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.

SAMs and sensor technologies

Quartz Crystal Microbalance (QCM):
Detection of adsorbed gases

Ex. cavitand tetrasulfides on Au(111)

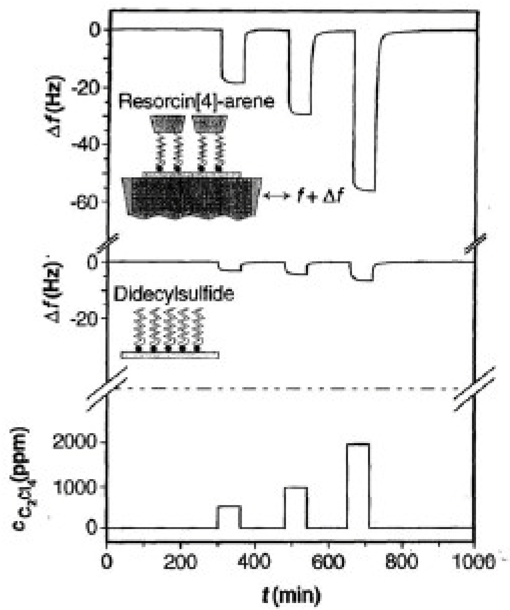
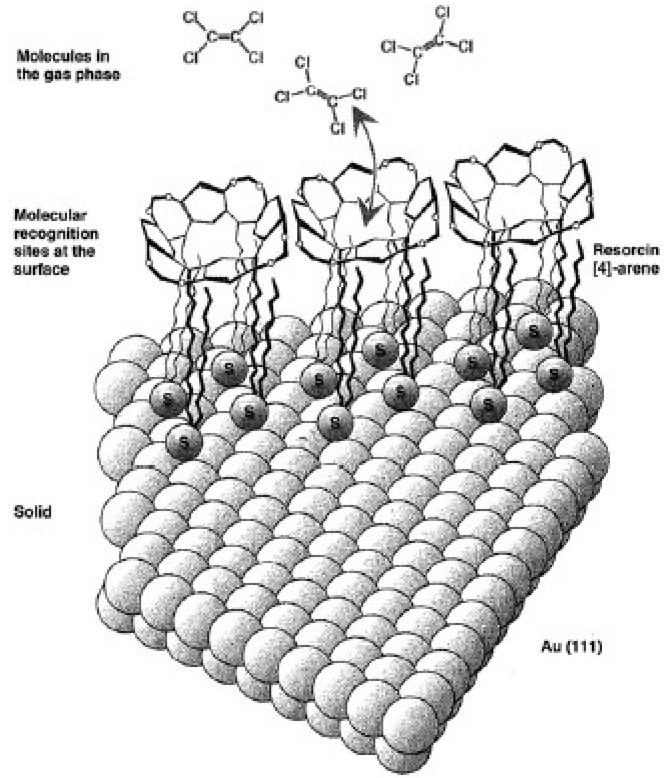
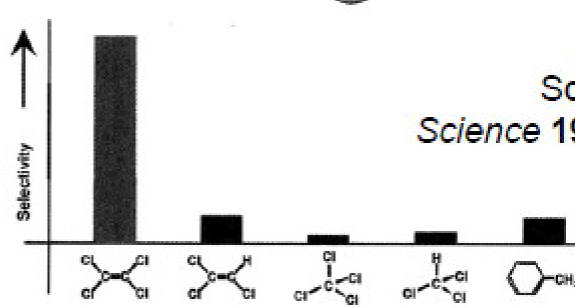


Fig. 4. Changes of frequencies Δf as a function of time t during exposure of monolayers of resorcin[4]arene and didecylsulfide to different concentrations $c_{C_2Cl_4}$ in synthetic air at T = 303 K. For simplification, the noise of the signal, ± (2 to 3) Hz (which mainly results from small fluctuations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





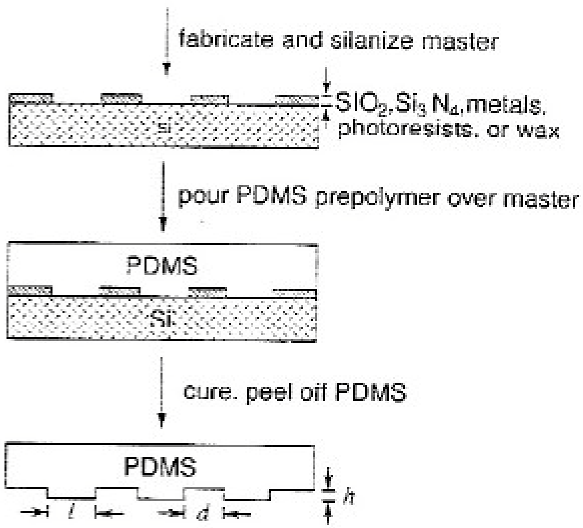
Schierbaum et al.
Science **1994**, *265*, 1413.

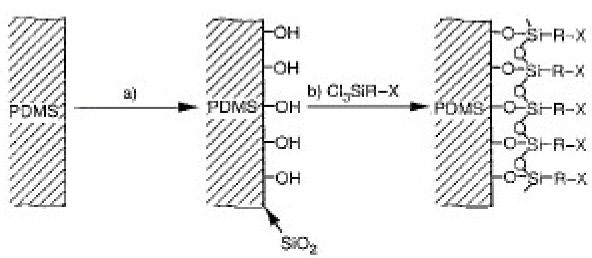
Surface Patterning using SAMs

Soft lithography: Microcontact printing (stamp-pad lithography)

Review: Xia and Whitesides, *Angew. Chem.* **1998**, *37*, 550.

Preparation and patterning of silicone (PDMS) stamp:





Application of SAM-forming compounds ("ink")

SAM Transfer Methods:

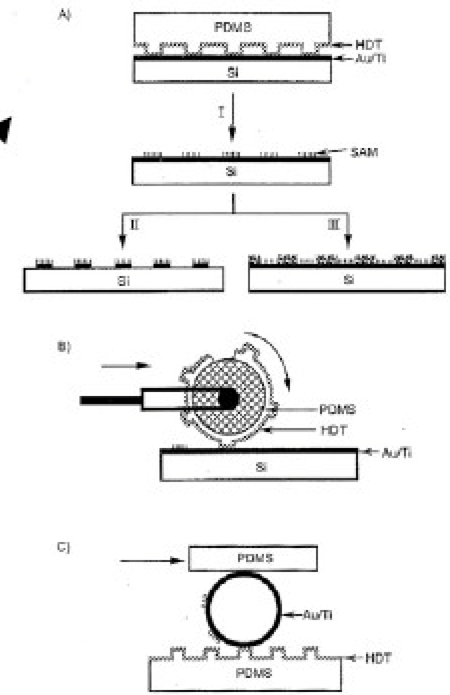
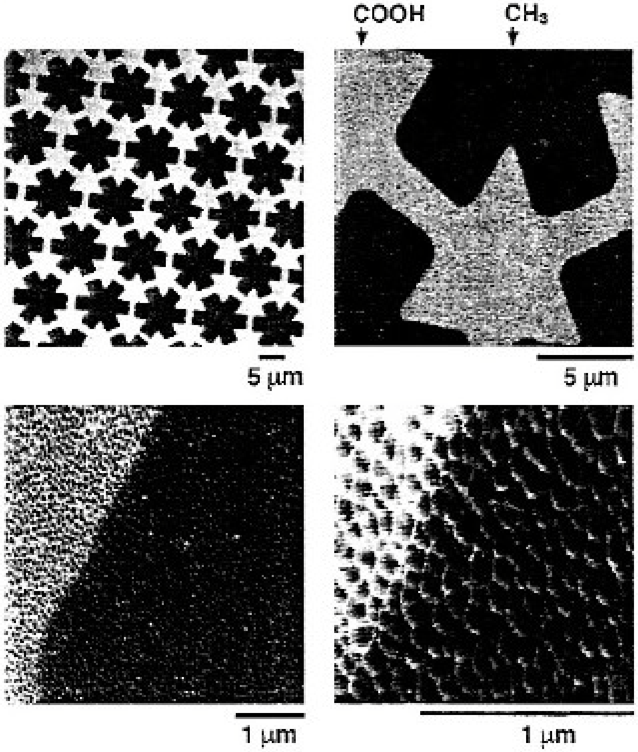


Figure 8. Schematic illustration of procedures for µCP of hexadecanethiol (HDT) on a gold surface: A) printing on a planar surface with a planar stamp (I: printing of the SAM, II: etching, III: deposition);[84] B) large-area printing on a planar surface with a rolling stamp;[illegible] C) printing on a nonplanar surface with a planar stamp.[illegible] After the "ink" (ca. 2 mM HDT in ethanol) was applied to the PDMS stamp with a cotton swab, the stamp was dried in a stream of N_2 (ca. 1 min) and then brought into contact with the gold surface (ca. 10–20 s).

Microcontact printing: scope and limitations

Chemical Force Microscopy images of patterned SAMs:



Stamp deformation:

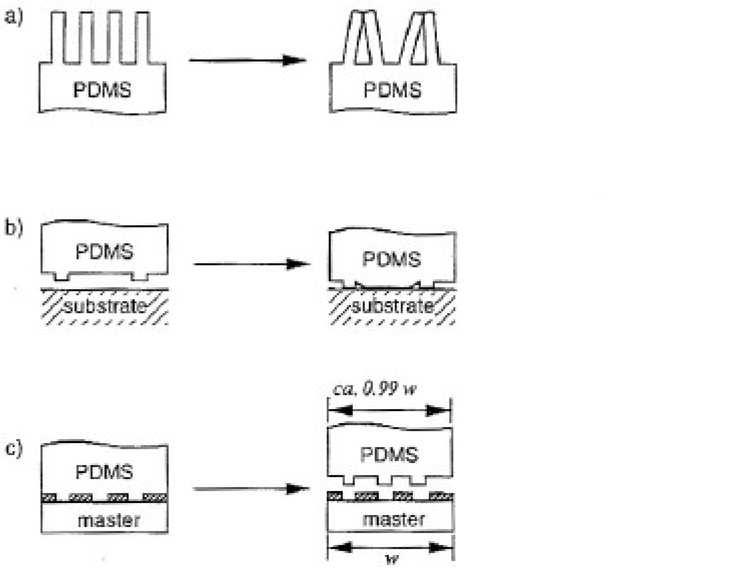
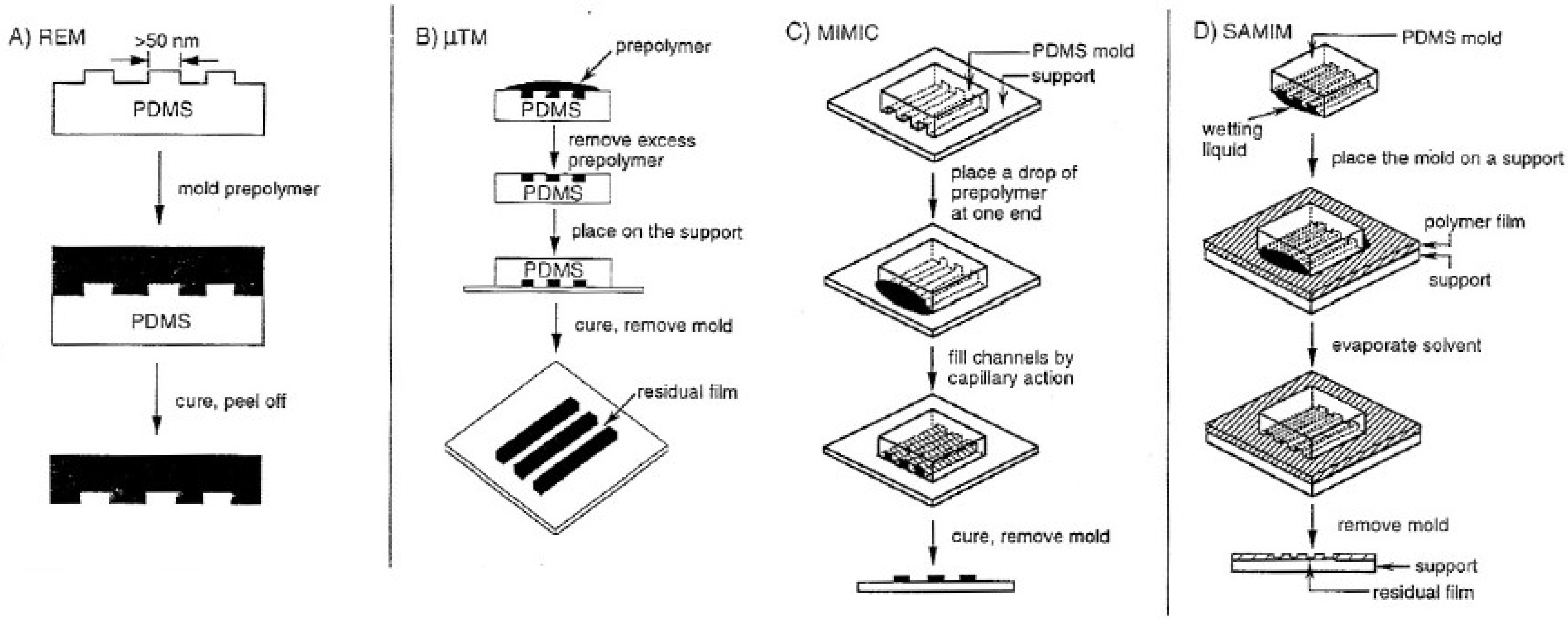


Figure 7. Schematic illustration of possible deformations and distortions of microstructures in the surfaces of elastomers such as PDMS. a) Pairing, b) sagging, c) shrinking.

Xia and Whitesides, *Angew. Chem.* **1998**, *37*, 550.

Micromolding: micropatterning in 3D



Replica molding	Microtransfer molding	Micromolding by capillary action	Solvent-assisted micromolding

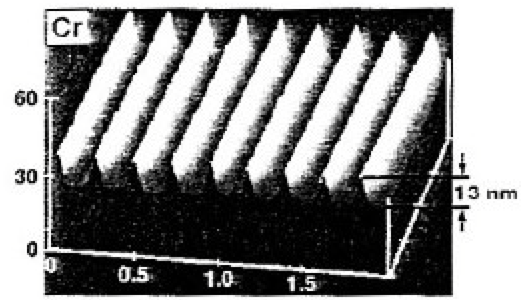
Xia and Whitesides, *Angew. Chem.* **1998**, *37*, 550.

Nanopatterned substrates by molding

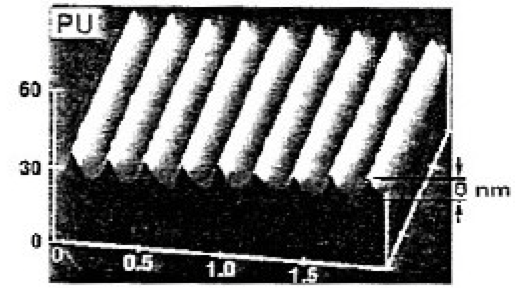
AFM images of nanostructured polyurethane

Replica mold

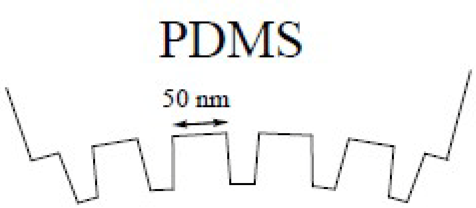
Master (Cr)



Polyurethane replica
(from PDMS mold)

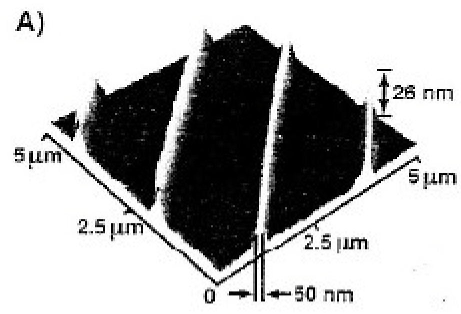


Reduced linewidth by stamp deformation:

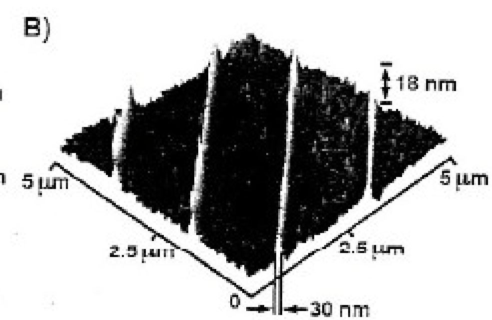


Mold after deformation

Master (Au)

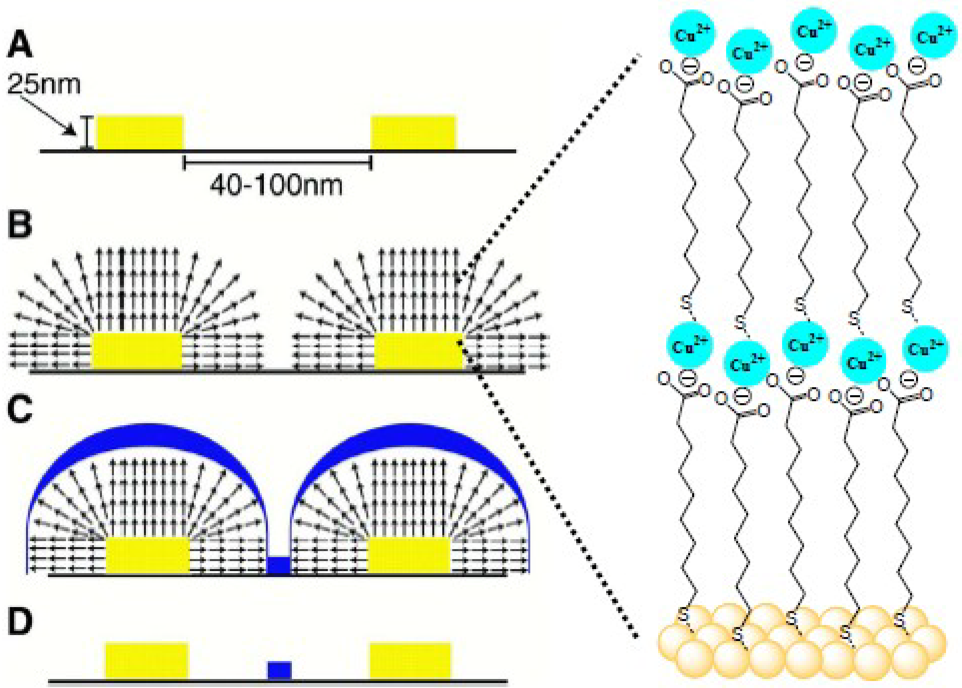


Polyurethane replica
(from PDMS mold)

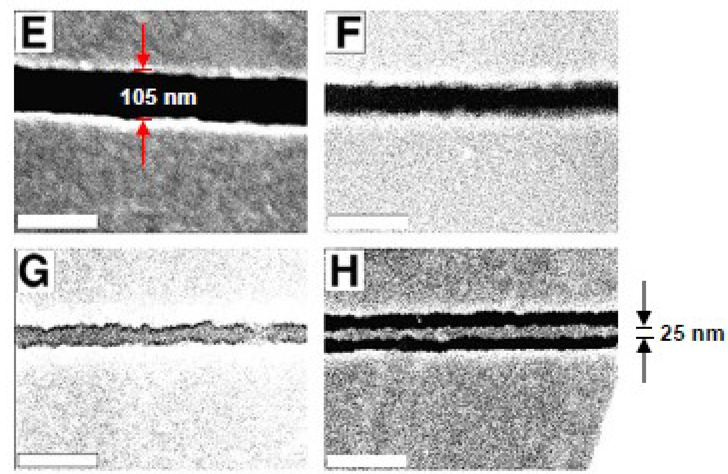


Xia et al, *Adv. Mater*. **1997**, *9*, 147.

Nanolithography using Layer-by-layer SAMs



Fabrication of nanosized gaps:



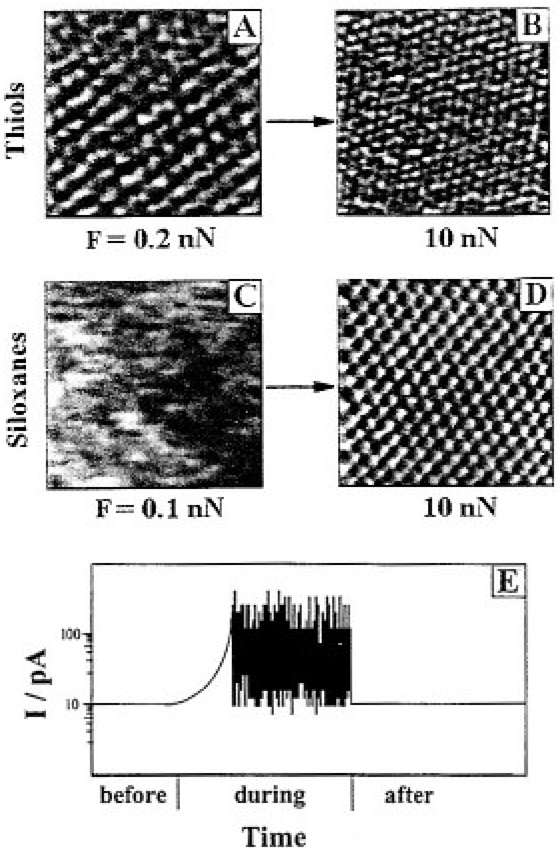
Molecule	Layers adsorbed	Multilayer thickness (nm) Calc.	Multilayer thickness (nm) Expt.
$HS(CH_2)_{10}COOH$	9	14	17
$HS(CH_2)_{10}COOH$	26	39	42
$HS(CH_2)_{15}COOH$	9	18	18
$HS(CH_2)_{15}COOH$	10	20	21
$HS(CH_2)_{15}COOH$	20	40	32

FE-SEM image of metal nanowire by lithography on LbL SAM resists:

Hatzor and Weiss, *Science* **2001**, *291*, 1019.

Nanopatterning by scanning probe lithography

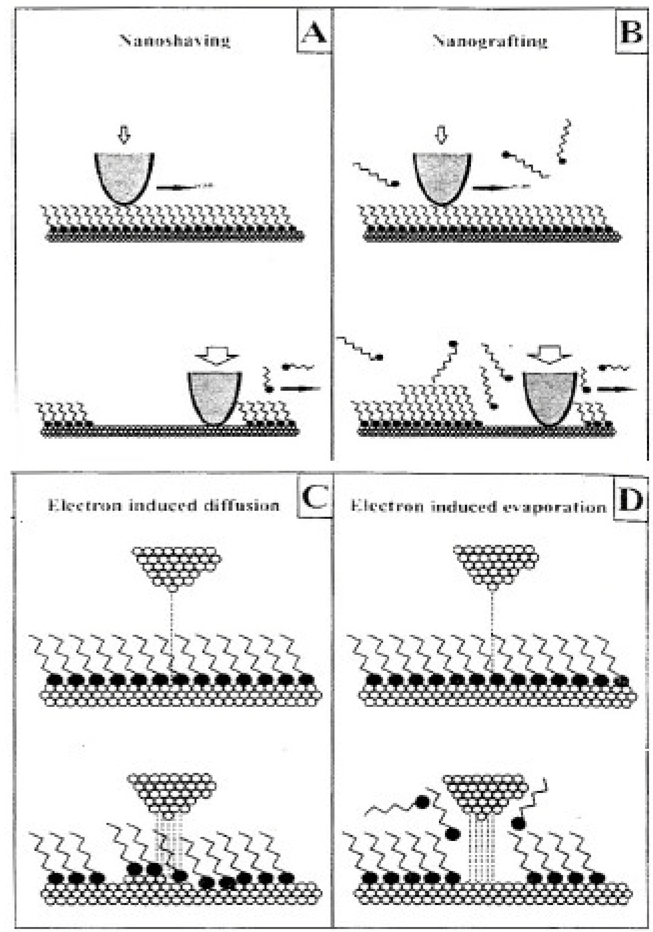
STM images above and below the threshold force



C18-thiols on Au (in EtOH)

C18-siloxane on mica (in EtOH)

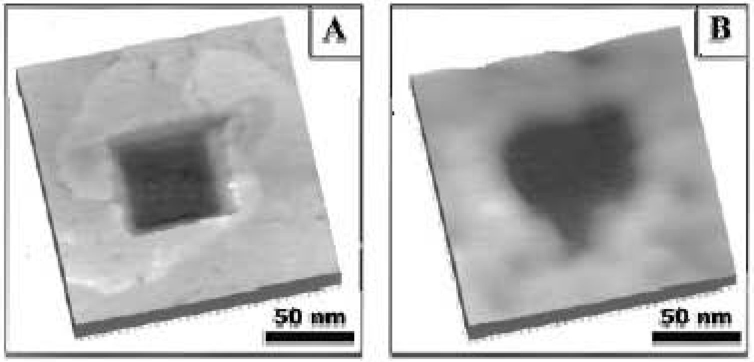
Modes of SPL



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

Nanopatterning by SPL

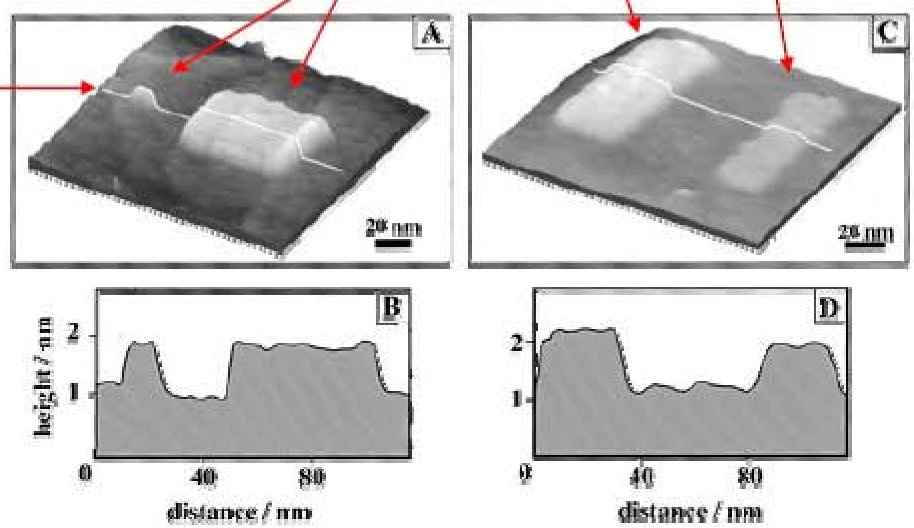
C18-thiol on Au(111) C18-siloxane on mica



"Nanoshaving" of
160 x 160 nm^2 area

C18 thiols C22 C18

AFM linescan

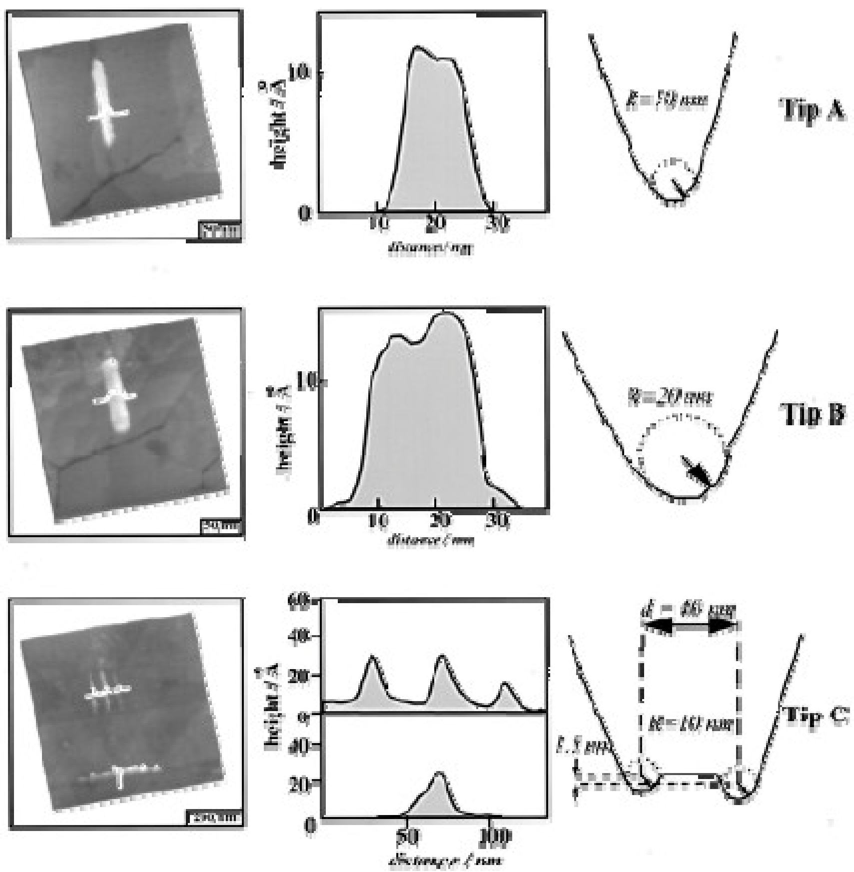


"Nanografting" of C18, C22 thiols onto C-10 thiol SAM

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

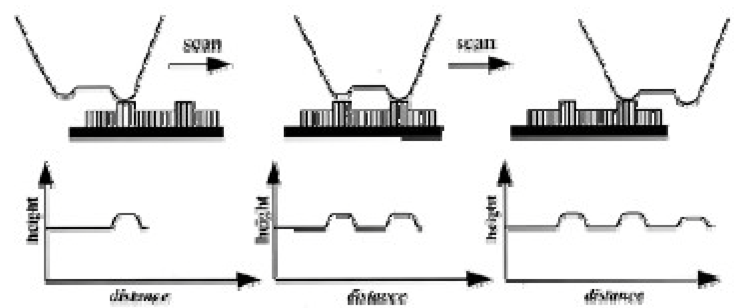
SPL: Probe tip characterization

C22-thiols grafted onto C10-thiol SAM



"Nanografting" at high loading force, followed by low-force imaging

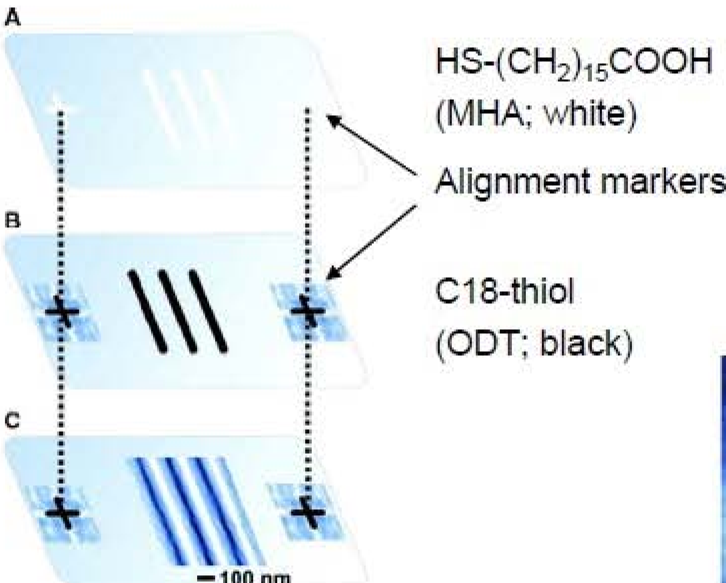
Double-line graft and imaging: deconvolution of observed pattern

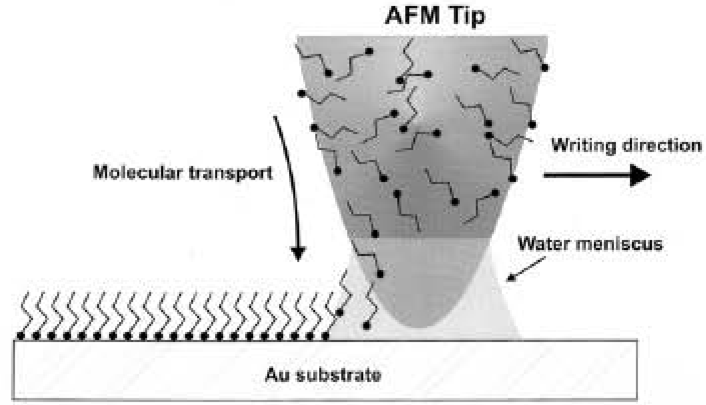


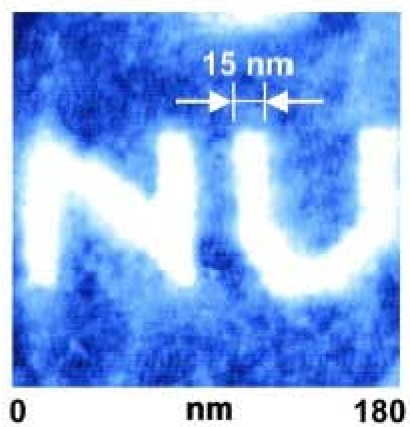
Liu, Xu, and Qian, *Acc. Chem*. Res. **2000**, *33*, 457.

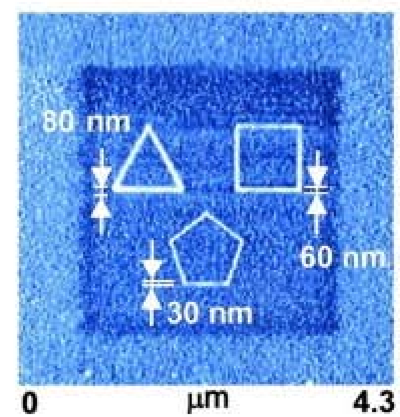
"Dip-pen" nanolithography (DPN)

Pattern alignment for DPN:





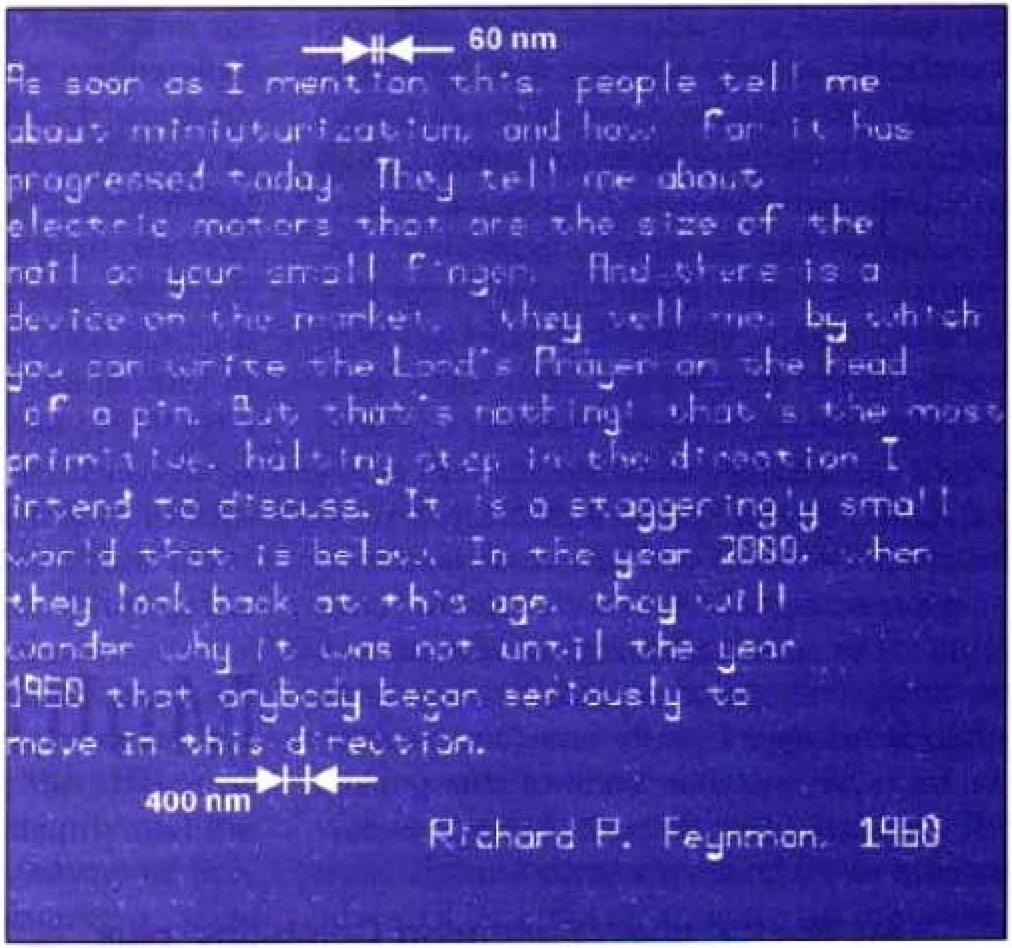




MHA written on Au substrate, followed by ODT background

Mirkin and coworkers, *Science* **1999**, *283*, 661; *Science* **1999**, 286, 523.

Feynman's vision



Tiny tribute. Text from a speech by physicist Richard Feynman, which was first delivered in 1959 and published in 1960, now comes nanosized.

Science **1999**, 286, 389.