Self-assembly and Nanotechnology 10.524

Lecture 3. Self-assembled Monolayers (SAM)

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& UML CHN/NCOE Nanomanufacturing Center)

Lecture 3: Self-assembled Monolayers (SAMs)

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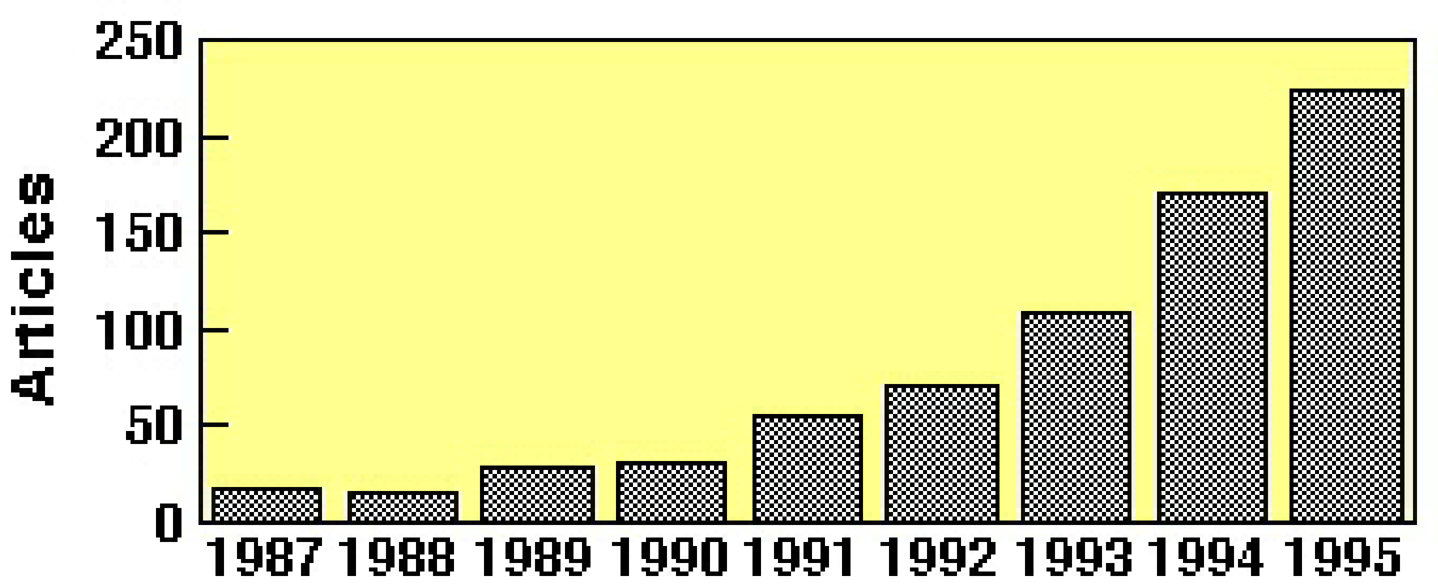
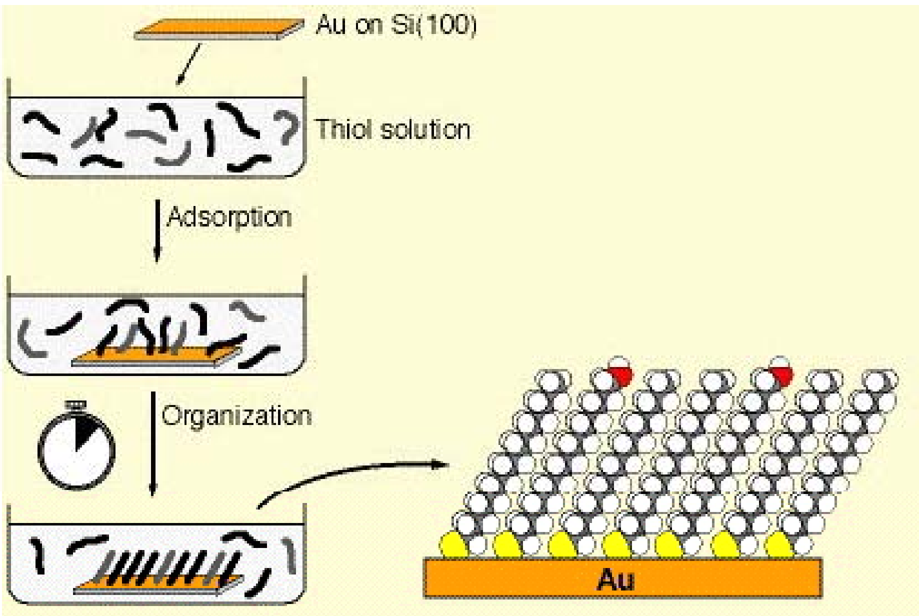
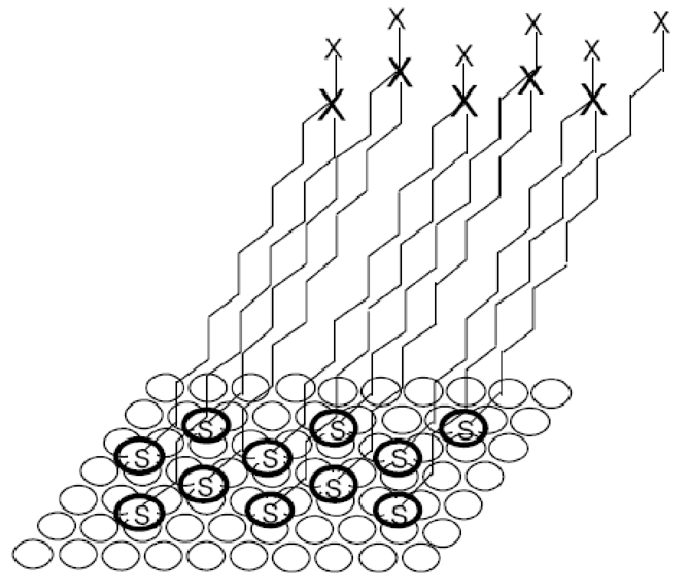


Figure. Number of published articles dealing with self-assembled monolayers per year, according to searches in the Chemical Abstracts and Science Citation Index databases

Lecture 3: Self-assembled Monolayers (SAMs)

Definition of monolayers





"SAMs are ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface" (or other surfaces such as liquid)

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

Lecture 3: Self-assembled Monolayers (SAMs)

Schematic of monolayers

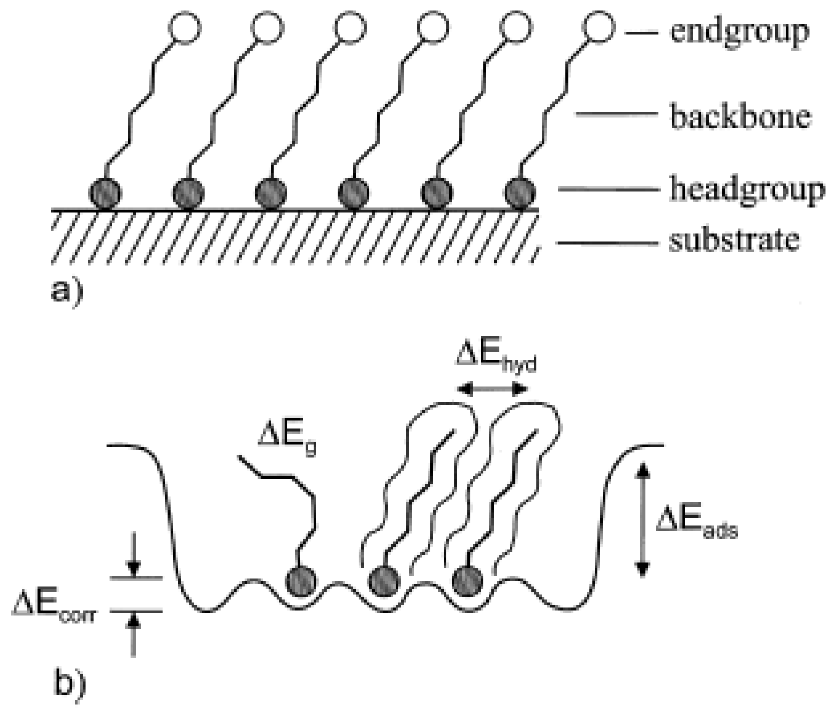
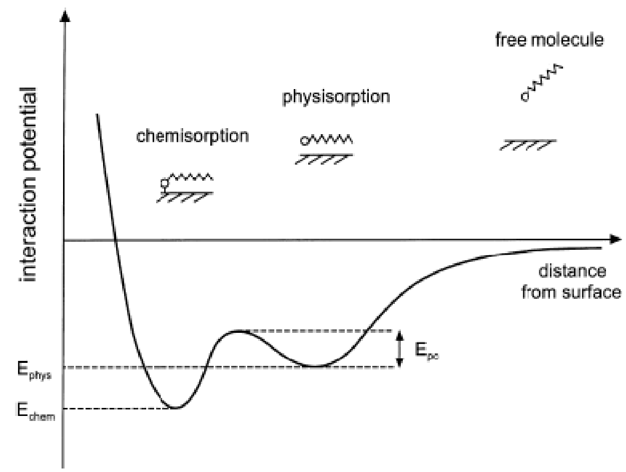


Fig. 2. (a) Schematic of SAM. Shaded circle indicates chemisorbing headgroup and open circle endgroup, which can be chosen from variety of chemical functionalities. (b) Schematic of different energies. ΔE_{ads} stands for adsorption energy, ΔE_{corr} corrugation of substrate potential experienced by molecule, ΔE_{hyd} van der Waals interaction of (hydrocarbon) tails, and ΔE_g energy of gauche defect (or, generally, deviation from fully stretched backbone).



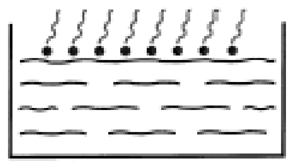
Schematic of interaction potential between decanethiol and bare Au (1 1 1) surface as function of distance

F. Schreiber, *Progress in Surface Science* **2000**, *65*, 151-256

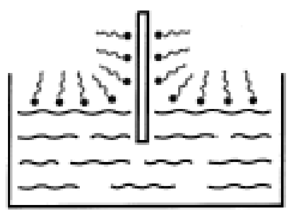
Lecture 3: Self-assembled Monolayers (SAMs)

Preparation of monolayers

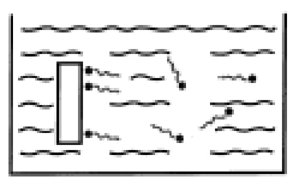
- Langmuir Films
  amphiphilic molecules
  at liquid/gas interface



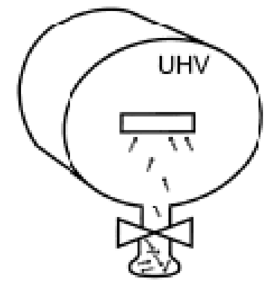
- Langmuir-Blodgett Films
  Langmuir films
  transferred onto solid substrate



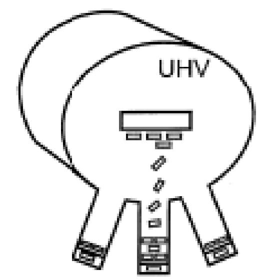
- Self-Assembled Monolayers
  grown from solution



- Self-Assembled Monolayers
  grown from vapor



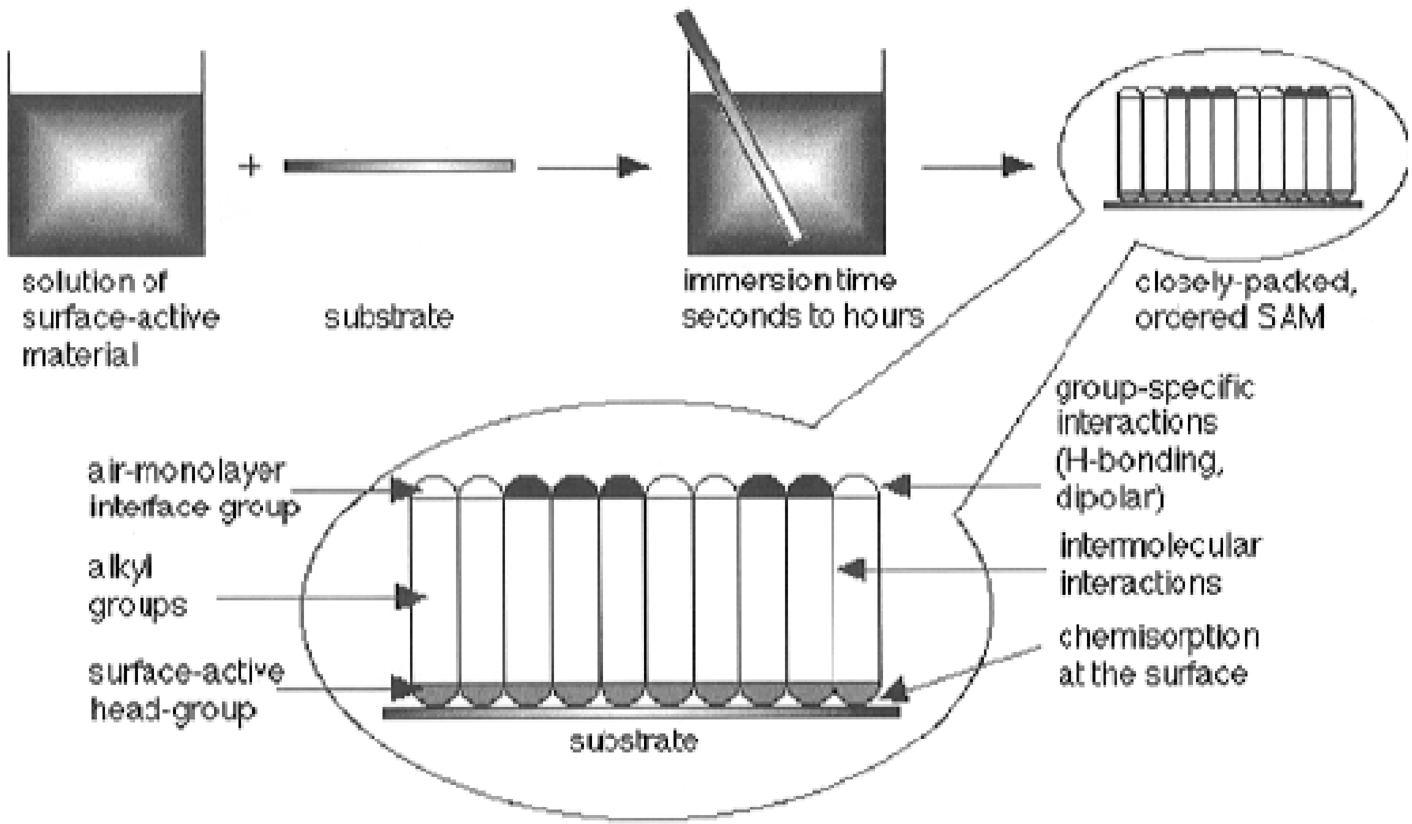
- Organic Molecular Beam Epitaxy
  similar to inorganic MBE



F. Schreiber, *Progress in Surface Science* **2000**, *65*, 151-256

Lecture 3: Self-assembled Monolayers (SAMs)

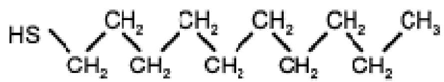
From solution: immersion technique

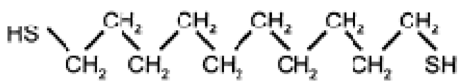


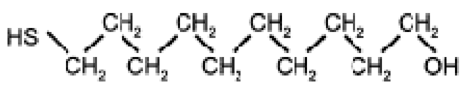
Abraham Ulman, *Chem. Rev.* **1996,** *96*, 1533-1554

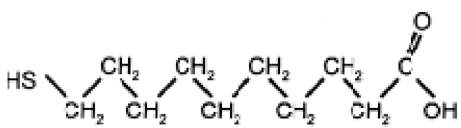
Lecture 3: Self-assembled Monolayers (SAMs)

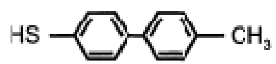
Some frequently used monolayers

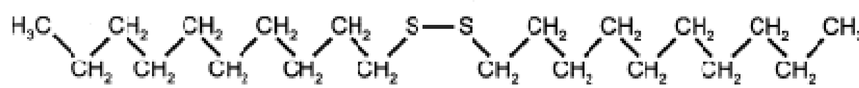
(1) 

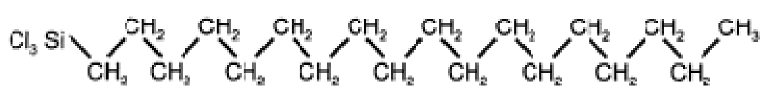
(2) 

(3) 

(4) 

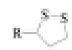
(5) 

(6) 

(7) 

F. Schreiber, *Progress in Surface Science* **2000**, *65*, 151-256

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_3O_4		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		
$R\text{-}N{\equiv}N^+(BF_4^-)$	GaAs(100)	52	
	Pd	52	
	Si(111):H	52	
RSH	Ag	26	53,54
	$Ag_{80}Ni_{20}$	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	

Self-assembly and Nanotechnology Love et al., *Chem. Rev.* **2005**, *105*, 1103-1169

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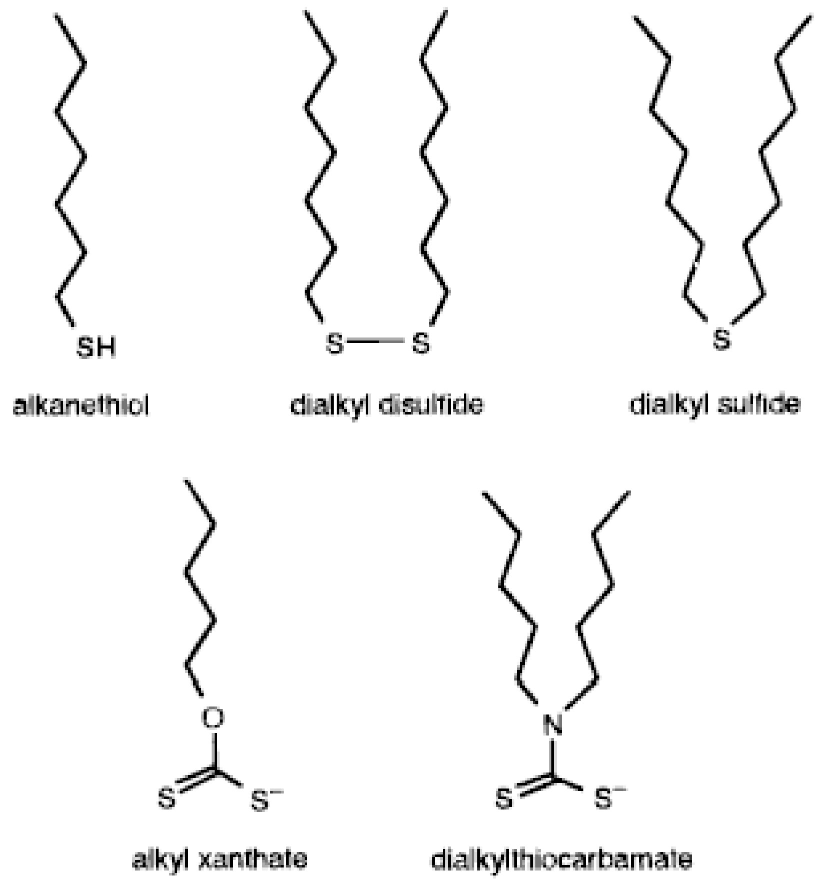
Lecture 3: Self-assembled Monolayers (SAMs)

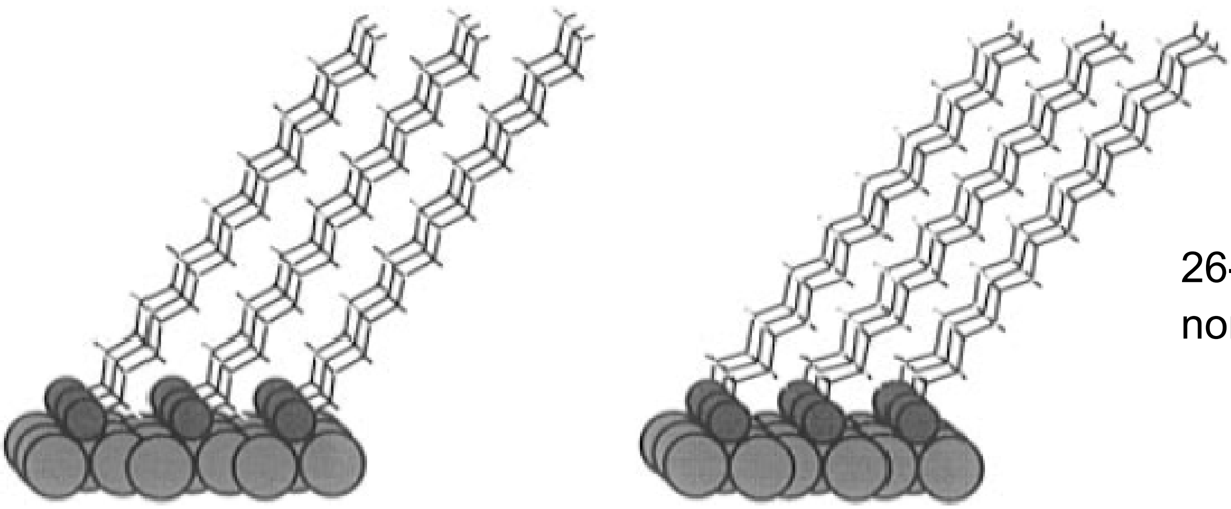
Surface-active organosulfur compounds on gold



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

Lecture 3: Self-assembled Monolayers (SAMs)

Chain tilting in SAMs of thiolates on Au(111)



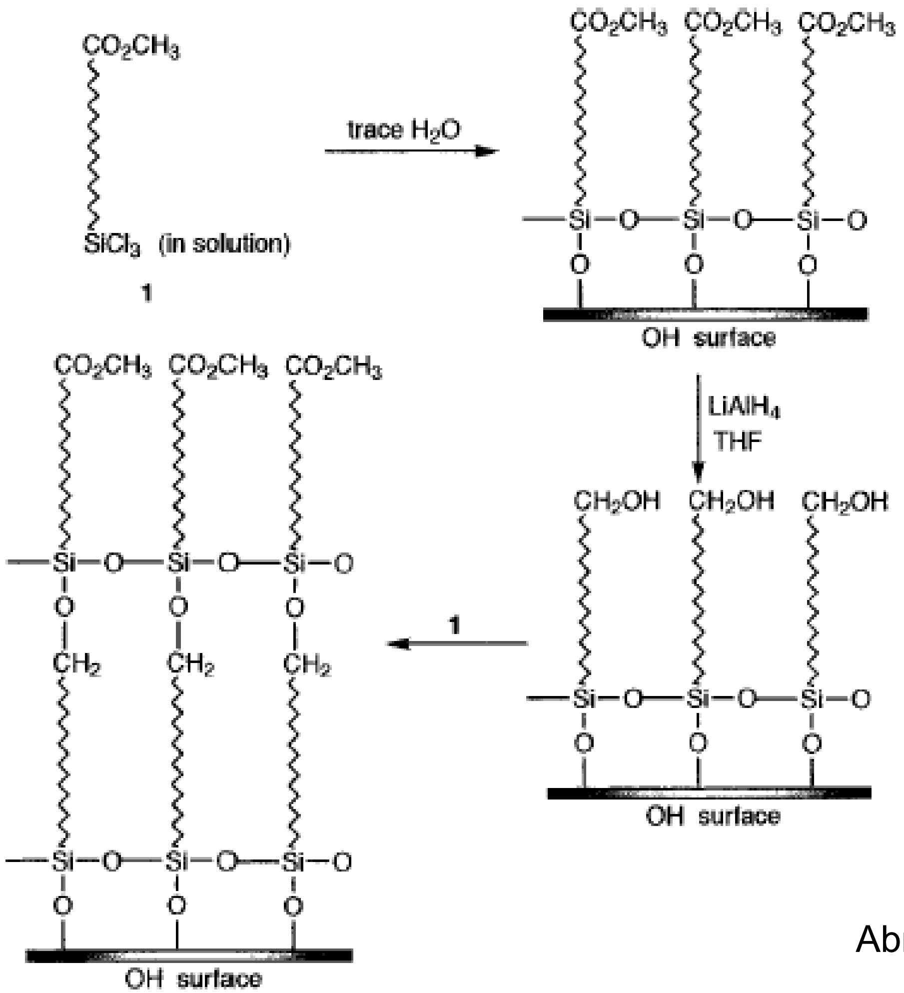
26-28° from the surface normal (or 11-14°)

Figure 11. A view of the tilt in a nine-molecule section of a fully covered $SC_{16}H_{33}$ monolayer on Au(111) minimized with a modified MM2 force field including the sp^3 chemisorption parameters (left, calculated stabilization energy −23.29 kcal mol^{-1}) and with the sp chemisorption parameters (right, calculated stabilization energy −22.25 kcal mol^{-1}). The gold atoms are shown in light gray having their full van der Waals radii. The sulfur atoms are shown in dark gray and are not drawn to scale.

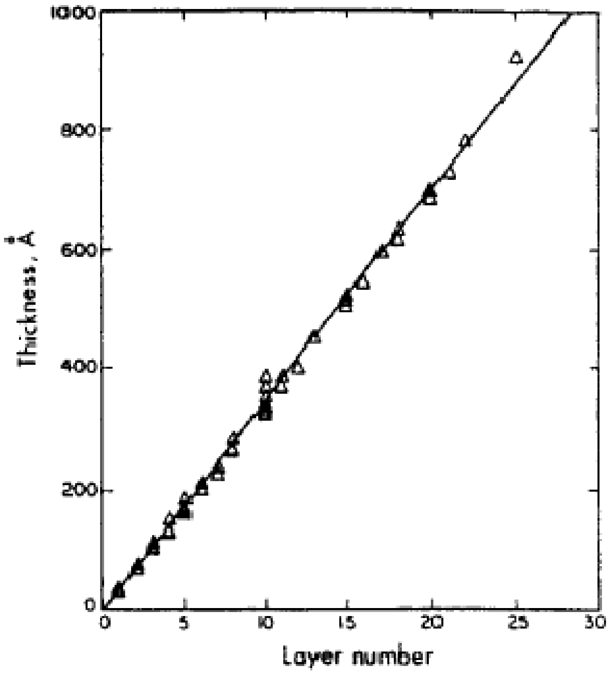
- This tilt is a result of the chains reestablishing VDW contact in an assembly with 5 Å S ••• S distance, larger than the distance of 4.6 Å, usually quoted for perpendicular alkyl chains in a close packed layer.

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

Self-assembled Multilayers



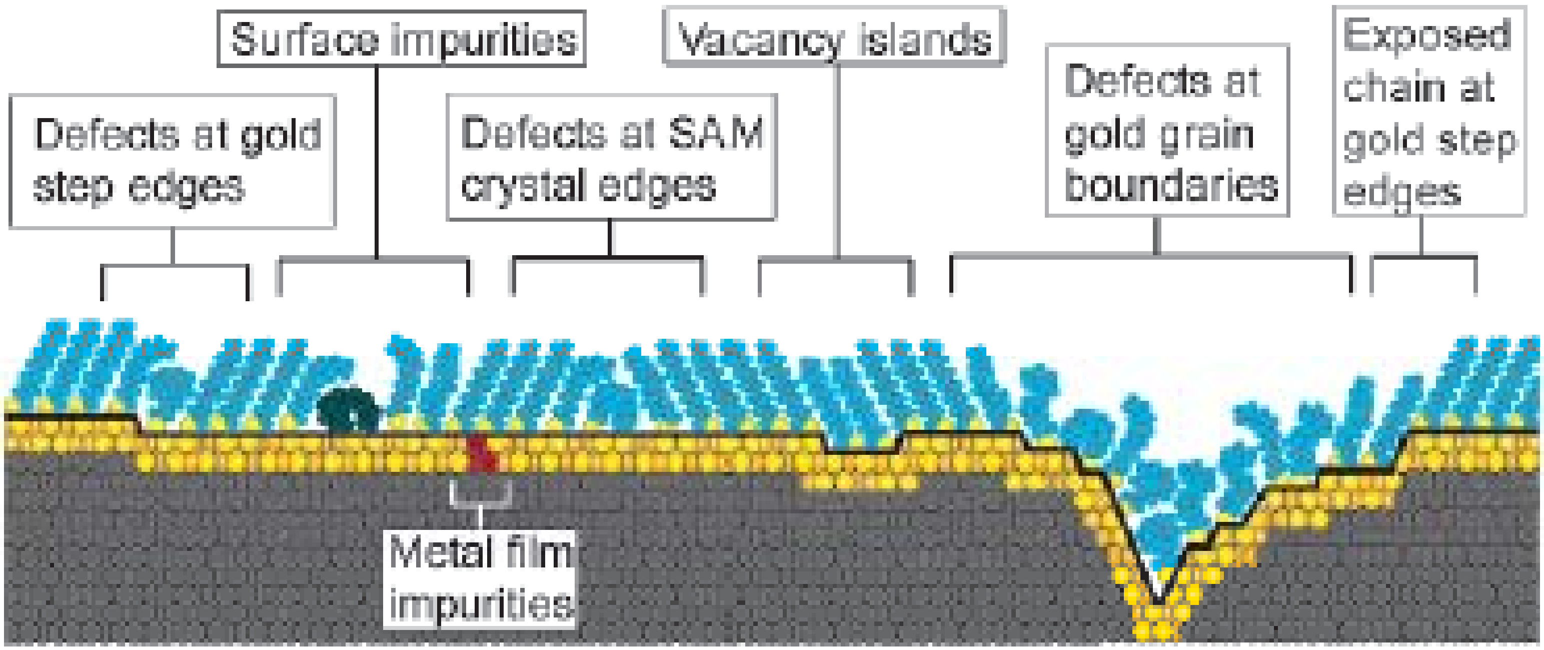
Construction of self-assembled multilayers



Film thickness vs layer number

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

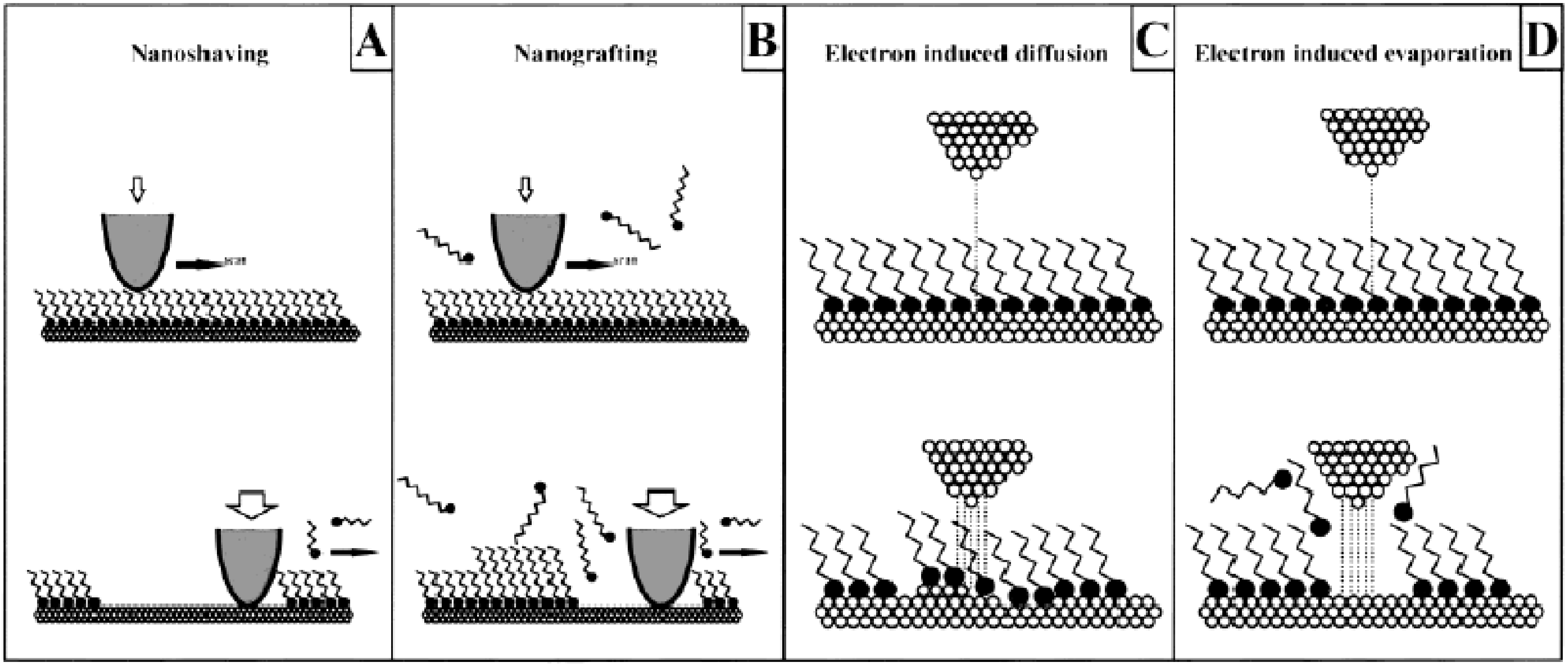
Defects in Self-assembled Monolayers (SAMs)



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.

Love et al., *Chem. Rev.* **2005**, *105*, 1103-1169

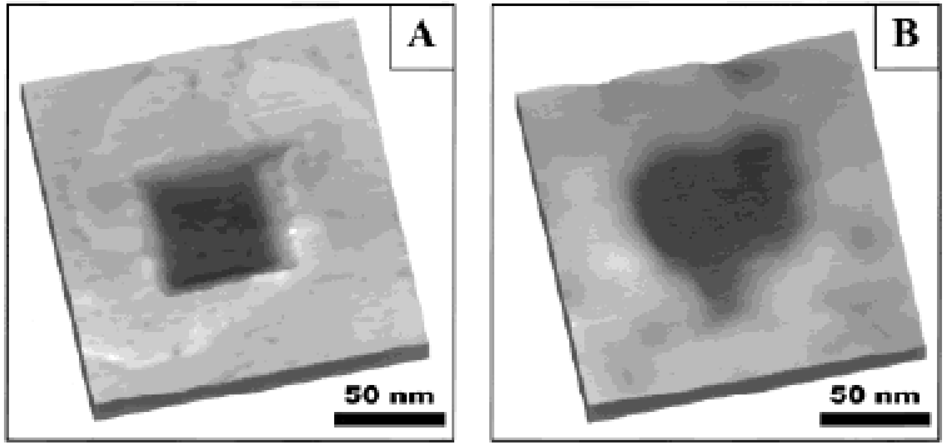
Scanning Probe Lithography Nanofabrication of SAMs



Schematic diagrams of four basic manipulation mechanisms using AFM (A and B) and STM (C and D). The imaging and fabrication modes are depicted in the top and bottom rows, respectively.

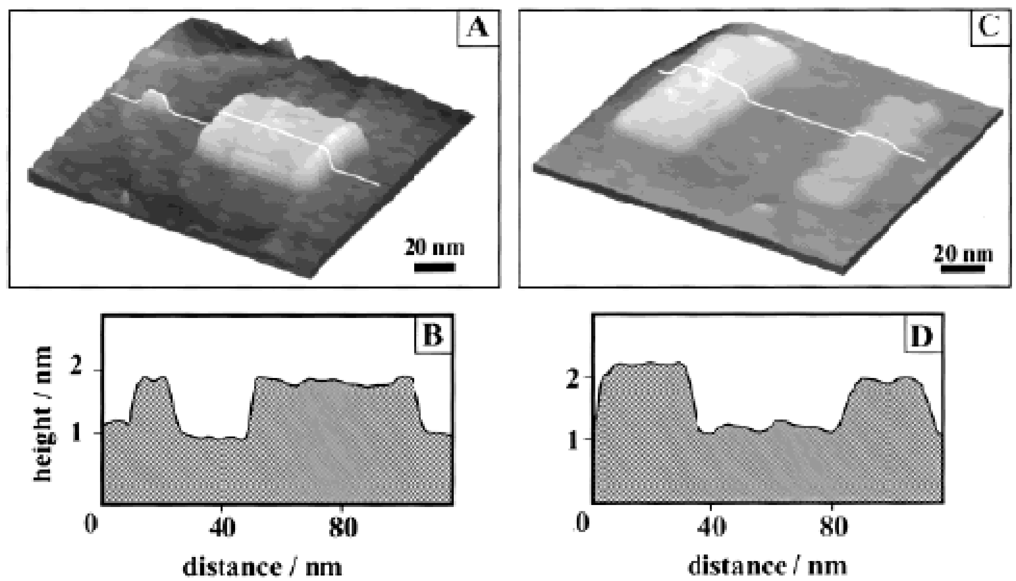
Liu, Xu, Qian. *Acc. Chem. Res.* **2000,** *33*, 457-466

Scanning Probe Lithography Nanofabrication of SAMs



(A) 160-160 nm2 topographic images of C18S/Au(111) with the thiols shaved away from the central 50-50 nm2 square.
(B) 160-160 nm2 topographic images of OTE/mica containing a heart-shaped pattern produced using nanoshaving.

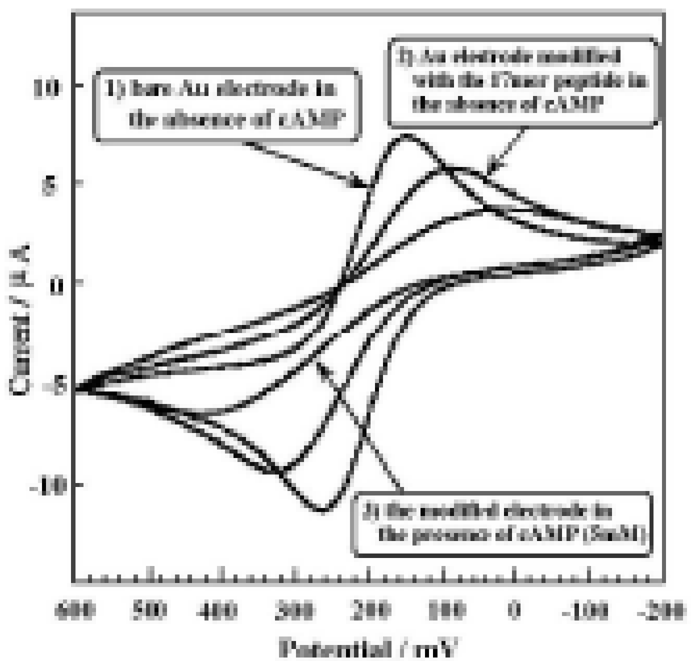
(A) Fabrication of two C18S nanoislands (3 - 5 and 50-50 nm2) in the matrix of a C10S monolayer using nanografting.
(C) Fabrication of multicomponent patterns using nanografting.



Liu, Xu, Qian. *Acc. Chem. Res.* **2000,** *33*, 457-466

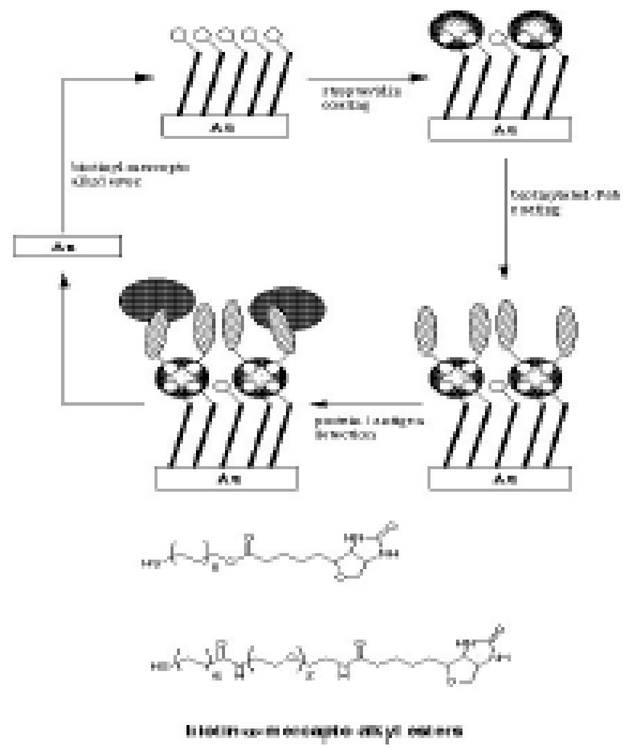
Sensing and Proteins Binding on SAMs-modified Electrodes

Electrochemical sensing by SAMs modified electrodes



Cyclic voltammogram of Au electrode modified with 17-mer peptide in the absence and presence of cAMP

Electrochemical studies of proteins on SAMs-modified electrodes



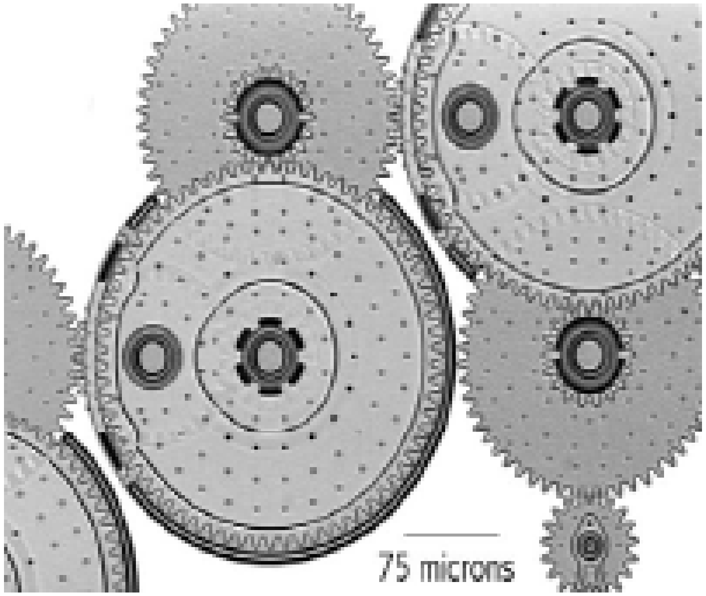
Reversible formation of a protein triple layer on SAM using biotinylated alkylthiols

Dojindo Molecular Technologies, Inc.

Self Assembled Monolayers(SAMs) in MEMS Devices

Common Failure Mechanisms in MEMS

- Fracture
- Creep
- Stiction
- Electromigration
- Wear
- Degradation of dielectrics
- Delamination
- Contamination
- Pitting of contacting surfaces
- Electrostatic discharge (ESD)



Dr. Lior Kogut, University of Western Ontario

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Self Assembled Monolayers(SAMs) in MEMS Devices

Advnatages of SAMs in MEMS

(a) Eliminate release stiction by effectively reversing the shape of the water meniscus;

(b) Reduce in-use stiction by three to four orders of magnitude with respect to the conventional oxidized release process;

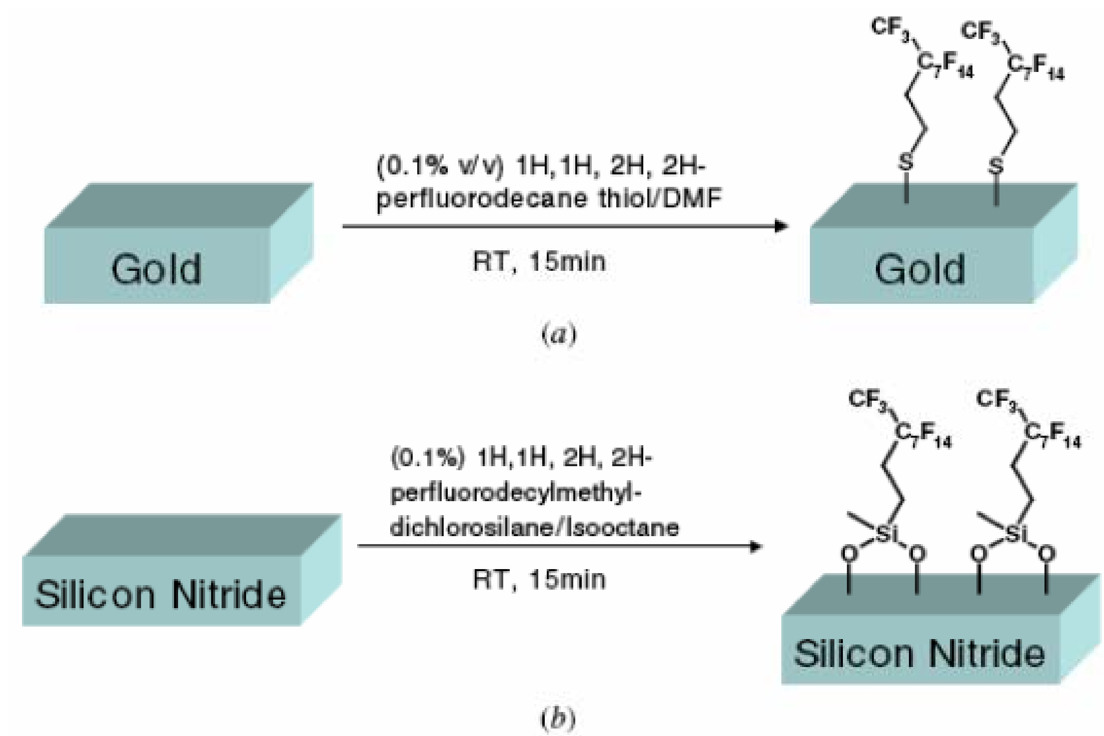
(c) Eliminate the need for large input signals or mechanical probing in the start-up phase in microengines;

(d) Reduce friction in microengines static friction value of 0.08 vs. 2.3 for oxide-coated surfaces;

(e) Reduce wear significantly over 40 million operation cycles have been achieved in touch-mode electrostatic actuators;

(f) Survive packaging environments thermally stable to 4000C in various, including oxygen containing, environments.

Self Assembled Monolayers(SAMs) in MEMS Devices



Contact angles of water droplets

	Without SAM coating	With SAM coating
Gold	70.6°	112.6°
Silicon nitride	36.7°	115.8°

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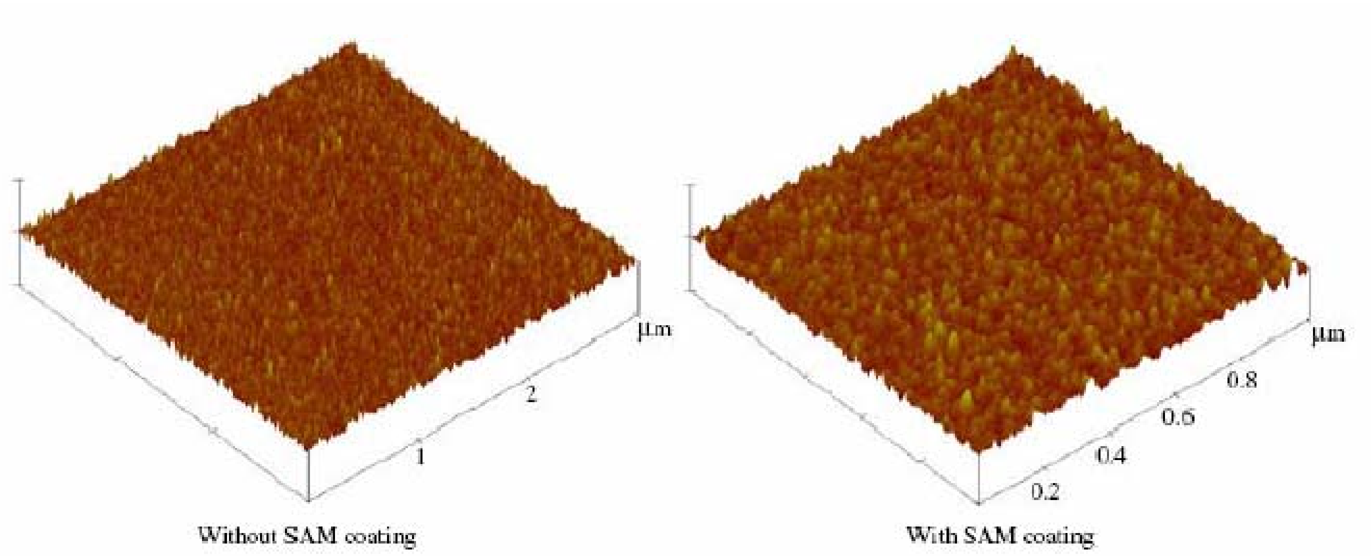
Self Assembled Monolayers (SAMs) in MEMS Devices

AFM images and roughness data of Silicon nitride surface



	Without SAM Coating	With SAM Coating
Roughness rms	0.542 nm	0.671 nm
Roughness peak to peak	5.274 nm	6.027 nm

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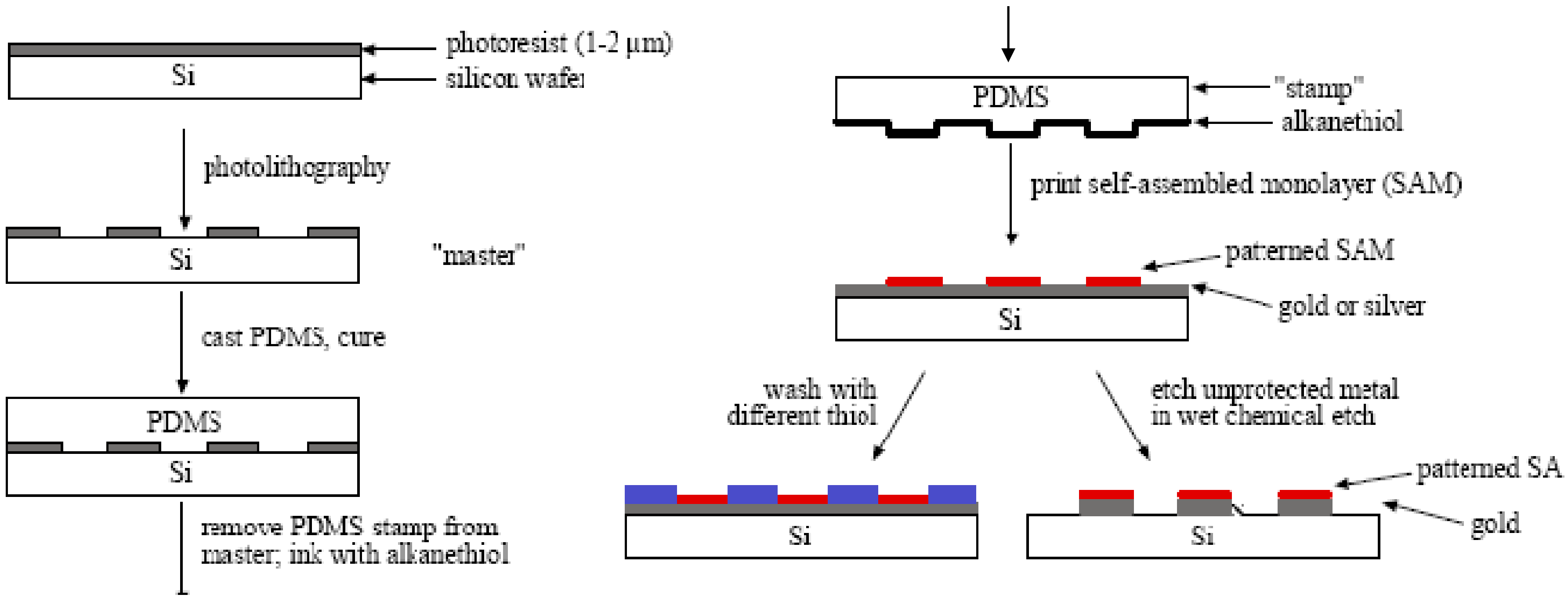
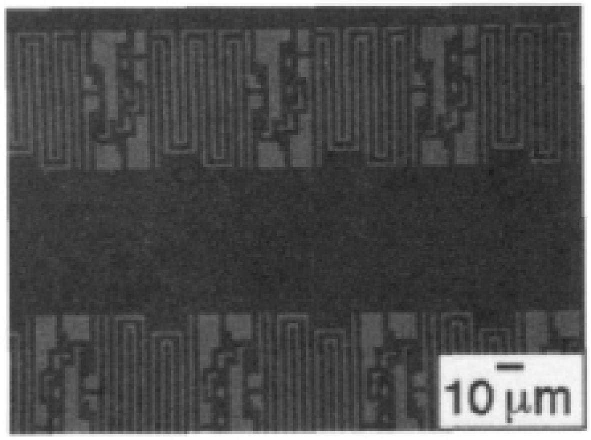
Case Study: Microcontact printing (μCP)

Schematic of microcontact printing (μCP)

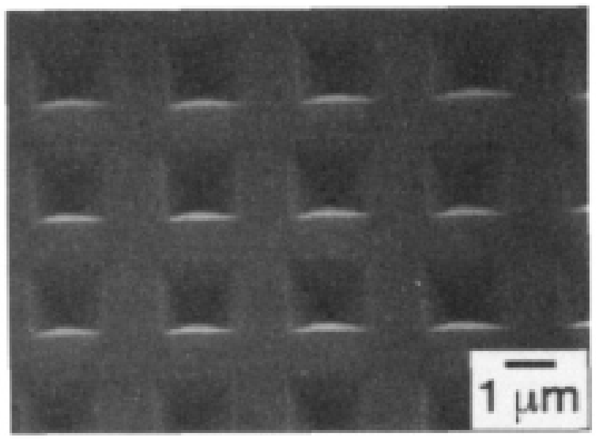


Kumar, Whitesides, *Appl. Phys. Lett.* **1993**, *63*, 2002

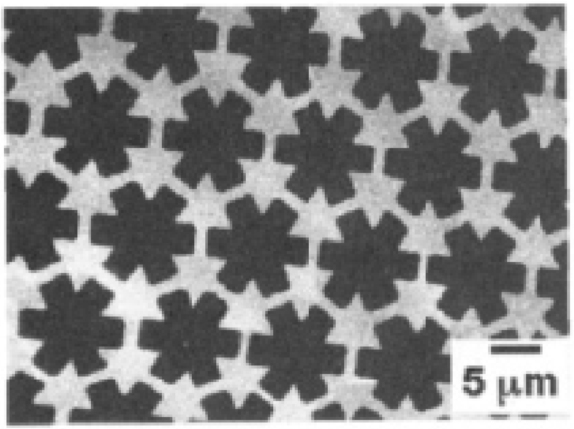
Case Study: Microstructures fabricated using µCP

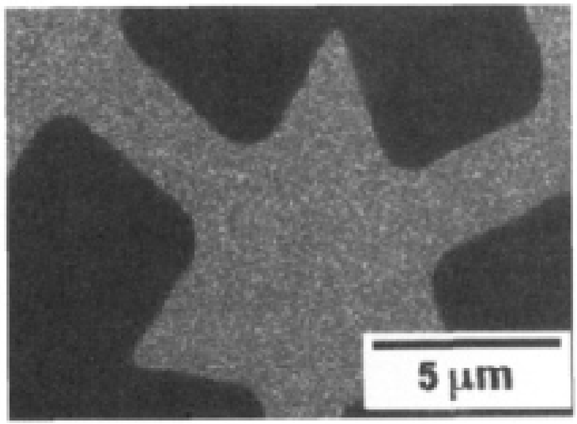


Gold structures generated by pCP and etching



Etched silicon structure produced through anisotropic etching of silicon (in KOW2-propanol) using a mask of gold produced through pCP and etching in a solution of cyanide ion.





AFM image of a series of alternating hydrophobic and hydrophilic lines and an electron micrograph of a corresponding region.

Kumar et al., *Acc. Chem. Res*. **1995**, *28*, 219-226

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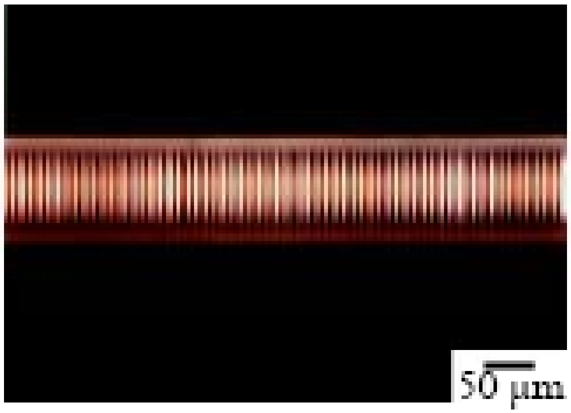
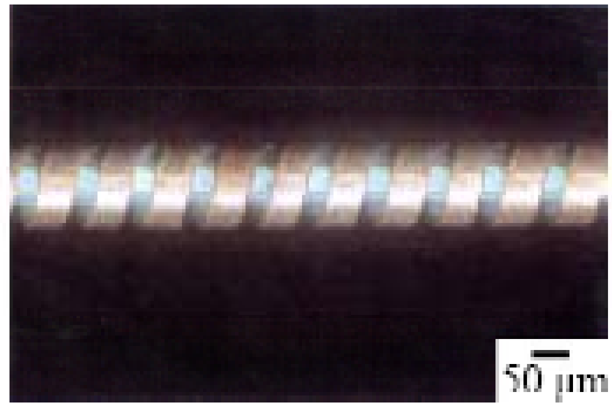
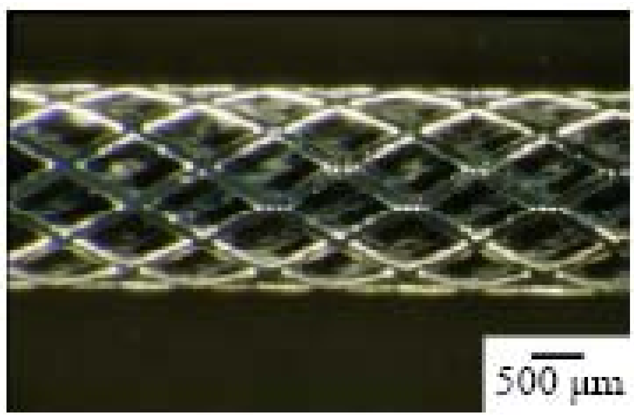
Case Study: Microstructures fabricated using µCP

Gold bands (3 µm) on an optical fiber



Copper coils (50 µm) on glass capillary





Free-standing silver mesh cylinder (~2 mm diameter)