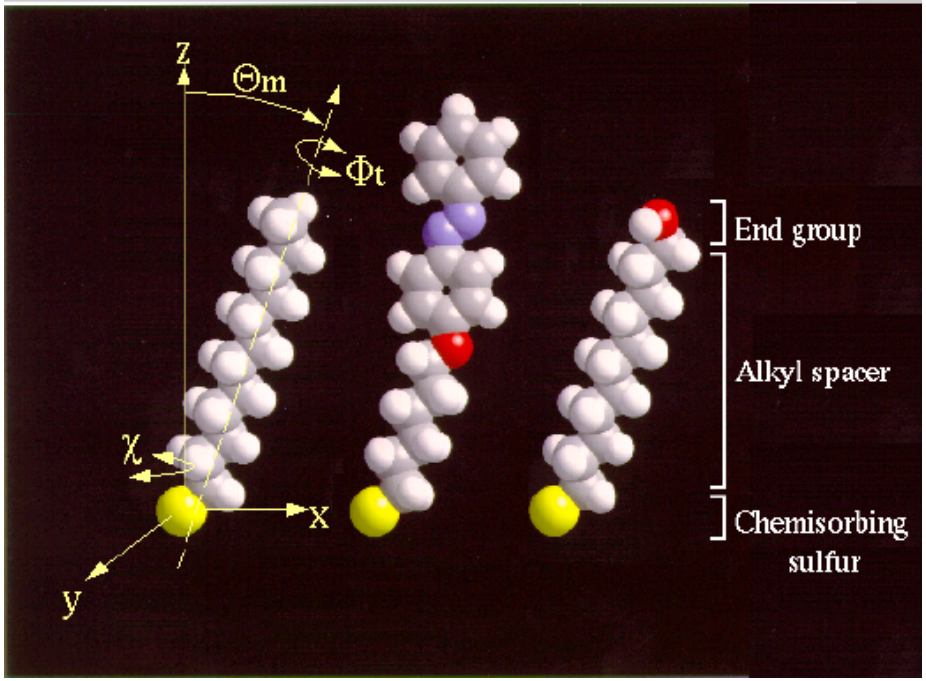
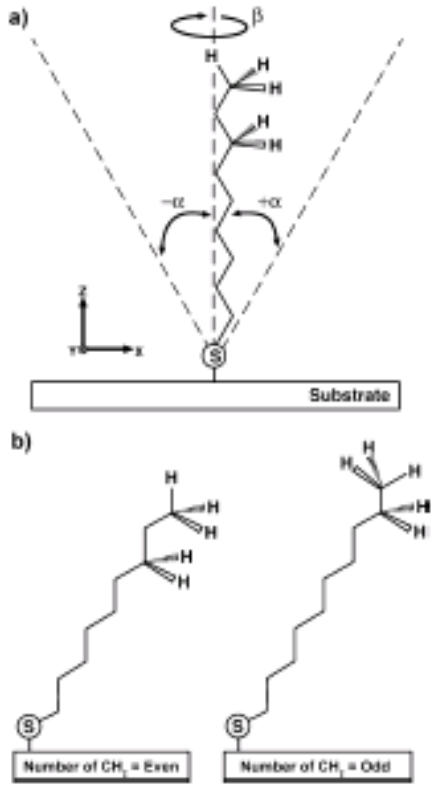
2D-SAMs







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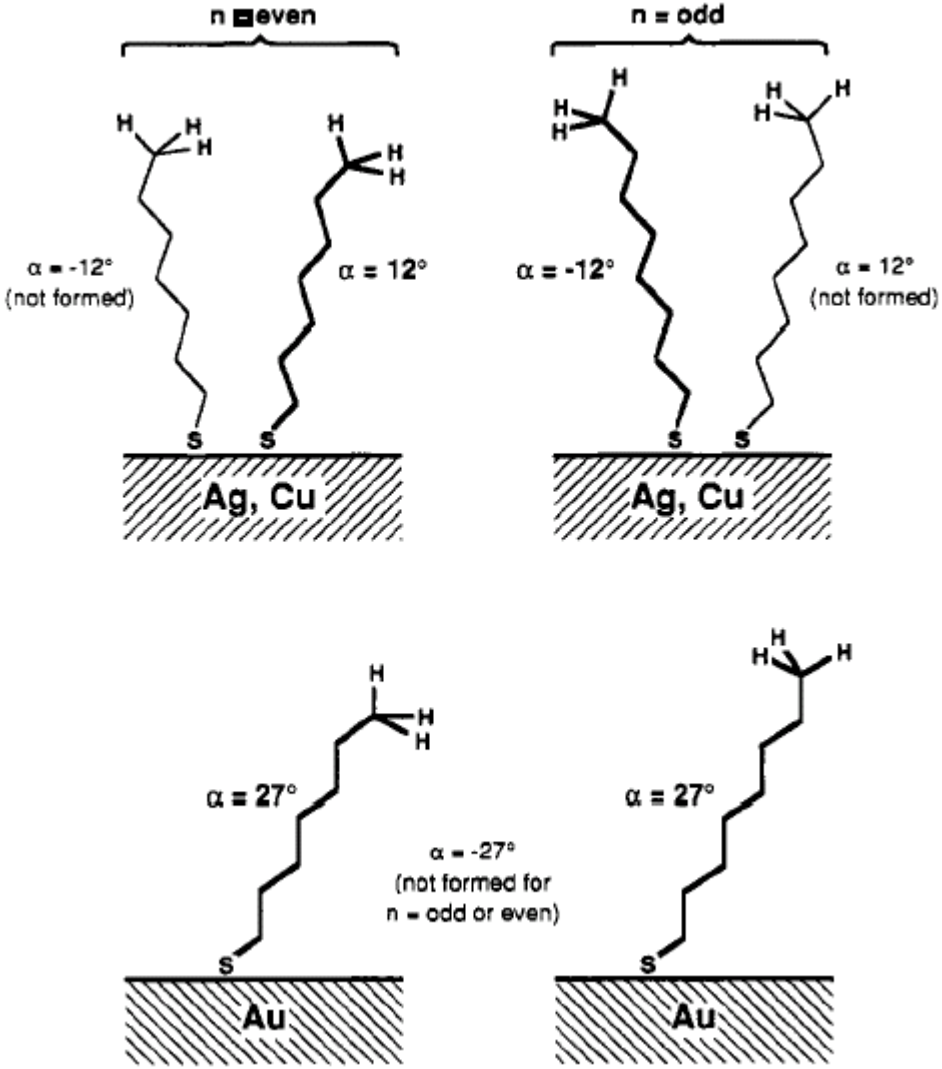
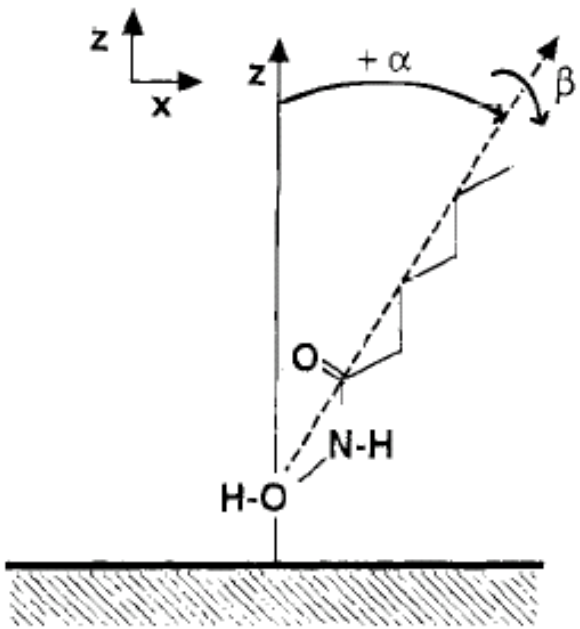
2D-SAMs





MOx	α	β
Cu	| 20°|	54°
Ag	-14°	38°
Al	| 8°|	47°
Ti	---	---

(RSH on Pd: $|\alpha| \approx 10°$)

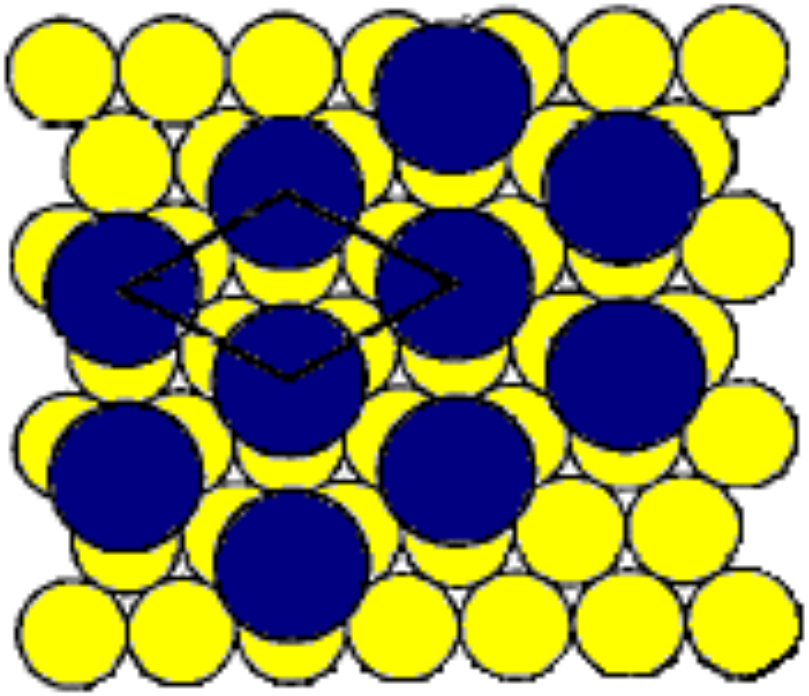
Folkers, John P.; et al. *Langmuir* **1995**, *11*, 813.

Laibinis, Paul E.; Whitesides,G. M.; et al. *J. Am. Chem. Soc.* **1991**, *113*, 152.

2D-SAMs

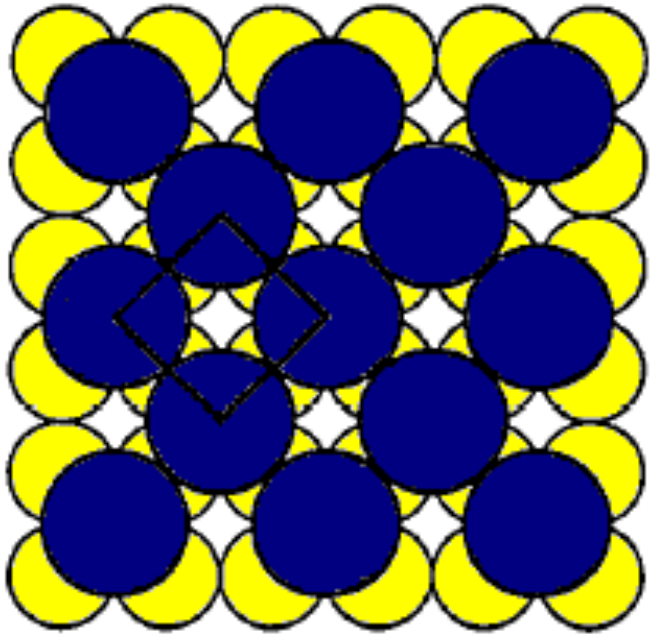
Structure of

$(\sqrt{3} \times \sqrt{3})R30°$



Au (111)

c(2x2)

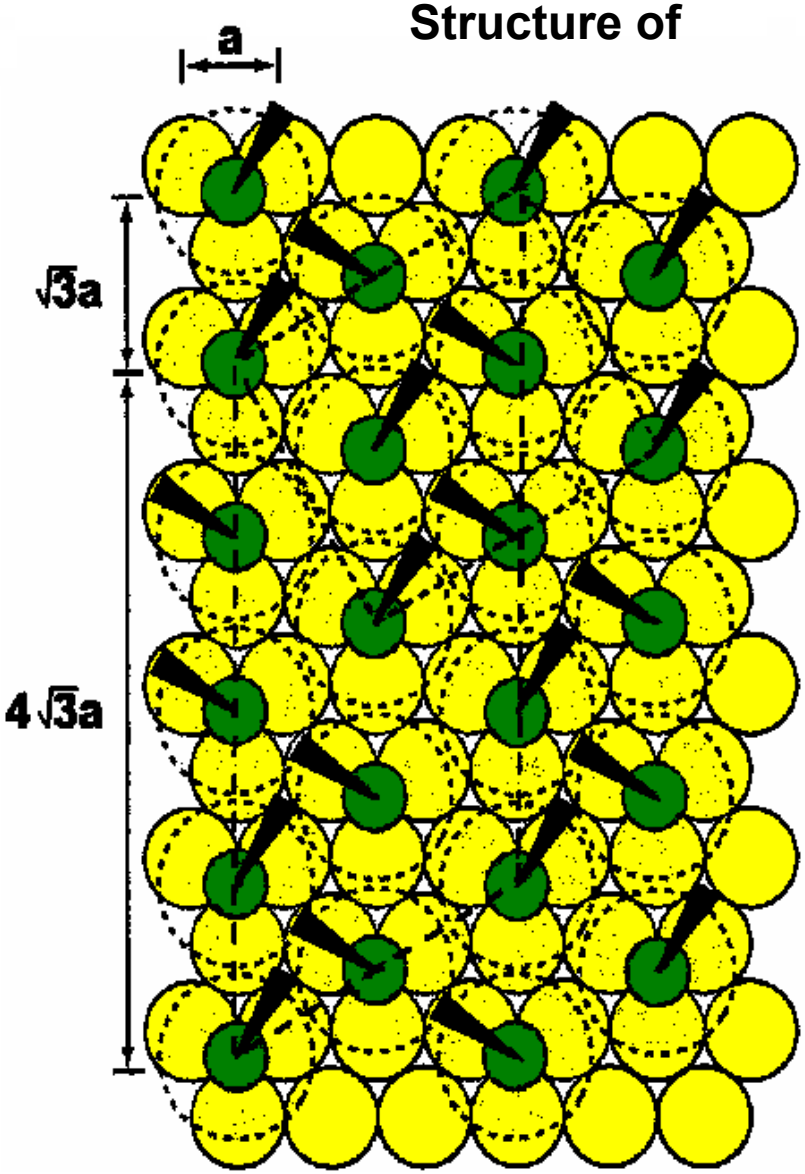


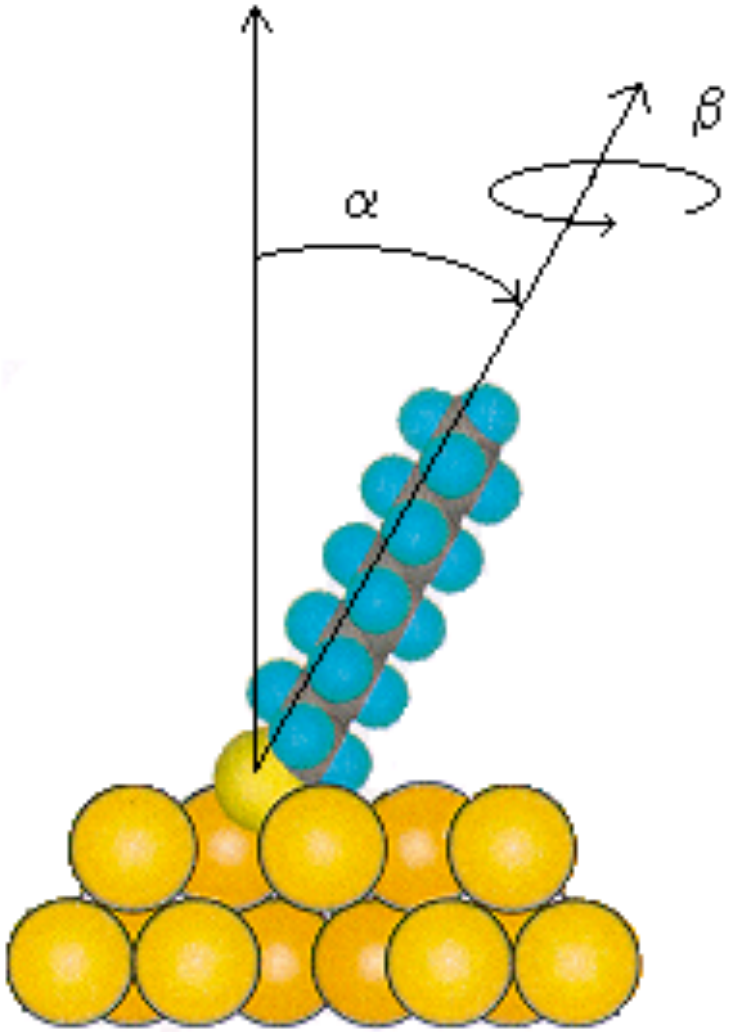
Au (100)

Dubois, L., *et al., J. Chem. Phys.* **1993**, *98*, 678.

2D-SAMs

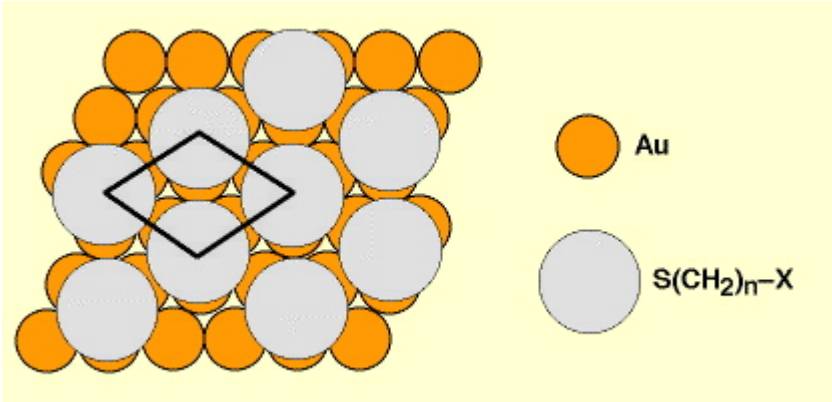
Structure of





2D-SAMs

alkanethiols on Au(111)



A schematic model of the √3 x √3R30° overlayer structure formed by alkanethiolate SAMs on Au(111).

2 mechanisms of chemisorption: a first fast (~ 1 min) followed by a slow one (~ 100 min)

S-S spacing of 4.97 Å

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STM

Scanning tunneling microscopy (STM) is a laboratory technique capable of obtaining atomic-scale resolution images of surfaces.

overcome about ten years later by Gerd Binnig and Heinrich Rohrer at the IBM Rüschlikon laboratory, who succeeded in creating an instrument with stable vacuum awarded in the 1986 Nobel Prize in physics

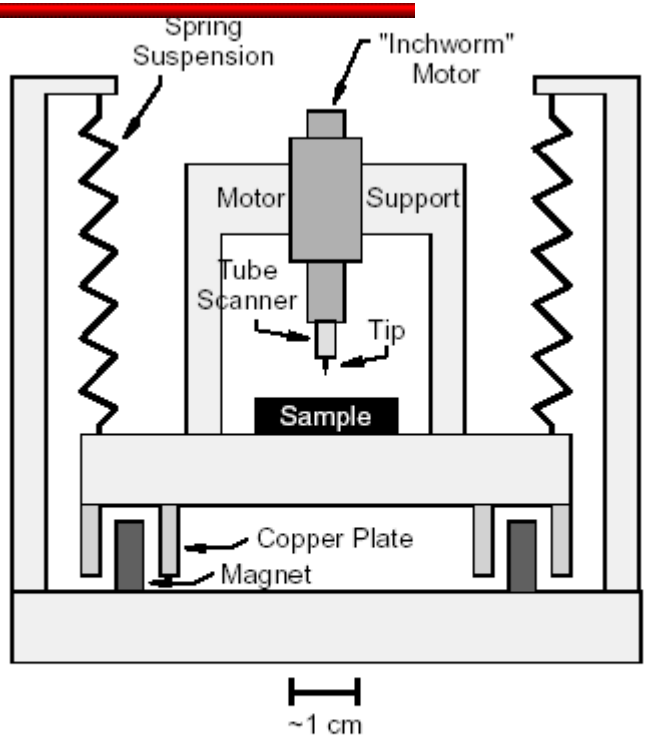
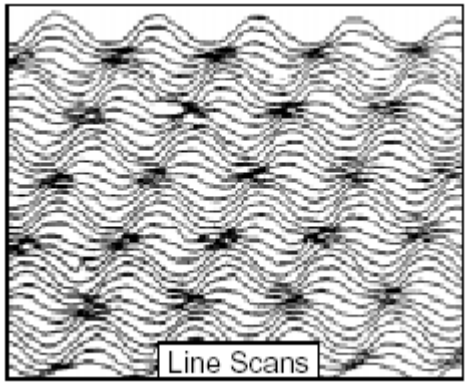
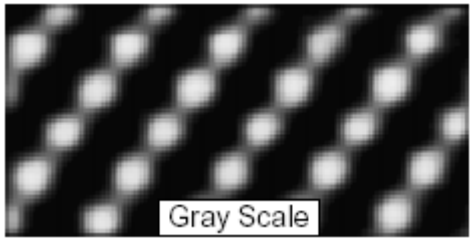
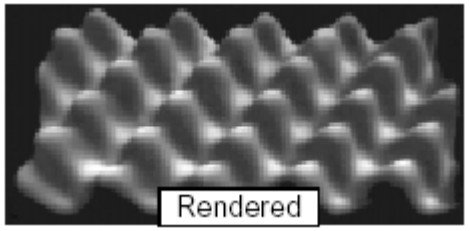


FIG. 3. Common elements of an STM, including a tip mounted on a piezoelectric tube scanner, a coarse approach mechanism (in this case an "inchworm" motor), and a damped vibration isolation system.

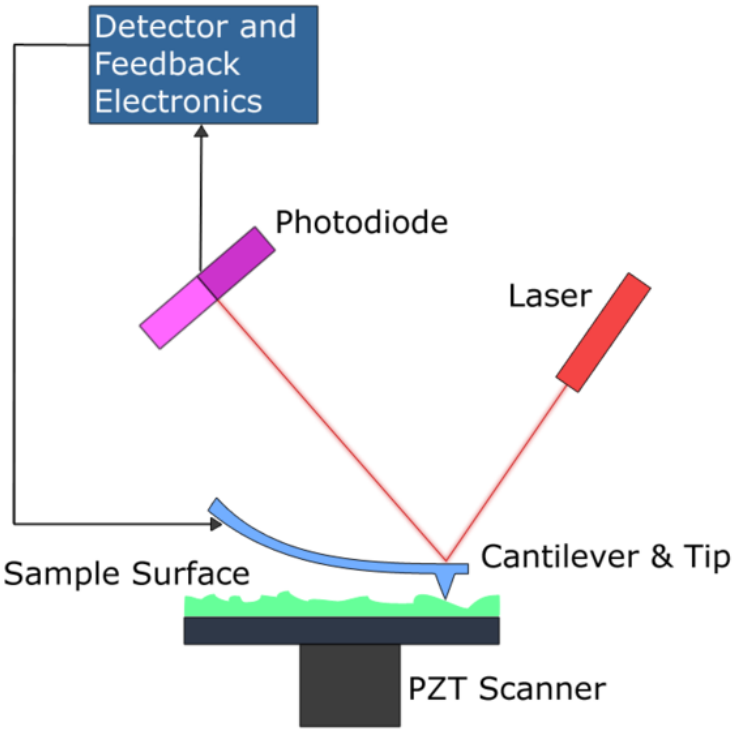






AFM

Atomic Force Microscopy,o Scanning Force Microscopy (SFM)



The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see Magnetic force microscope (MFM)), Casimir forces, solvation forces etc.

2D-SAMs

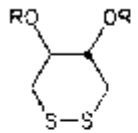
Adsorption of Bifunctional Organic Disulfides on Gold Surfaces

Ralph G. Nuzzo* and David L. Allara*

Bell Laboratories, Murray Hill, New Jersey 07974

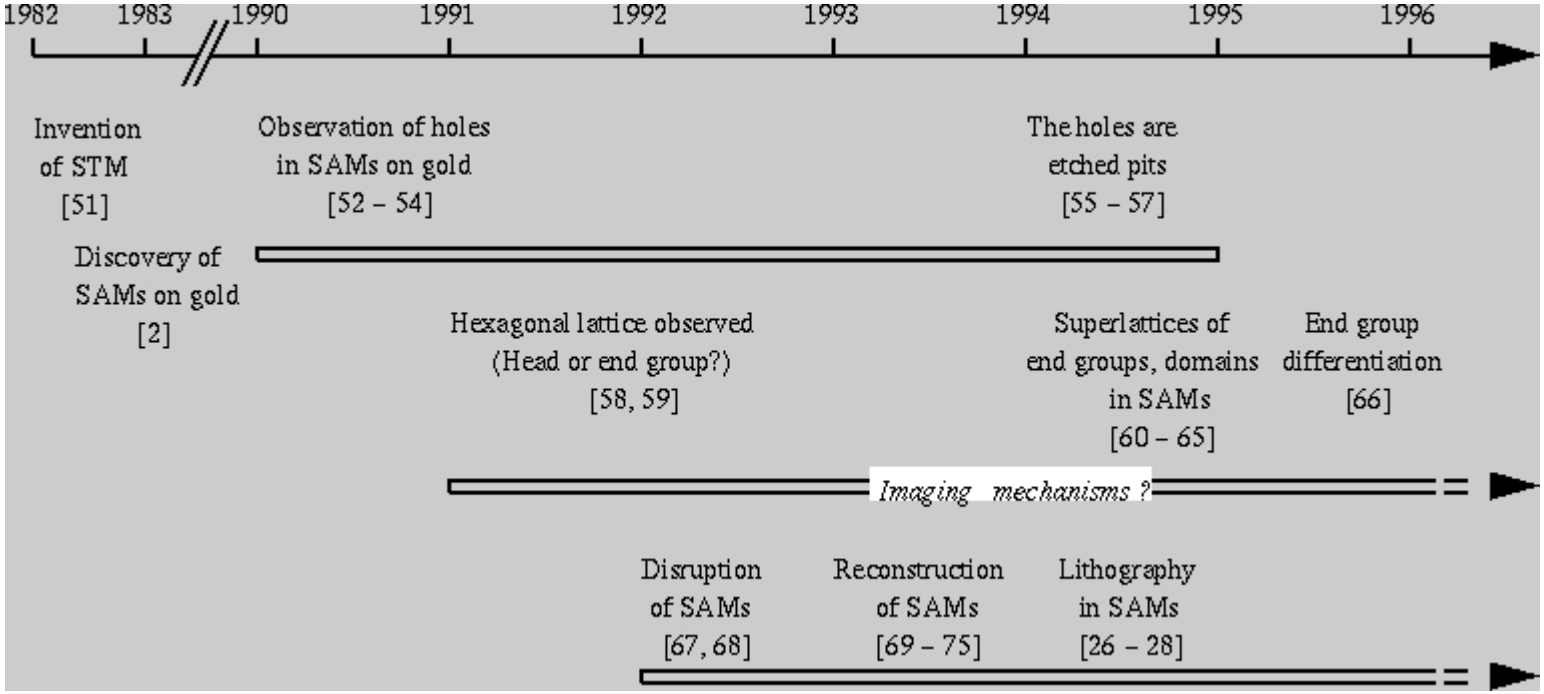
Received January 20, 1983

Table I. Solution Adsorption of Organic Disulfides on Evaporated Gold Films at Room Temperature

 *a,b* R =	thickness of film by ellipsometry,[a–c] Å	estimated max vert extension of adsorbed molecules with attachment at the S–S group,[f] Å	contact angle of water, deg[i]
$CF_3(CF_2)_6CO$ (1a)	10.5 ± 1.0[d]	15.5, 11[g]	104 ± 1
$CH_3(CH_2)_{14}CO$ (1b)	20.5 ± 1.0[e]	25	96 ± 1
$O_2NC_6H_4CO$ (1c)	9.5 ± 2.5	12.5	52 ± 2
CH_3CO (1d)	7.0 ± 2.5	8	47 ± 1
CF_3CO (1e)	4.0 ± 0.5	9	57 ± 1
H (1f)	5.0 ± 0.5	6	34 ± 1
$(HO_2C(CH_2)_2S)_2$ (2)	4.0 ± 0.5	6[h]	13 ± 2
$(CH_3(CH_2)_{11}S)_2$ (3)	21.5 ± 1.0	22[h]	99 ± 1

J. Am. Chem. Soc. **1983**, *105*, 4481-4482.

2D-SAMs



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2D-SAMs

surface analysis and spectroscopic/physical characterization

RAIRS, reflectance absorption infrared spectroscopy
Raman spectroscopy
XPS: X-ray photoelectron spectroscopy
HREELS: high-resolution electron energy loss spectroscopy
NEXAFS: near edge X-ray absorption fine structure spectroscopy diffraction
helium atom scattering
X-ray diffraction
contact angle goniometry
optical ellipsometry
SPR: surface plasmon resonance spectroscopy
mass spectrometry
SPM: scanning probe microscopy (AFM, STM)

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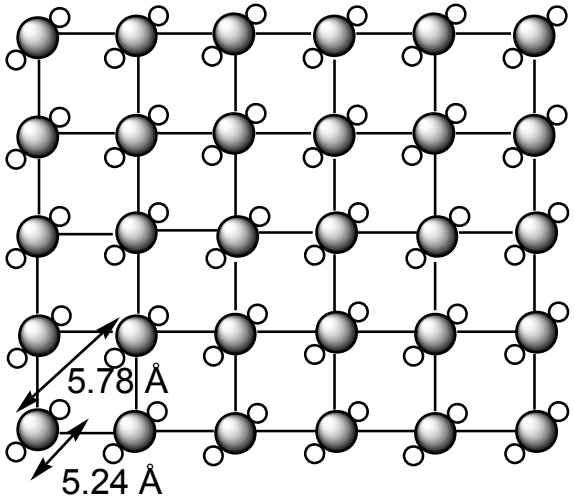
2D-SAMs

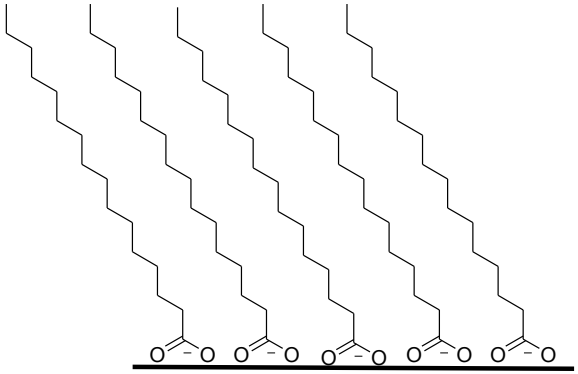
$C_nH_{2n+1}COOH$ on AgO



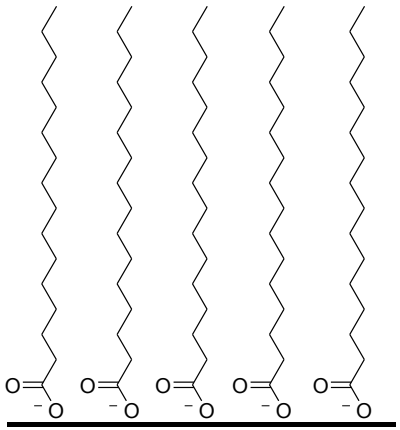
driving force: formation of a surface salt between the carboxylate anion and a surface metal anion.

The p(2x2) adsorption scheme of fatty acids on AgO. The filled circles are the carboxylate carbon atoms, while the small, hollow circles are carboxylate oxygen atoms.

The alky chains are in all-trans extended configuration, and are tilted 26.7° from the surface normal.



AgO



Al_2O_3

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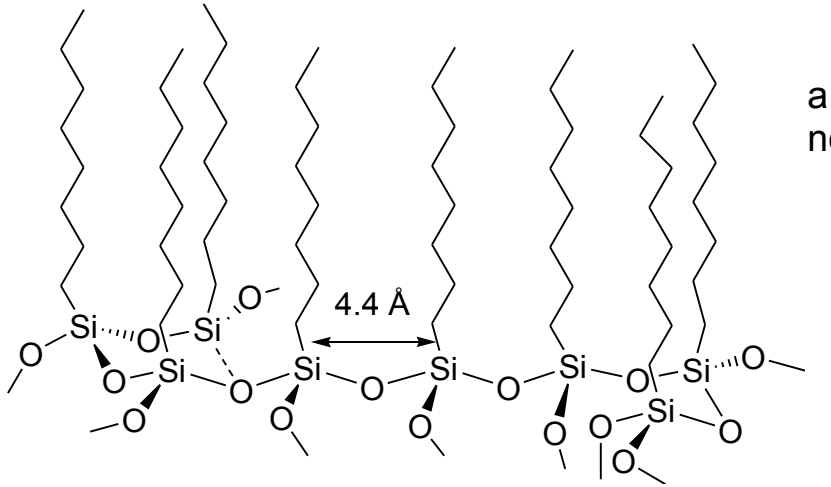
2D-SAMs

alkylsilanes on: SiO_2, Al_2O_3, quartz, glass, mica, ZnSe, GeO, Au

driving force: in situ formation of polysiloxane



a tilt angol of about 10° from the normal has been observed

A schematic description of a polysiloxane at the monolayer-substrate surface.

The reproducibility of alkyltrichlorosilane monolayers is still a problem since the quality of the monolayer formed is very sensitive to reaction conditions.

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Esempi di substrati-leganti

$Au\text{-}P(Ph)_3$

$Au\text{-}SR$

$Au\text{-}NR_2$

$Ag\text{-}SR$

$Ag\text{-}NR_2$

$Ag\text{-}N{\equiv}CR$

$Al_2O_3\text{-}OOCR$

$Si\text{-}OOCR$

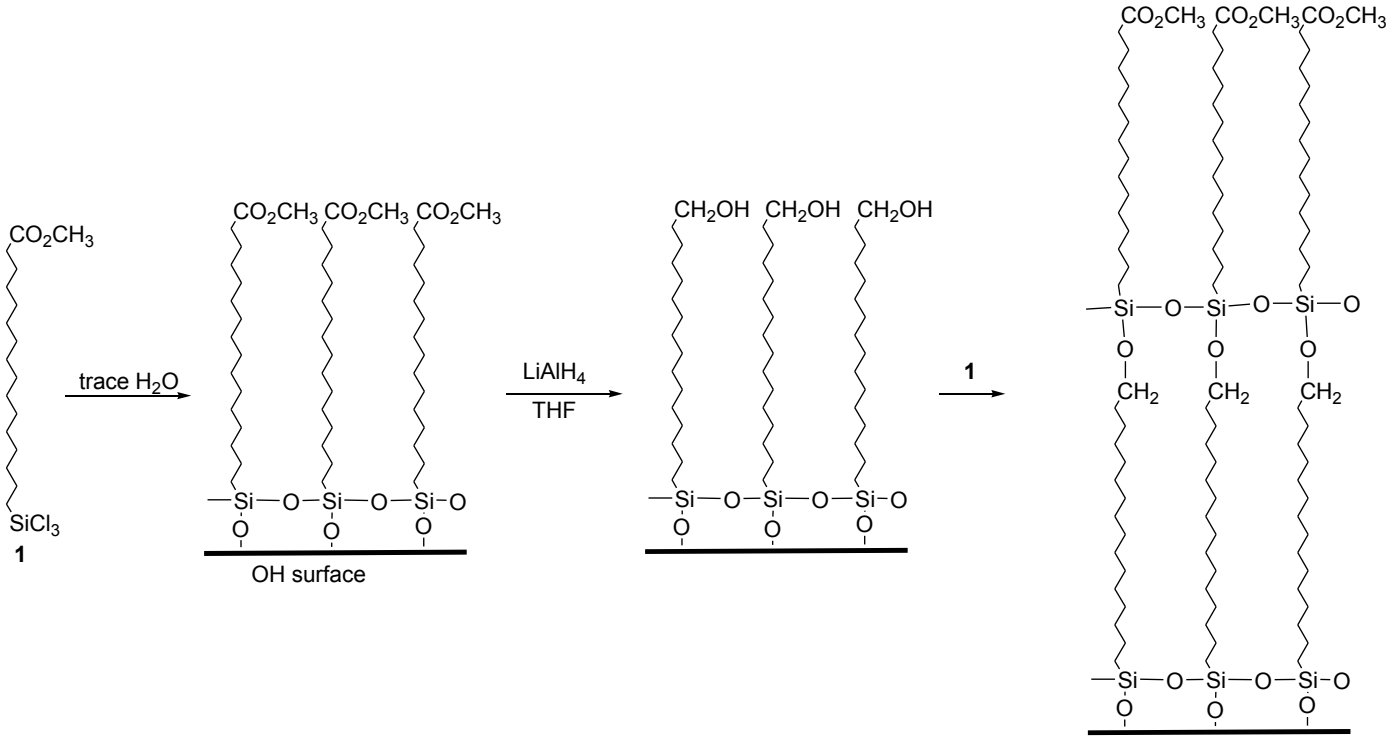
$CdS\text{-}SR$

$CdS\text{-}P(Ph)_3$

$CdS\text{-}O{=}P(Ph)3$

2D-SAMs

modification of surface properties
construction of self-assembled multilayers



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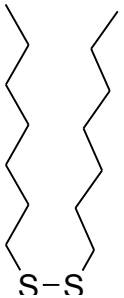
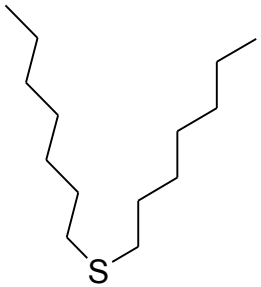
2D-SAMs

organosulfur adsorbates on gold

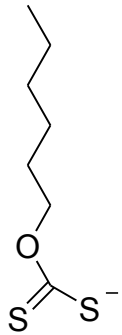
alkylthiol



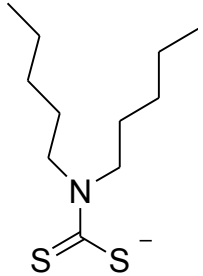
dialkyl disulfide



dialkyl sulfide



alkyl xanthate



dialkylthiocarbamate

also on: Ag, Cu, Pt, Hg, Fe,
nanoparticles as: γ-Fe_2O_3, GaAs, InP

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Structure of a CH_3S Monolayer on Au(111) Solved by the Interplay between Molecular Dynamics Calculations and Diffraction Measurements

R. Mazzarello,[1,2] A. Cossaro,[3] A. Verdini,[3] R. Rousseau,[1] L. Casalis,[4] M. F. Danisman,[5] L. Floreano,[3] S. Scandolo,[2] A. Morgante,[3,6] and G. Scoles[1,4,5]

PRL **98,** 016102 (2007)

Calcoli ab initio e misure di Raggi X a basso angolo GXRD sono in accordo con:

1. Sono stabili strutture in cui un singolo atomo di oro coordina due atomi di zolfo (motivo RS-Au-RS)
   Stabilizzate dalla presenza di ADATOM

2. Sono stabili strutture a ponte (Au-S-Au)
   Stabilizzate dalla presenza di VACANZE

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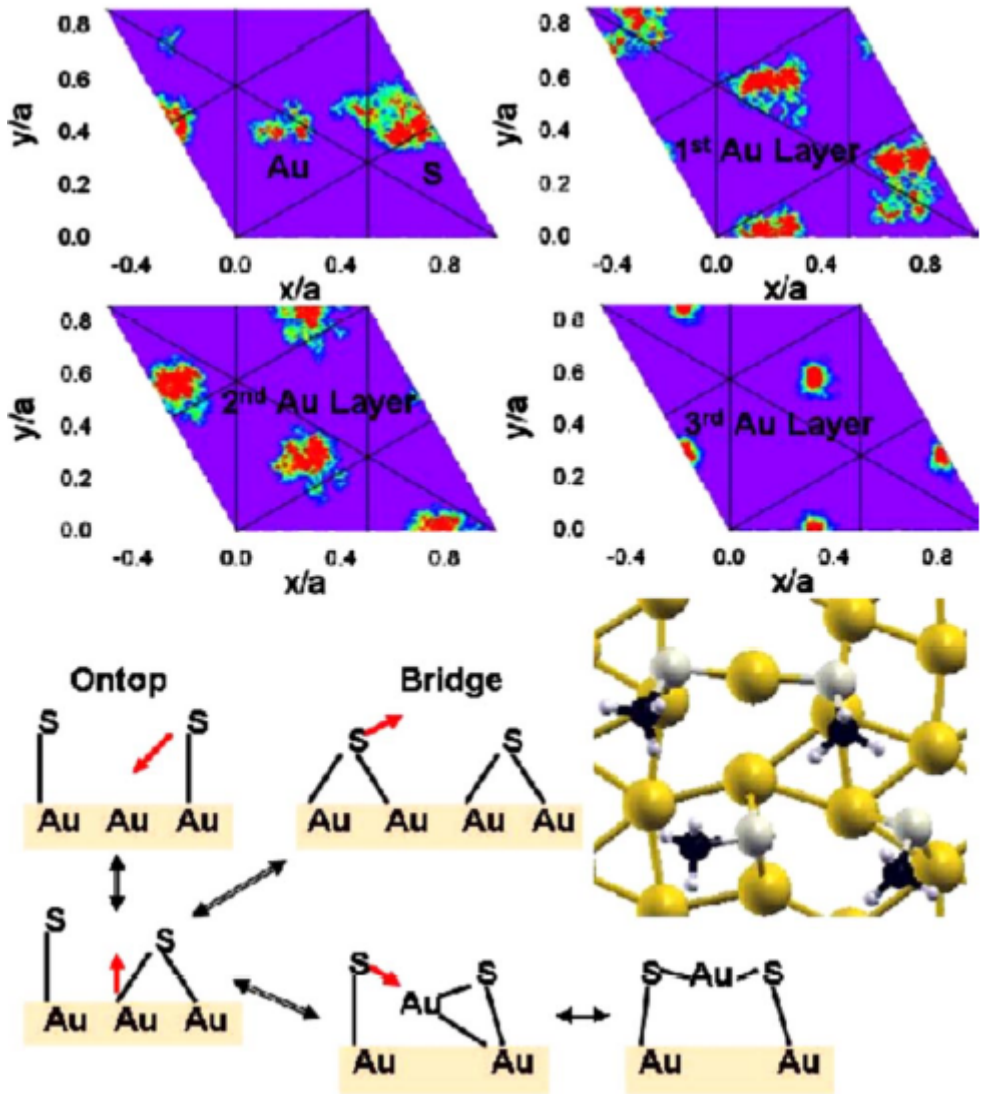
PRL **98,** 016102 (2007)



X-ray Diffraction and Computation Yield the Structure of Alkanethiols on Gold(111)

A. Cossaro,[1] R. Mazzarello,[2] R. Rousseau,[2*] L. Casalis,[3] A. Verdini,[1] A. Kohlmeyer,[4] L. Floreano,[1] S. Scandolo,[5] A. Morgante,[1,6]† M. L. Klein,[4] G. Scoles[2,3,7]

15 AUGUST 2008 VOL 321 SCIENCE 943

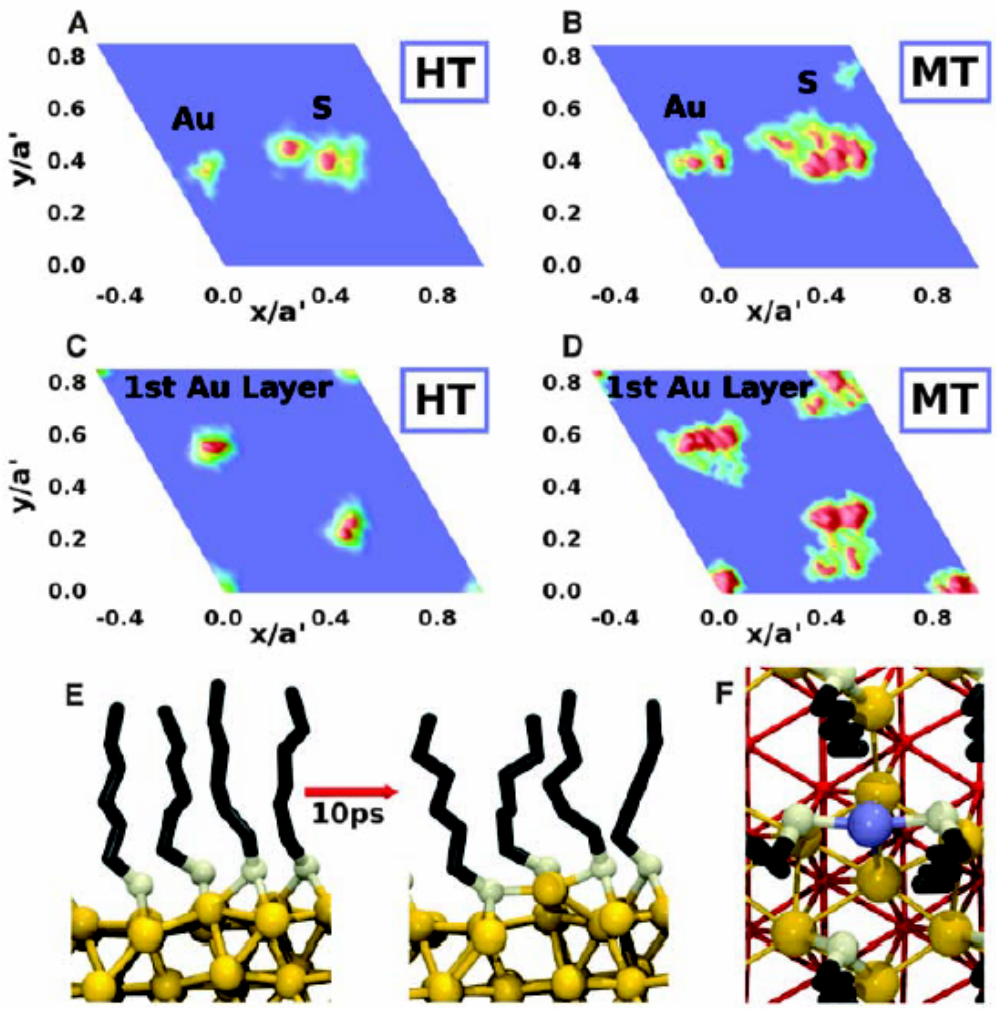
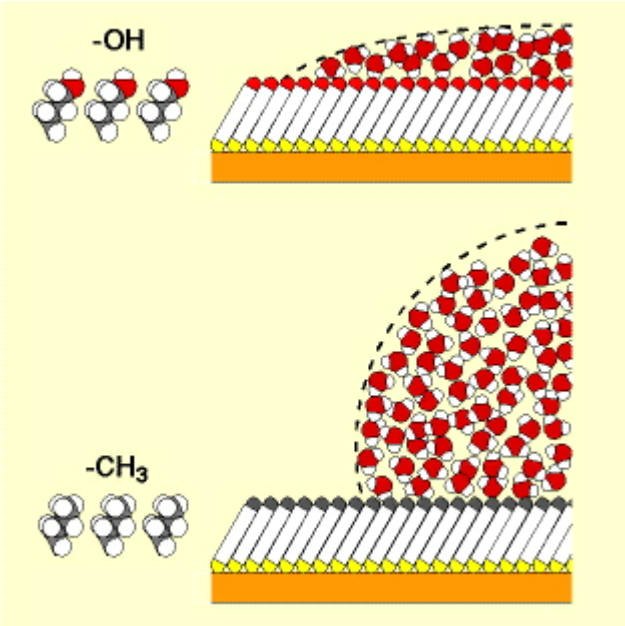


Fig. 1. Top view of the Au(111) surface and selected MD results.

2D-SAMs

wetting behaviour



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BAGNABILITA'

Perchè un tessuto asciuga bene l'acqua mentre un altro sembra rifiutarla? Perchè l'acqua si raccoglie in grosse gocce su di una superficie unta e forma invece un film aderente su di una superficie pulita? Una goccia di un liquido che venga deposta su di una superficie solida vi aderisce in modo maggiore o minore a seconda della natura del liquido e di quella del solido. Per comprendere questo fenomeno bisogna considerare che le molecole di un liquido sono soggette ad una **forza di coesione** che le mantiene unite le une alle altre, ma esiste anche una **forza di adesione** che rappresenta la forza con cui le molecole del liquido aderiscono alla superficie di un materiale con cui vengono in contatto. Quando le forze di adesione sono grandi rispetto alle forze di coesione, il liquido tende a bagnare la superficie, quando invece le forze di adesione sono piccole rispetto a quelle di coesione, il liquido tende a "rifiutare" la superficie. A questo proposito si parla di bagnabilità fra liquidi e solidi. Per esempio, l'acqua bagna il vetro pulito, ma non bagna la cera.

1 - **Misura dell'angolo di contatto.** Deponete una goccia di un liquido su di una superficie liscia di un solido. A seconda della bagnabilità del liquido nei confronti di quel solido, la goccia formerà un determinato angolo di contatto con il solido. In riferimento alla figura 10, se l'angolo di contatto è inferiore a 90°, il solido viene definito bagnabile, se l'angolo di contatto è maggiore di 90°, il solido viene definito non bagnabile. Un angolo di contatto pari a zero indica completa bagnabilità. Per misurare l'angolo di contatto usate un goniometro ed un righello. Fare una fotografia

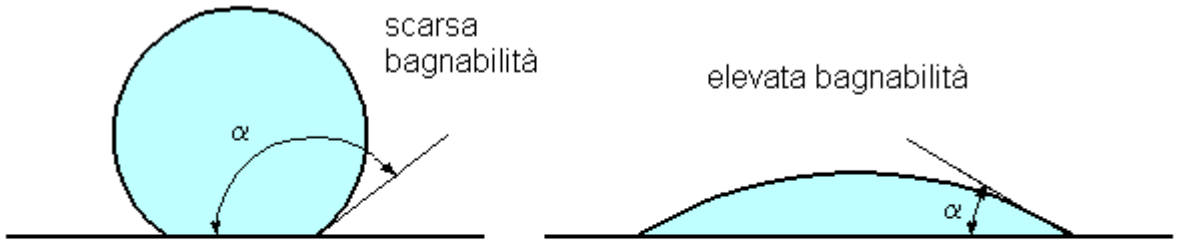
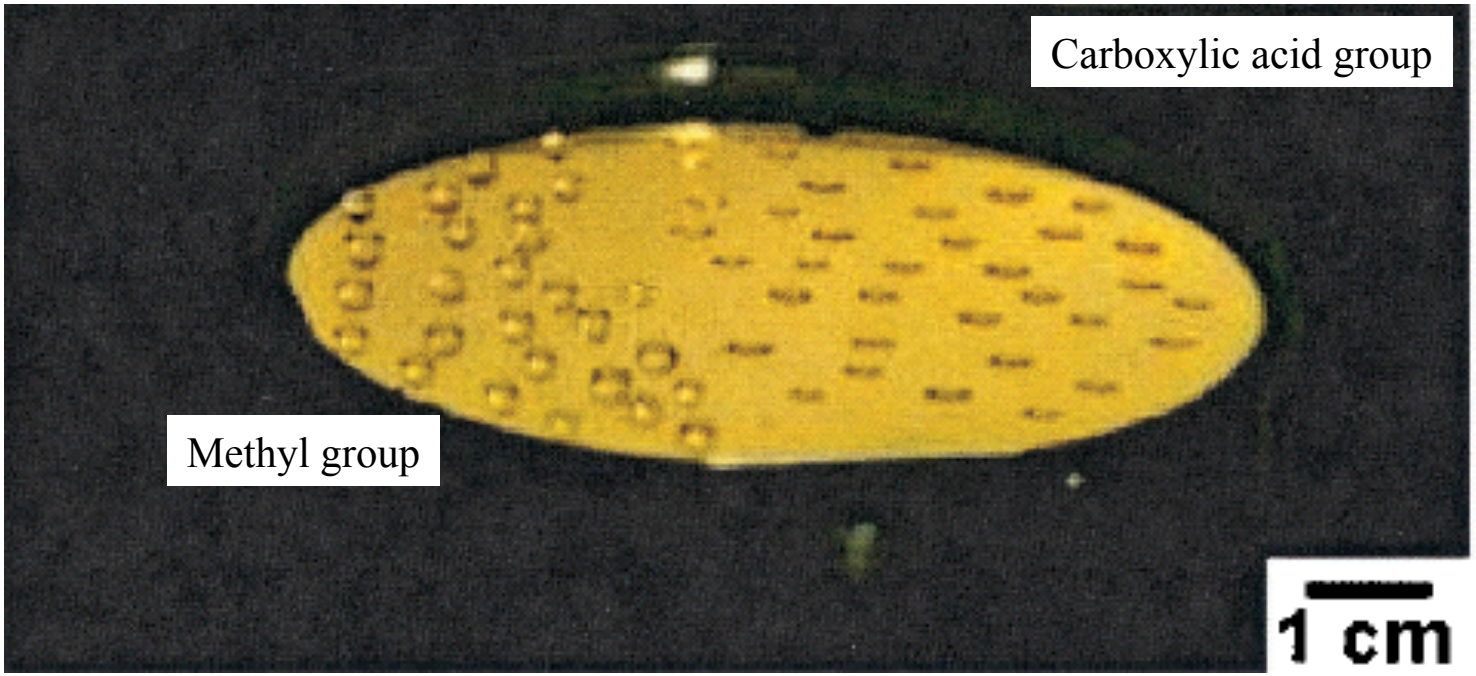


Figura 10 - L'angolo di contatto di un liquido con un solido viene utilizzato come indice di bagnabilità. Per $\alpha < 90°$ il liquido bagna la parete (es: acqua su vetro), per $\alpha > 90°$ il liquido non bagna la parete (es: mercurio su vetro). Se $\alpha = 0°$ si dice che il liquido bagna perfettamente la parete.

Changing Functional Groups

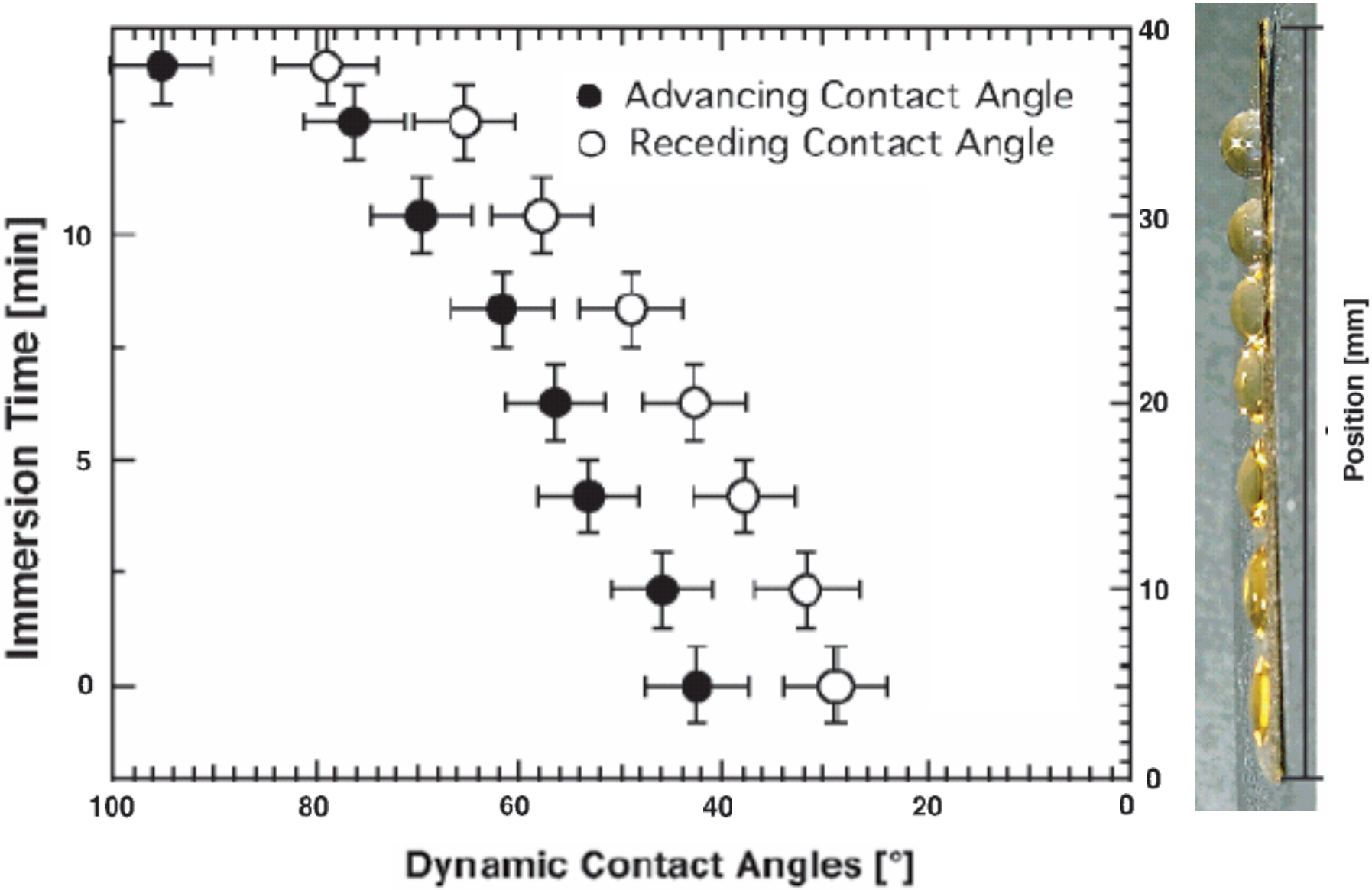
Surface Polarity

Low → High



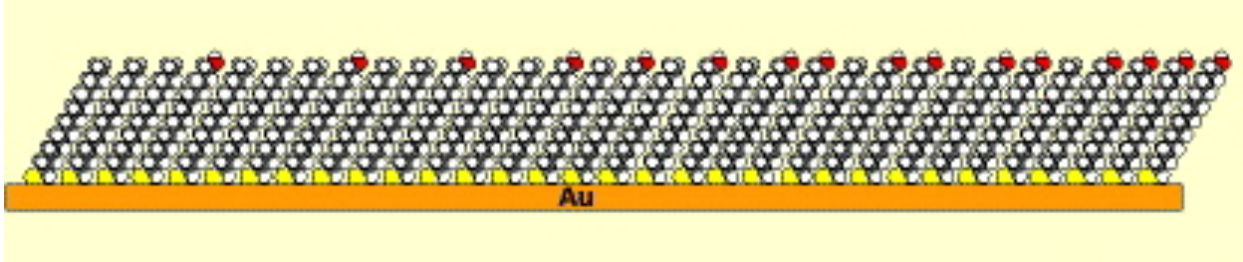
Nuzzo, R., *PNAS*. **2001**, *9*, 4827.

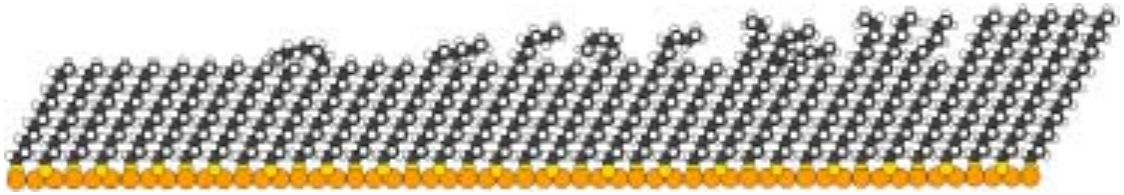
Surface-Chemical Gradients



Morgenthaler, S., *et al., Langmuir.* **2003**, *19*, 10459.

2D-SAMs





surfaces with different funtional groups have been reported, for example: CF_3, $CH{=}CH_2$, $C{\equiv}CH$, Cl, Br, CN, OH, OCH_3, NH_2, $N(CH_3)_2$, SO_3H, $Si(OCH_3)_3$, COOH, $COOCH_3$, $CONH_2$, etc.

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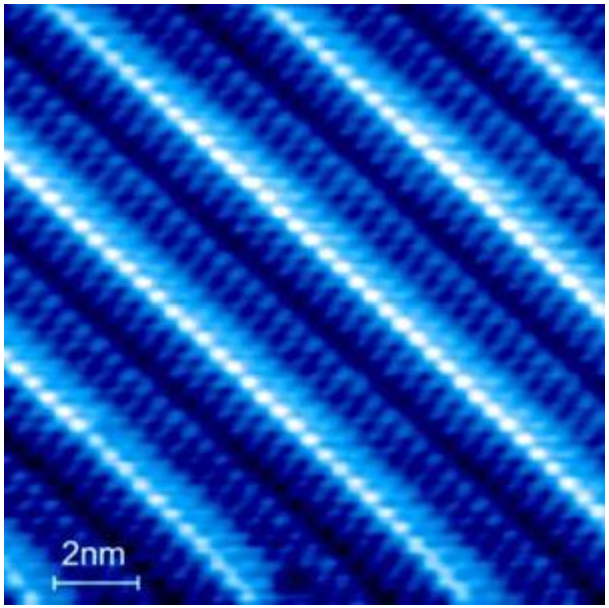
2D-SAMs

Langmuir **1998**, *14*, 6693–6698

Flat Lying Pin-Stripe Phase of Decanethiol Self-Assembled Monolayers on Au(111)

R. Staub, M. Toerker, T. Fritz, T. Schmitz-Hübsch, F. Sellam, and K. Leo*

decanethiol physisorbed on Au(111), gas phase



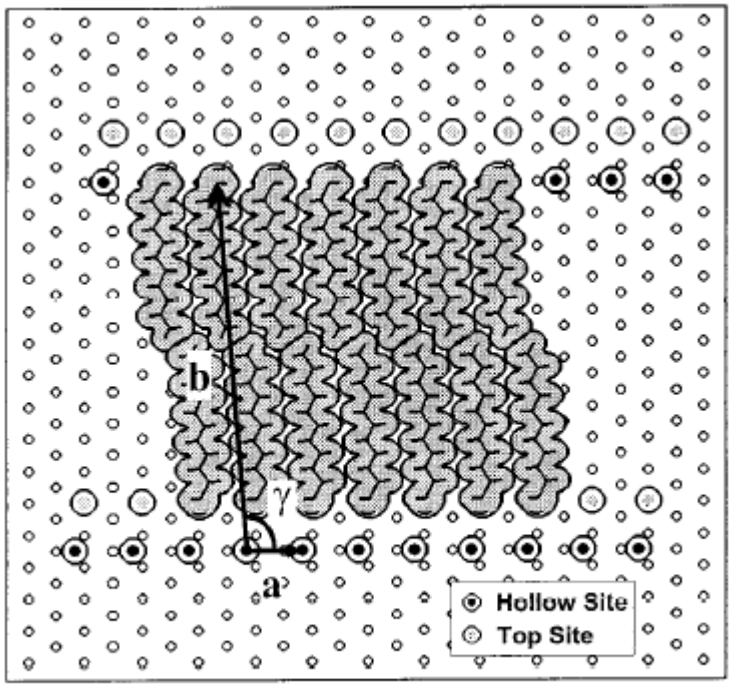
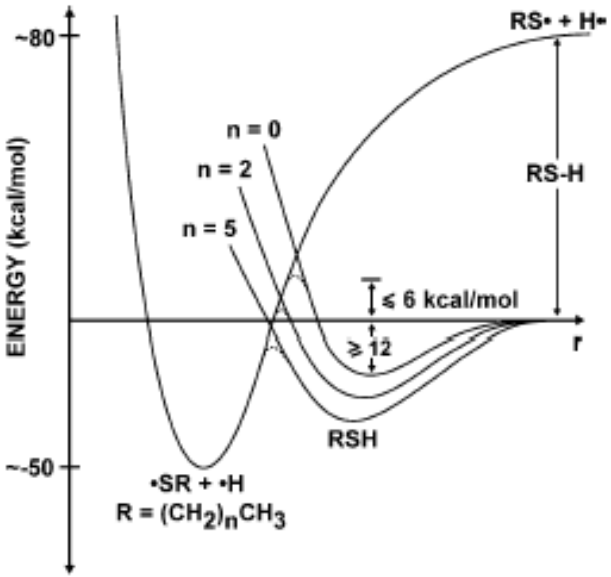


Figure 6. Real space structure model for the 11.5 × √3 pin-stripe structure of decanethiol.

2D-SAMs



Schematic one-dimensional energy diagram showing the effect of chain length on the barrier for activation of the S-H bond of *n*-alkanethiols on gold. For short chain lengths (*n* 0-2), the transition from a physisorbed state to a chemisorbed state is an activated process.

2D-SAMs

defects on SAMs

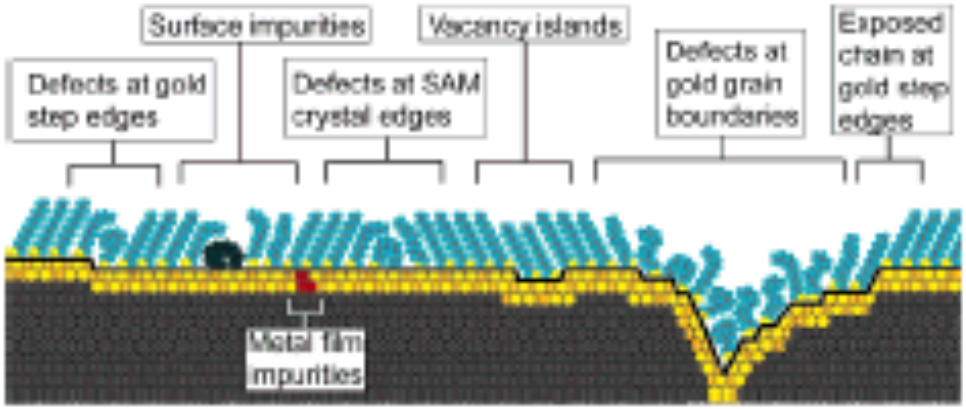


Figure 7. Schematic illustration of some of the intrinsic and extrinsic defects found in SAMs formed on polycrystalline substrates. The dark line at the metal–sulfur interface is a visual guide for the reader and indicates the changing topography of the substrate itself.

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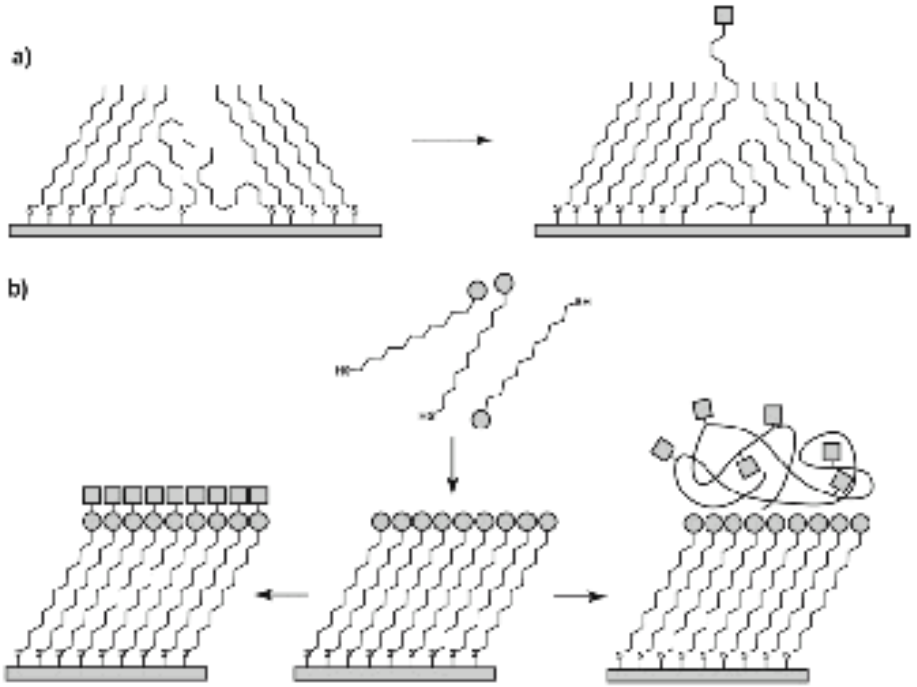
2D-SAMs

surface modifications

Scheme 1. General Strategies for Modifying the Interfacial Composition of SAMs after Formation[a]



[a] (a) Insertion of a functional adsorbate at a defect site in a preformed SAM. (b) Transformation of a SAM with exposed functional groups (circles) by either chemical reaction or adsorption of another material.

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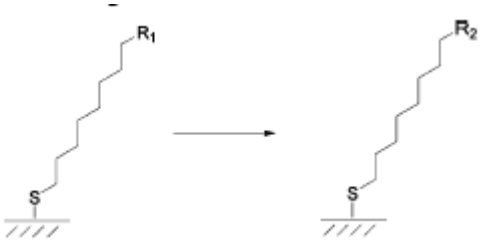
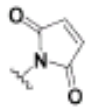
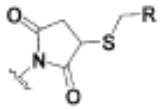
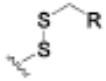
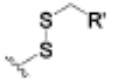
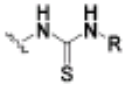
2D-SAMs

surface modifications



Surface Group (R_1)	Ligand	Complex Formed (R_2)	Reference
			347
			348-350
			355
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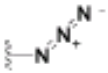
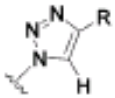
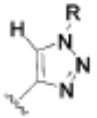
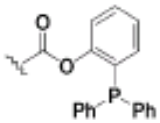
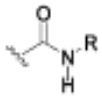
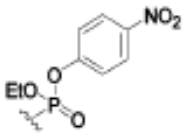
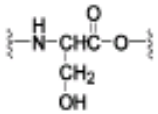
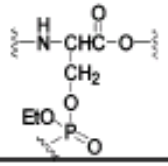
			354
			356
			357,358
			359,360

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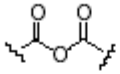
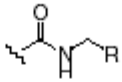
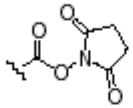
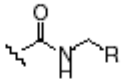
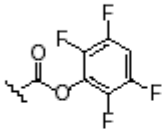
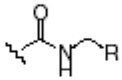
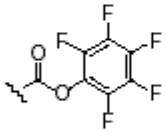
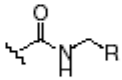
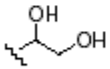
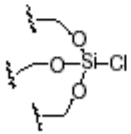
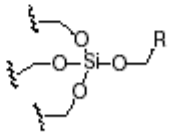
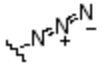
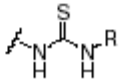
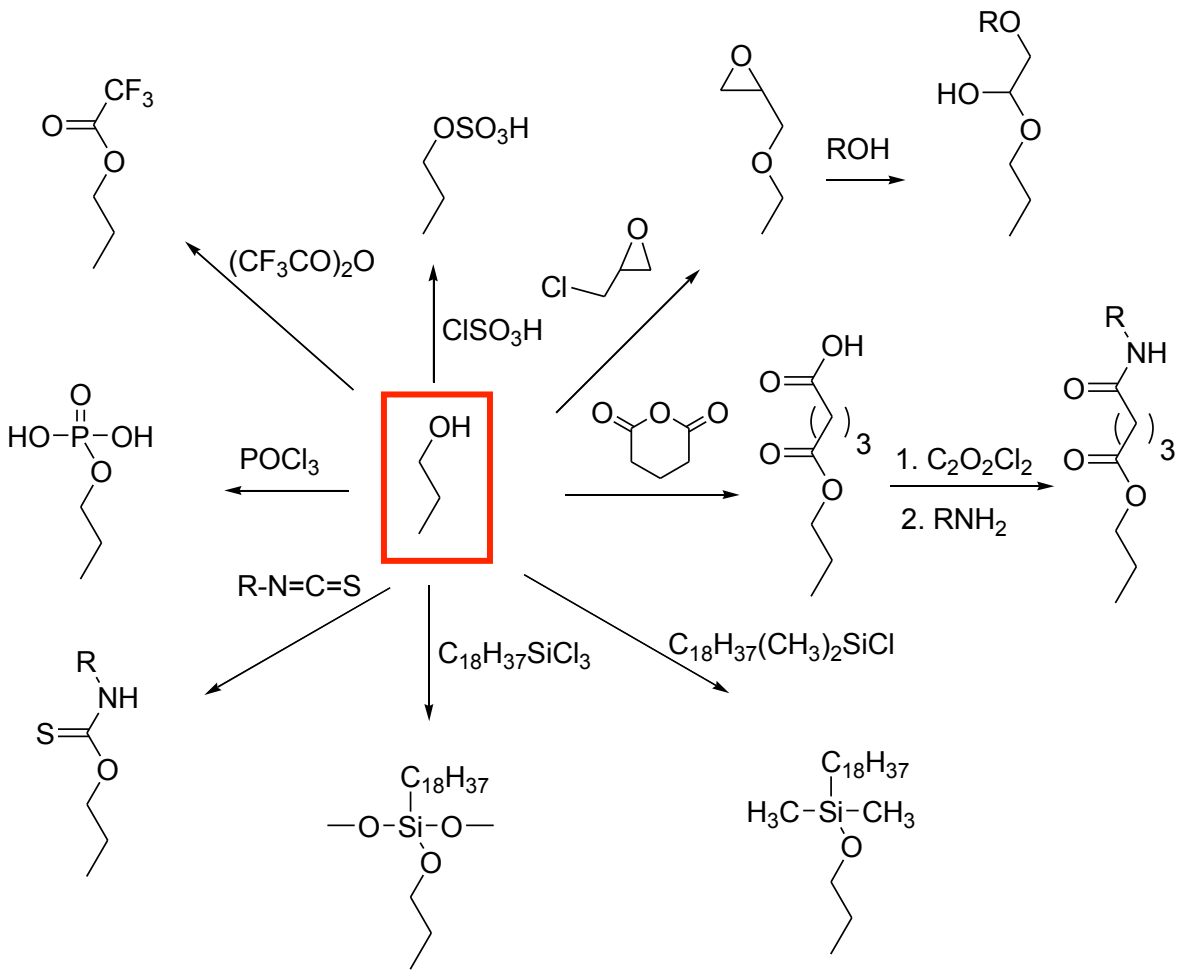
Table 4.2 Selected Methods for SAMs Functionalization via the Formation of Activated Species

Surface bound reactive group	Activated species	Reagent	Product	Reference
				57
				72
				59
				58
				61–63
				64
				71, 78

2D-SAMs

surface modifications



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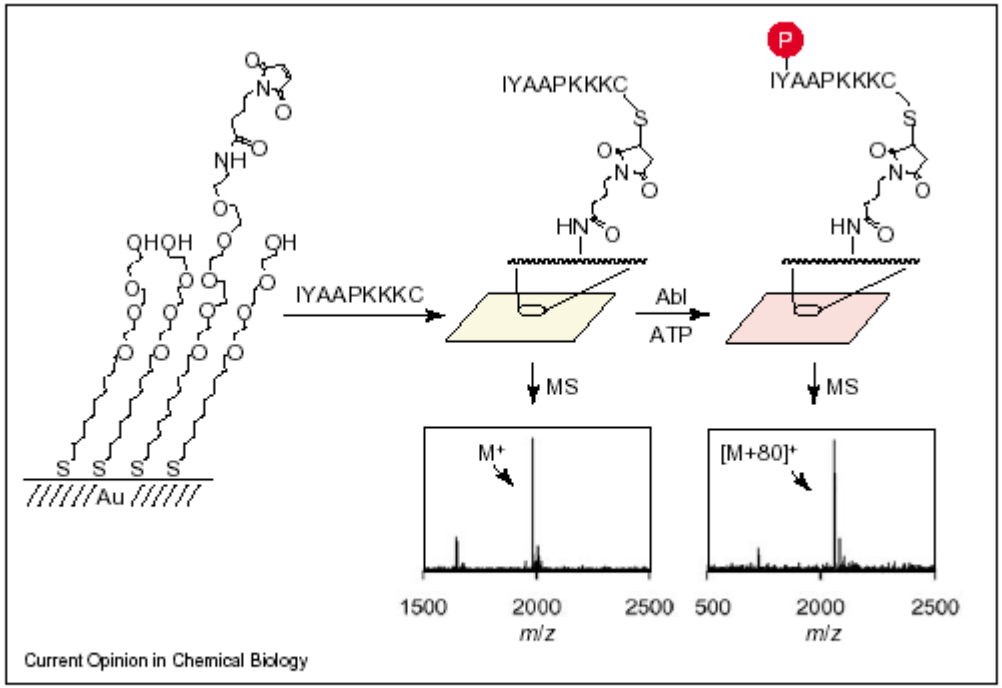


Design of peptide arrays for characterizing enzyme activities by MALDI-TOF MS. A peptide substrate for Abl kinase was immobilized to a maleimide-presented self-assembled monolayer (SAM). The monolayer was treated with Abl kinase and phosphorylation was characterized by MALDI-TOF MS.

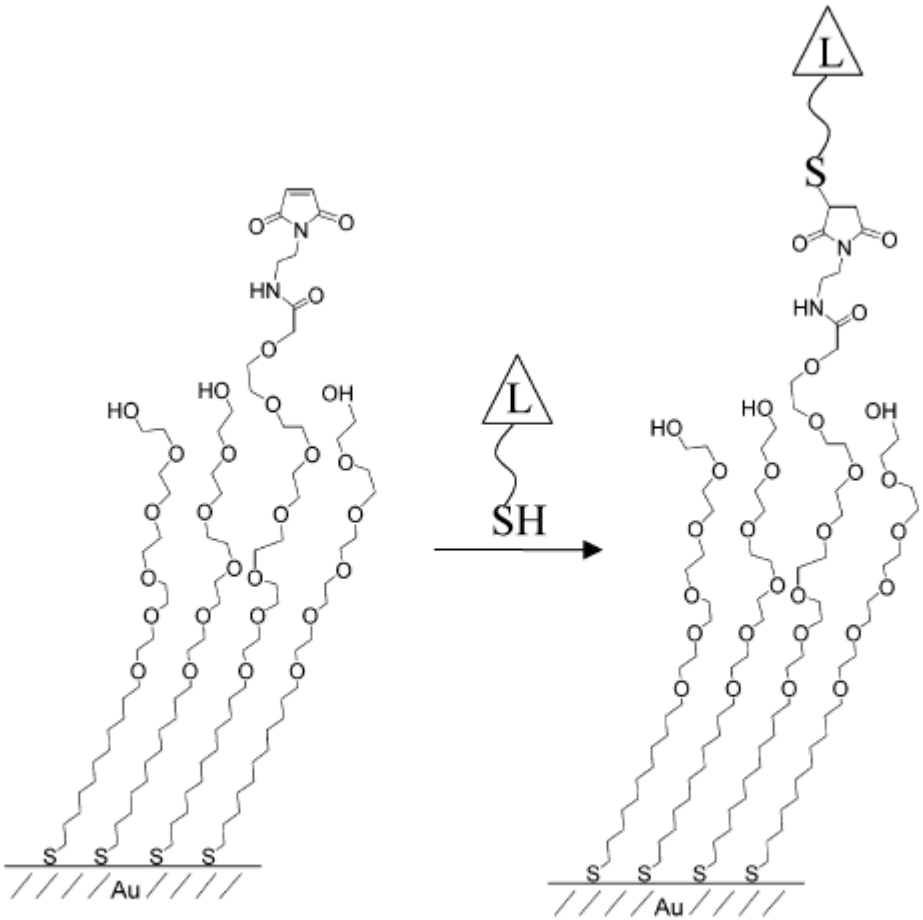


Figure 1. Structure of a self-assembled monolayer used to immobilized thiol-terminated ligands. The maleimide groups react selectively with thiol groups in a contacting solution while the penta(ethylene glycol) groups prevent the nonspecific adsorption of protein to the monolayer.

B. T. Houseman, E. S. Gawalt, M. Mrksich *Langmuir* **2003,** *19,* 1522-1531

Label-Free Detection of Protein–Protein Interactions on Biochips**

*Woon-Seok Yeo, Dal-Hee Min, Robert W. Hsieh, Geoffrey L. Greene, and Milan Mrksich**

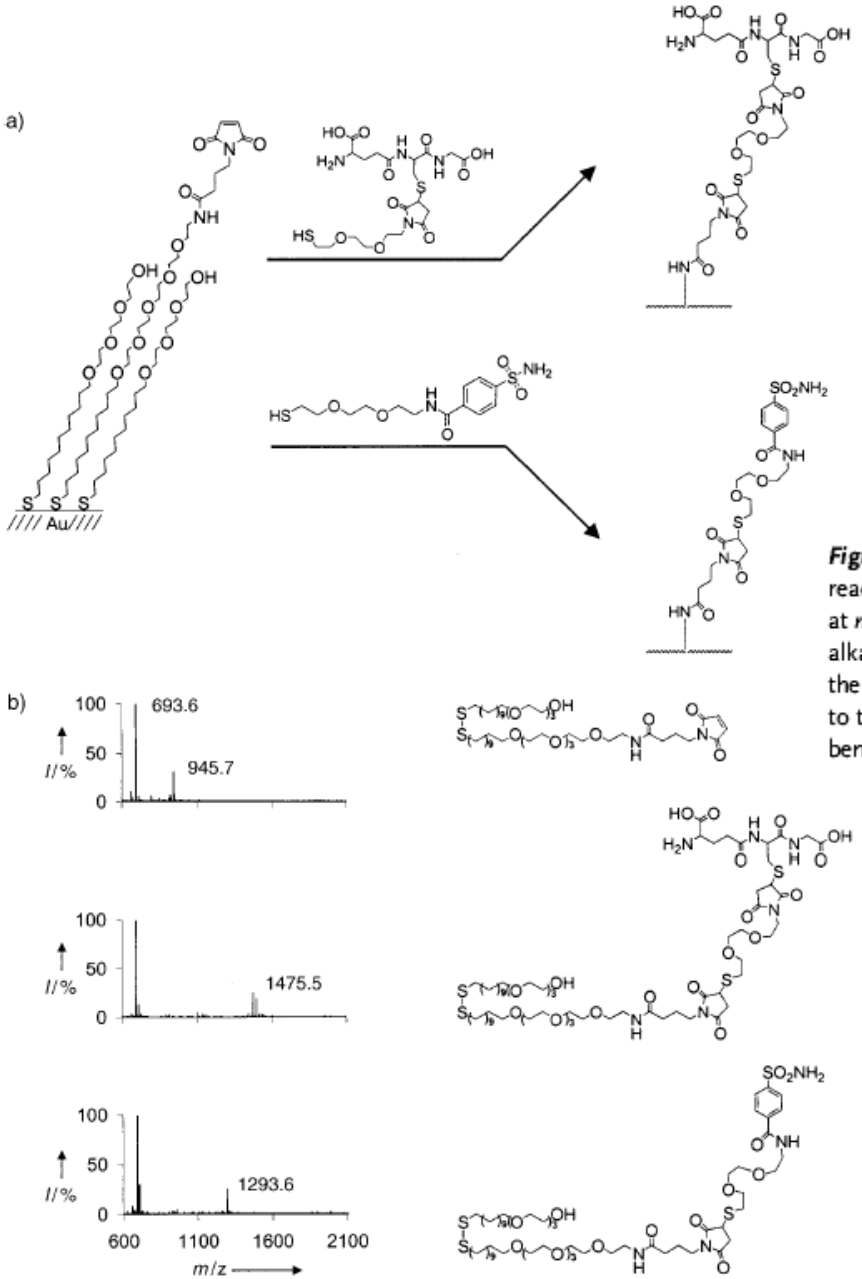
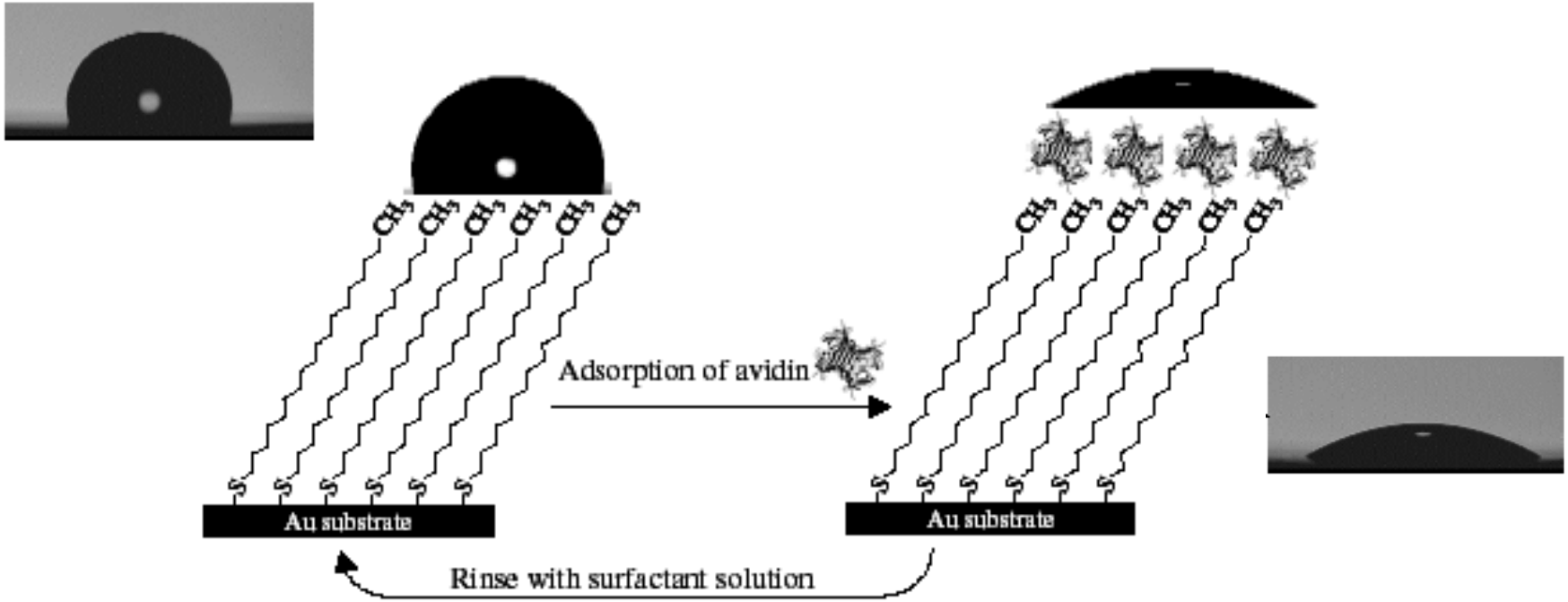


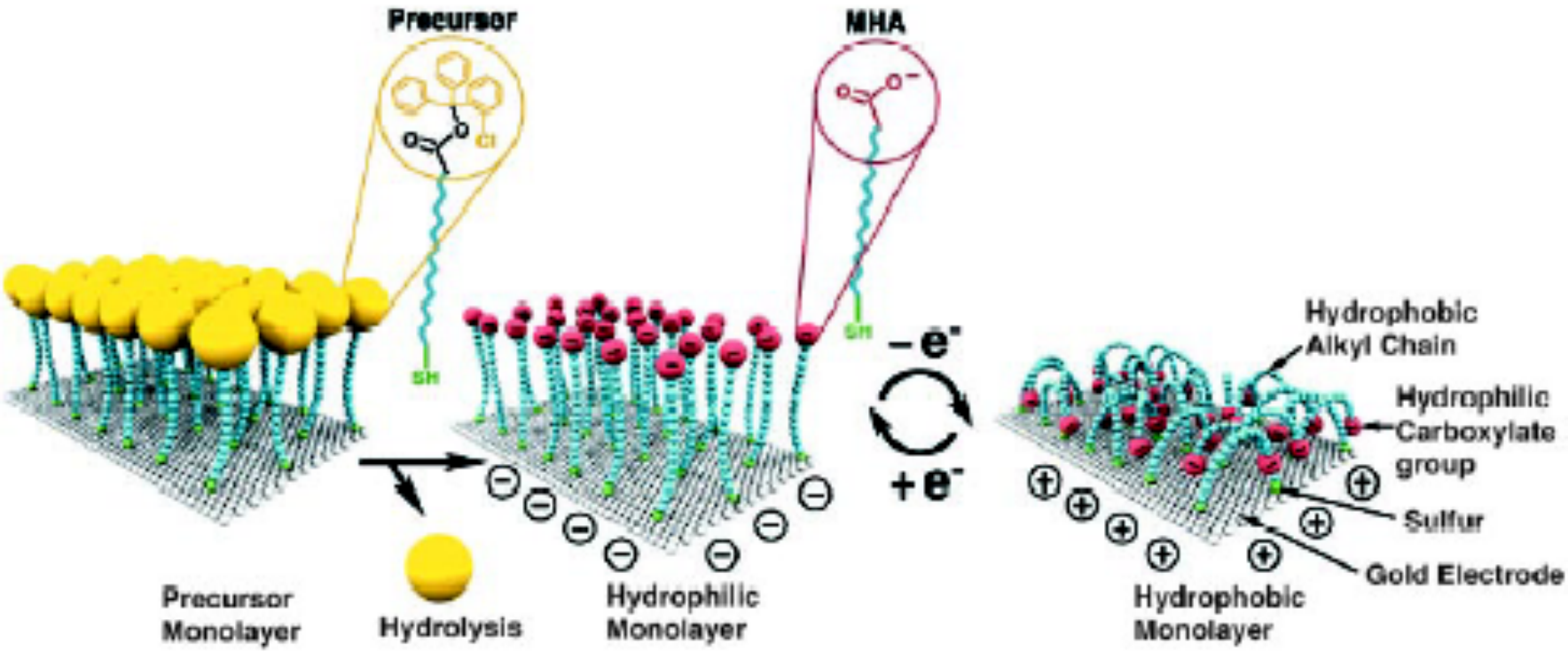
Figure 1. a) Protein-capture ligands were immobilized onto a maleimide-terminated SAM by reaction of the thiol-tagged ligands. b) MS data for the initial monolayer (top) displayed a peak at m/z 945.7, which corresponds to the mixed disulfide derived from a maleimide-terminated alkanethiolate and a tri(ethylene glycol)-terminated alkanethiolate. After treatment with ligands, the original peak disappeared and gave rise to a new peak at m/z 1475.5, which corresponds to the glutathione-conjugated product (middle) or at m/z 1293.6, which corresponds to the benzenesulfonamide-conjugated product (bottom).

Reversible Hydrophobic/Hydrophilic Surfaces



Deval, J., *et al.*, *J. Micromech. Microeng.* **2004**, *14*, 91.

Reversible Hydrophobic/Hydrophilic Surfaces

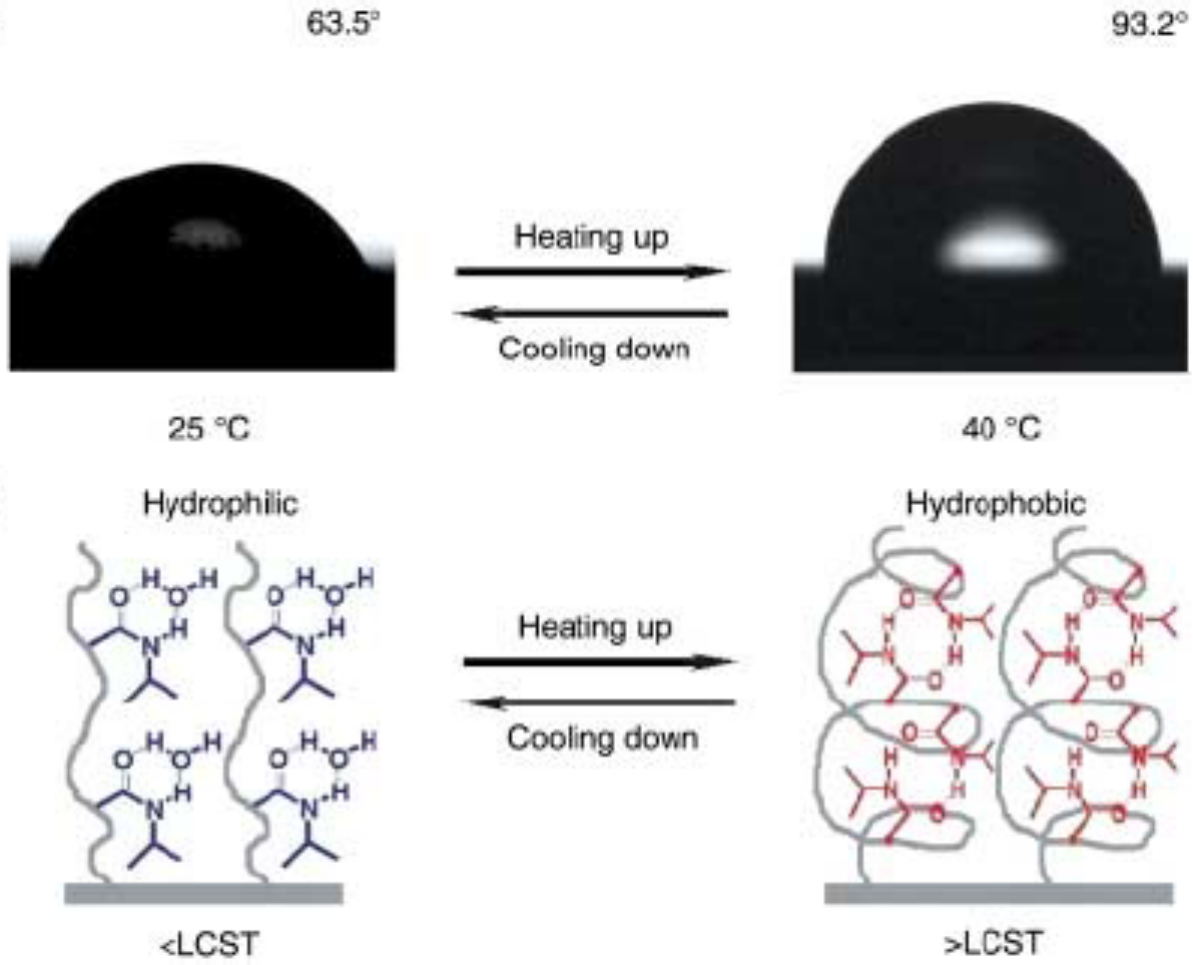


Change Potential

Lahann, J., *et al., Science.* **2003**, *299*, 371.

Controlling Wettability

surface of poly(N-isopropylacrylamide)



Sun, T., *et.al., Angew. Chem.* **2004**, 116, 361.

2D-SAMs

reactivity on surfaces

- effect of chain organization: esters at the end of long chains are hydrolized faster than esters at the end of shorter chains but slower than similar esters in solutions.
- lateral steric effect
- position of reactive sites
- partitioning of reactants in the organic interface

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2D-SAMs

noncovalent modifications

- non specific adsorption of molecules
  van der Waals and electrostatic forces
  hydrophobic SAMs (formed from alkanethiols) adsorb proteins

- fusion of vesicles
  hydrophilic functional groups (i.e. OH) promote the adsorption and rupture of vesicles.
  hydrophobic SAMs (i.e. alkyl groups) promote the formation of hybrid bilayers that are excellent dielectric barriers. These structures provide a useful model system for studying the structure and function of cell membranes.

- selective deposition onto SAMs
  pH control

- modifications via molecular recognition - multivalency
  functional groups that bind through a network of hydrogen bonds, metal-ligand interactions, electrostatic interactions, or hydrophobic interactions – this modification is reversible

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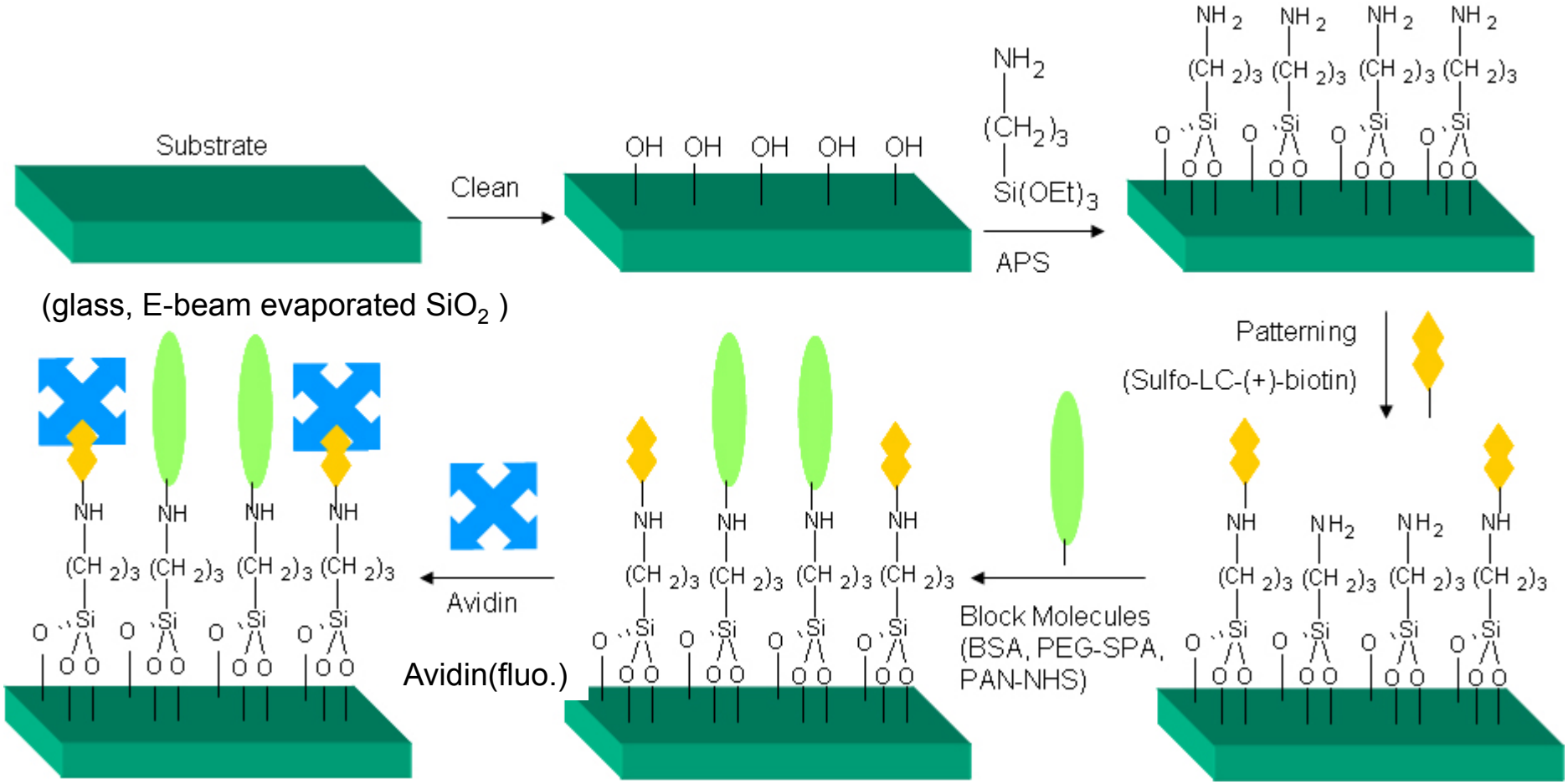
2D-SAMs

model bioassay



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