

# Alkanethiolate Protected Silver Clusters

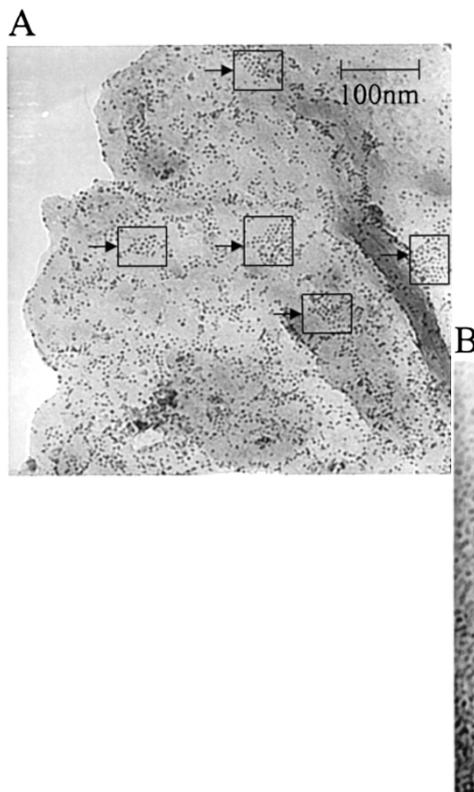


Figure 46. Transmission electron micrographs of octanethiol-capped Ag cluster. (A) Soluble portion of Ag-OT and slow evaporation leading to ordering. The observed (111) planes are marked. Absence of a long-range order is attributed to the polydispersity of the particles. (B) Insoluble portion after sonication in toluene. Uniform size distribution is observed.

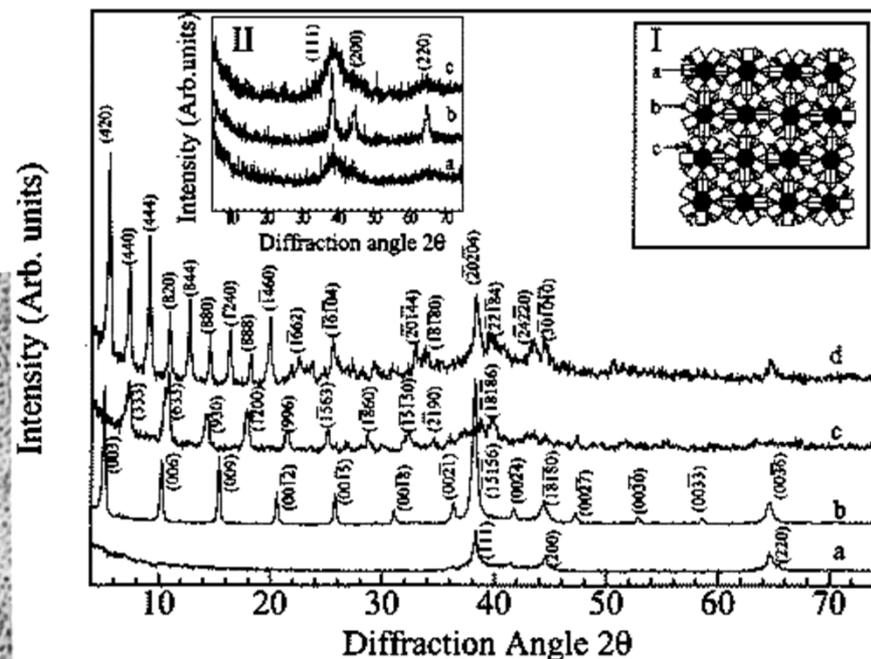


Figure 46.1 Cu K XRD patterns of (a) Ag-BT, (b) Ag-PT, (c) Ag-OT, and (d) Ag-ODT. A schematic of the super-lattice is shown in inset I. The cluster cores and the organized and unorganized alkyl chains are represented by a, b, and c, respectively. The shape of the cluster cores observed in TEM15 and the ordering of the alkyl chains seen in IR are considered in preparing this schematic. Inset II shows the XRD patterns of the Au clusters capped with (a) BT, (b) OT, and (c) ODT. The reflections are labeled.

# Microcontact Printing, $\mu$ CP (Whitesides et al.)

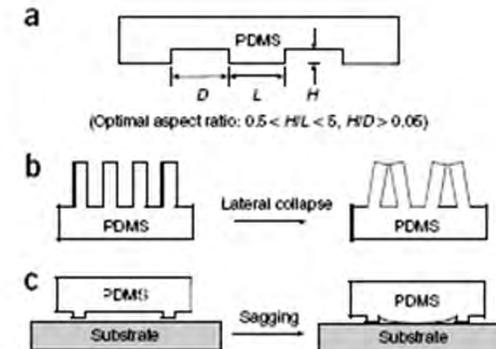
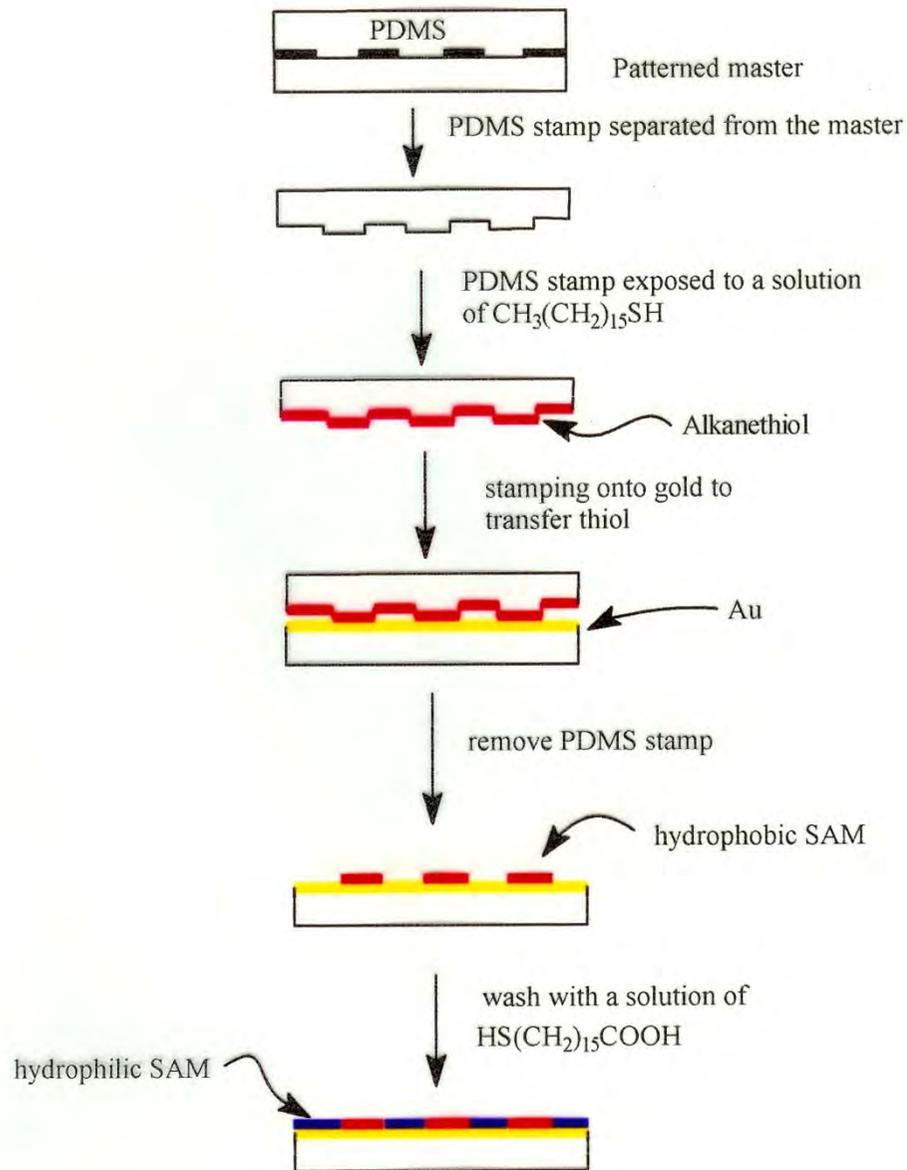
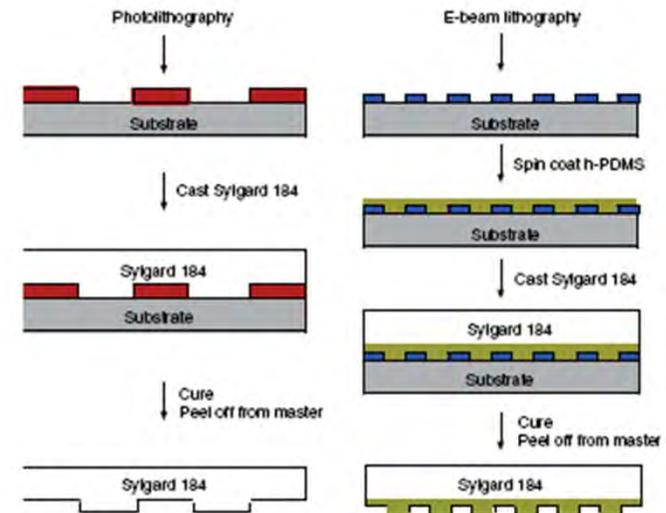
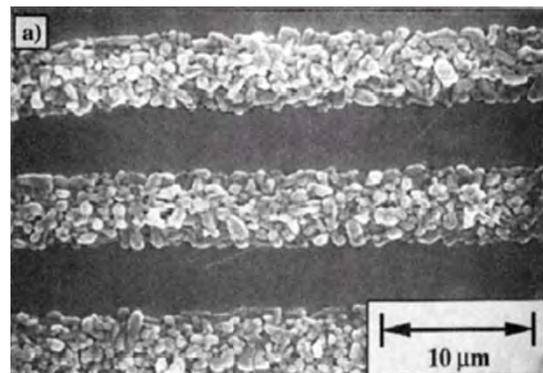
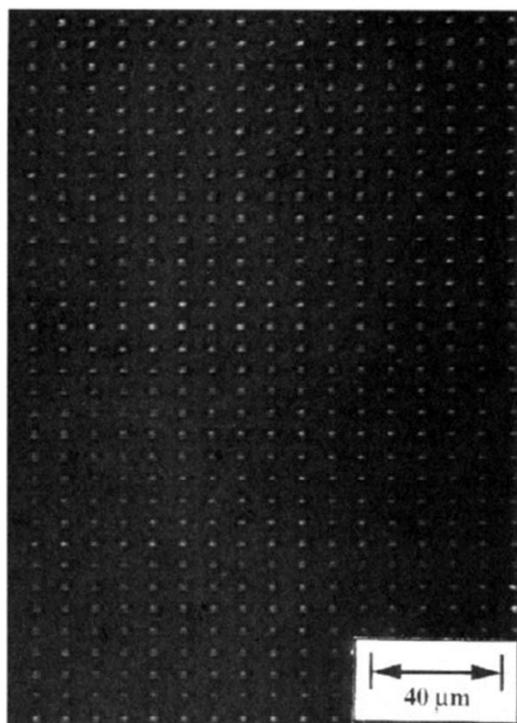
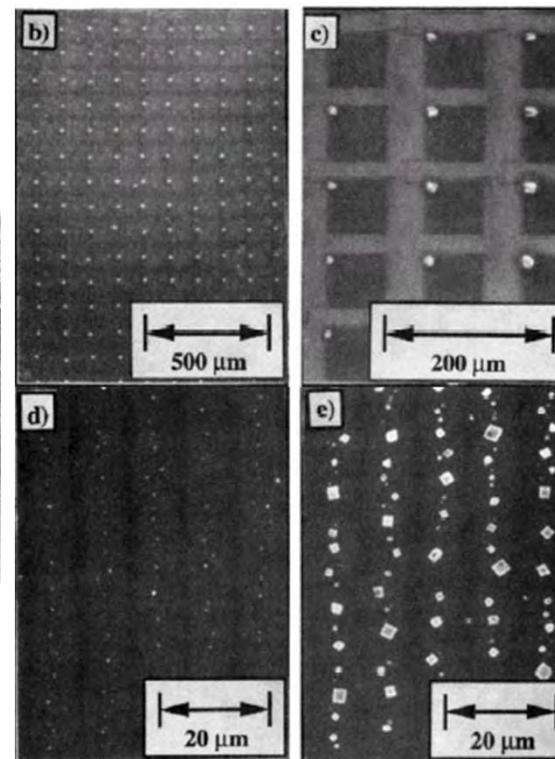


Figure 3 | Schematic illustrations of a PDMS stamp (a) and two possible problems that may arise from the softness of an elastomer: (b) lateral collapse of relief structures (or commonly known as 'pairing') with aspect ratios  $H/L > 5$ ; and (c) sagging of recessed structures with aspect ratios  $H/L < 0.5$ .





Langmuir, 1994, V. 10 (5)  
P. 1509



Optical photograph taken of condensed drops of water that formed on a pattern surface on cooling. The surface consisted of an array of hydrophilic circles ( $2\mu\text{m}$  in diameter, SAM formed from  $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ ) in a hydrophobic field (SAM formed by rubber stamping the adsorption of  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ ). The substrate was a thin ( $100\text{\AA}$ ) layer of gold deposited on a Ti-primed ( $10\text{\AA}$ ) glass slide. The thin film on glass system is an optically transparent substrate that is useful for optical microscopy since light can be transmitted through the substrate.

Langmuir, 1994, V. 10 (5) P. 1507

Patterned crystallization. (a)  $\text{LiClO}_4$  crystallized from a saturated solution of methanol that formed on the hydrophilic (SAM formed from  $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ ) regions of a patterned substrate. The hydrophobic regions were formed by rubber stamping the adsorption of  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ . (b, c) Arrays of crystals of  $\text{CuSO}_4$  that formed on hydrophilic regions from 1 M, Aqueous solutions. Crystals that formed from patterned solution of KI are shown in parts d and e. The concentration of KI was 0.1 and 3 M for the solutions used to prepare parts d and e, respectively. The liquid in each case was evaporated in an oven at  $65^\circ\text{C}$ .

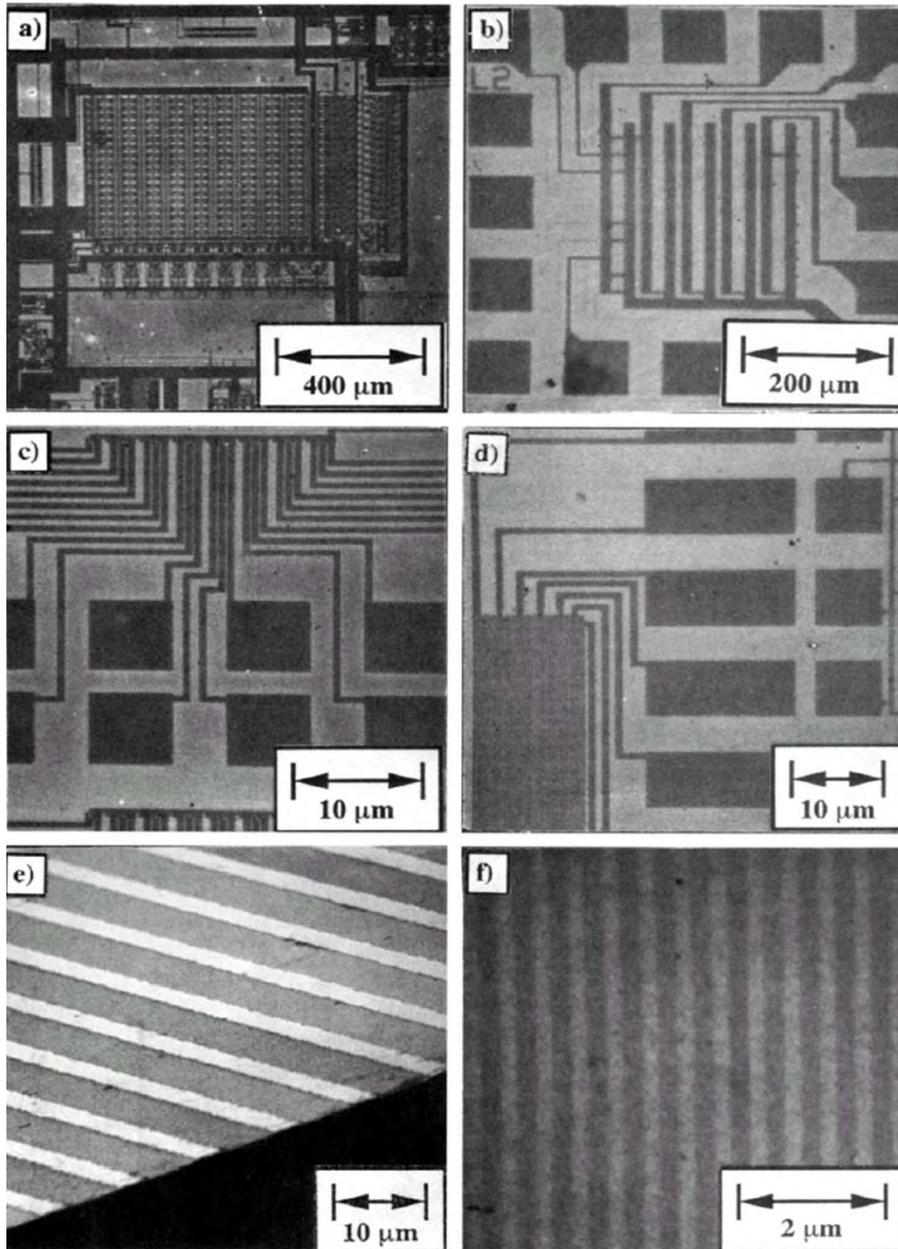
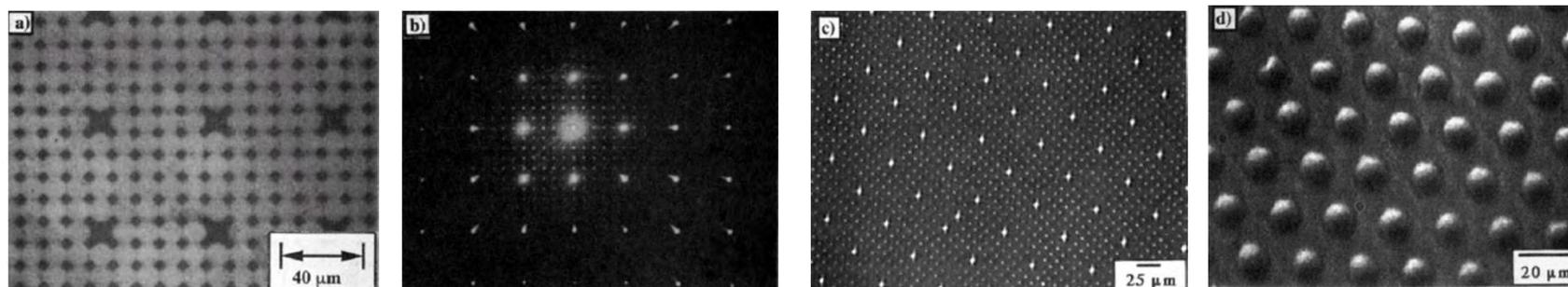
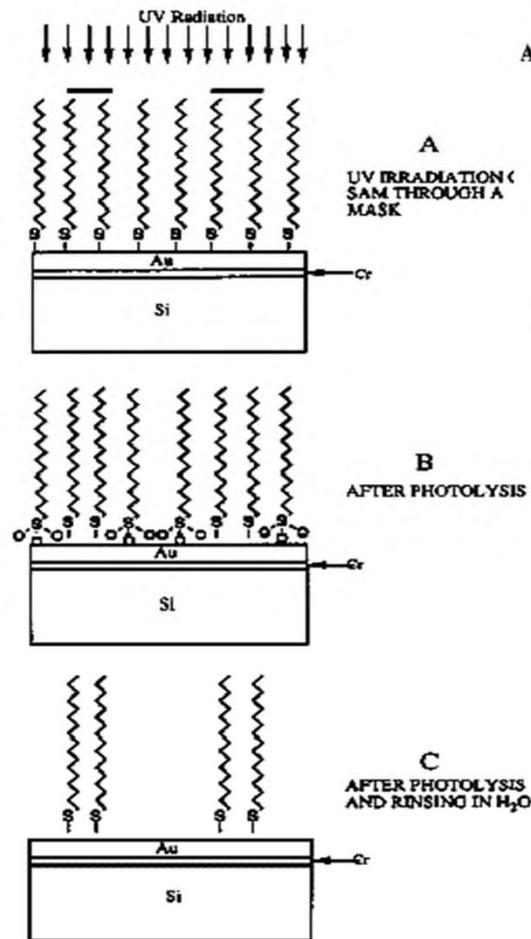


Figure 48.2 SE micrographs of several types of structures formed through rubber stamping and chemical etching (a-d). (e) Fracture profile of a series of gold lines supported on a silicon wafer. The width of the gold lines is  $2\mu\text{m}$ , and the thickness of the gold is  $2000\text{\AA}$ . The tilt allows observation of the thickness of the gold and the resolution of the edge. (f) The smallest features that are currently accessible using rubber stamping. The width of the lines is  $0.2\mu\text{m}$ . Although the arrays with features on scales of  $1\mu\text{m}$  or greater are easy to produce, the arrays of submicrometer ( $0.2\mu\text{m}$ ) lines are not routinely reproducible through rubber stamping by hand: they represent best-case examples, and the view shown was chosen from regions of lower fidelity. More precise mechanical control should allow these arrays to be produced with better reproducibility.

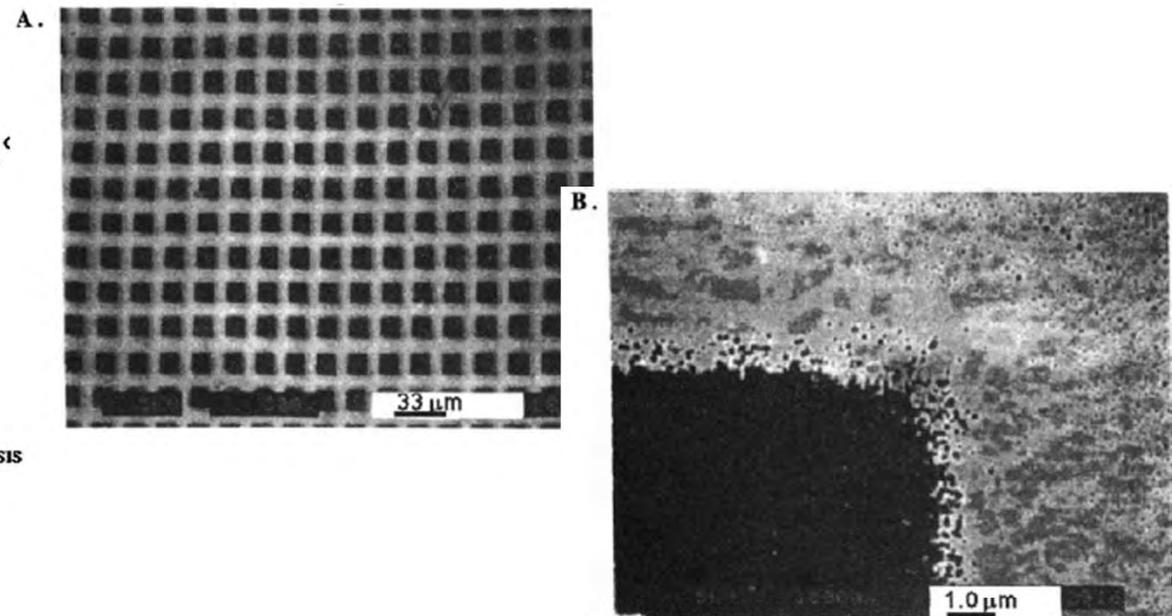


Langmuir, 1994, V. 10 (5) P. 1508

Figure 48.3 (a) SE micrograph of a surface having hydrophobic (light) and hydrophilic (dark) regions. The hydrophobic regions were formed by patterning the adsorption of  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  using a rubber stamp. The remaining regions were rendered hydrophilic by washing with a 1 mM solution of  $\text{HS}(\text{CH}_2)_{15}\text{CO}_2\text{H}$ . The surface has two lattices with different periodicities and lateral geometries. (b) A diffraction pattern of a He:Ne laser ( $\lambda=632.8\text{nm}$ , 1mW) reflected off the surface after formation of a condensation figure. Note that both lattices of the surface are distinguishable in the diffraction pattern. (c) An optical photograph taken of drops of hexadecane (light areas in the figure) left behind on hydrophilic patches of a patterned surface. The surface consisted of an array of hydrophilic circles and crosses (the SAM was formed from  $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ ) in a hydrophilic field (this SAM was formed first by application of a stamp of PDMS, like the one used in (a), inked with  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  to the gold surface.) The SAM was formed on a gold substrate similar to Fig. 48. The photograph was taken with light in transmission through this film within 30s of emergence of the substrate from a phase separated solution of 100 $\mu\text{L}$  of hexadecane in 10mL of water. (d) An optical photograph of drops of hexadecane wetting hydrophobic areas of a patterned surface under water. The surface consisted of an array of hydrophobic circles (this SAM was formed first by application of a PDMS stamp inked with  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  to the gold surface) in a hydrophilic field (the SAM was formed from  $\text{HS}(\text{CH}_2)_{15}\text{COOH}$ ). The SAM was formed on a gold substrate similar to Fig. 48. The photograph was taken with light in transmission through this film while the patterned gold film remained in the aqueous portion of solution of 100 $\mu\text{L}$  of hexadecane in 10mL of water. The microscope objective lens was also immersed in this phase during capture of the image.

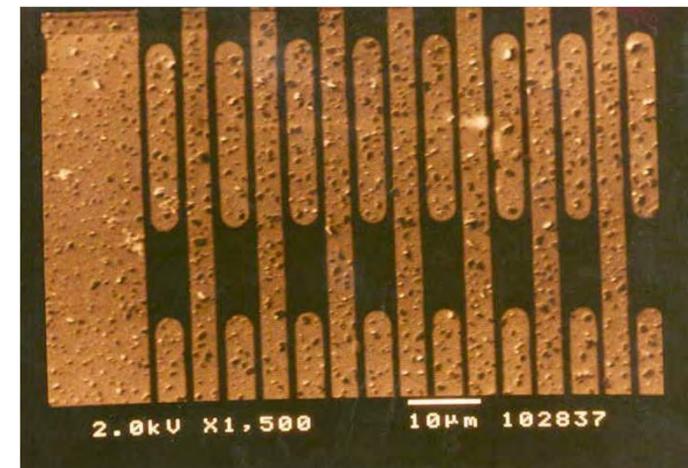
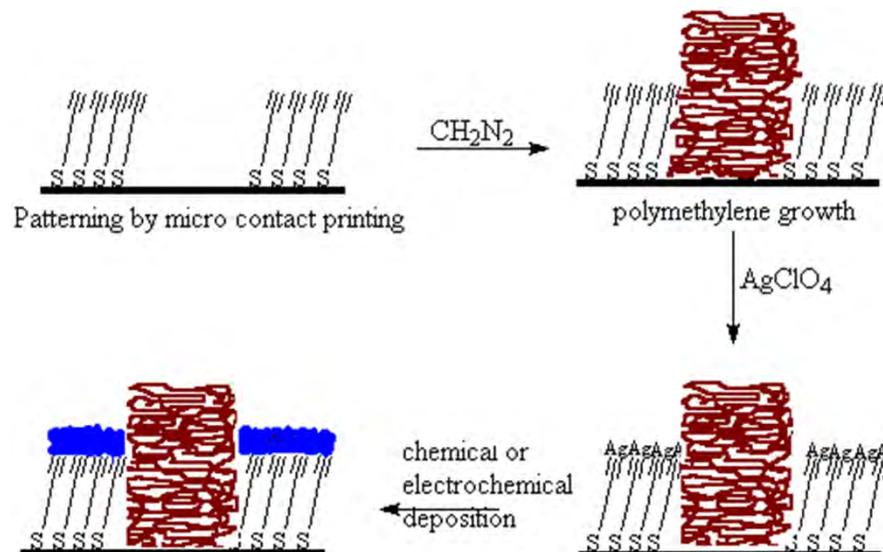
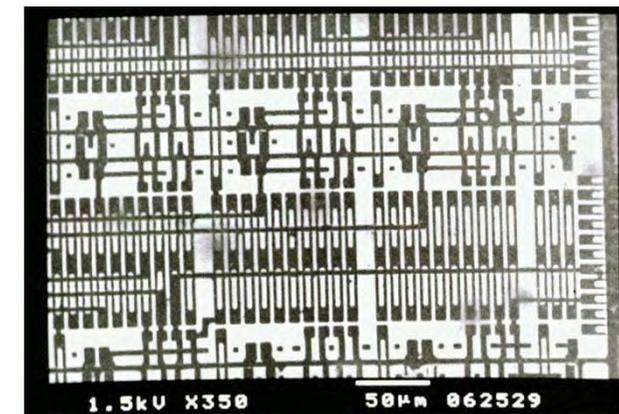
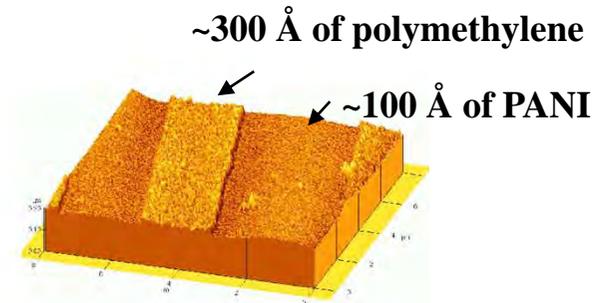
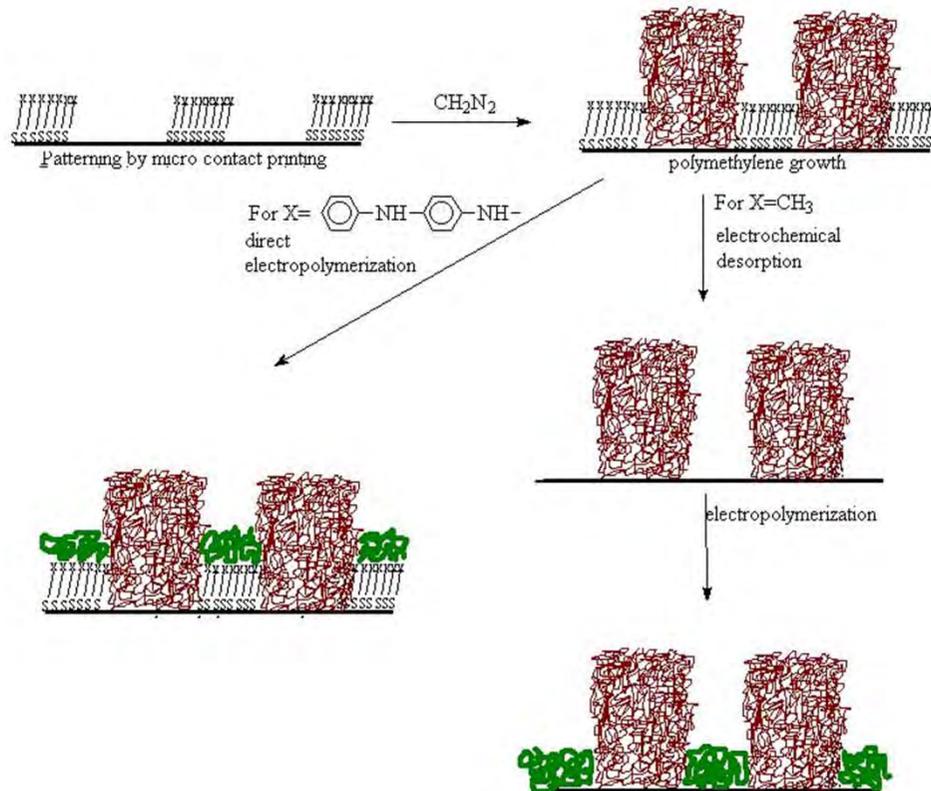


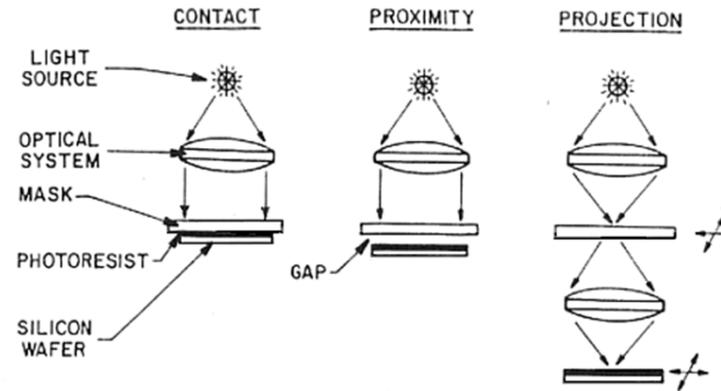
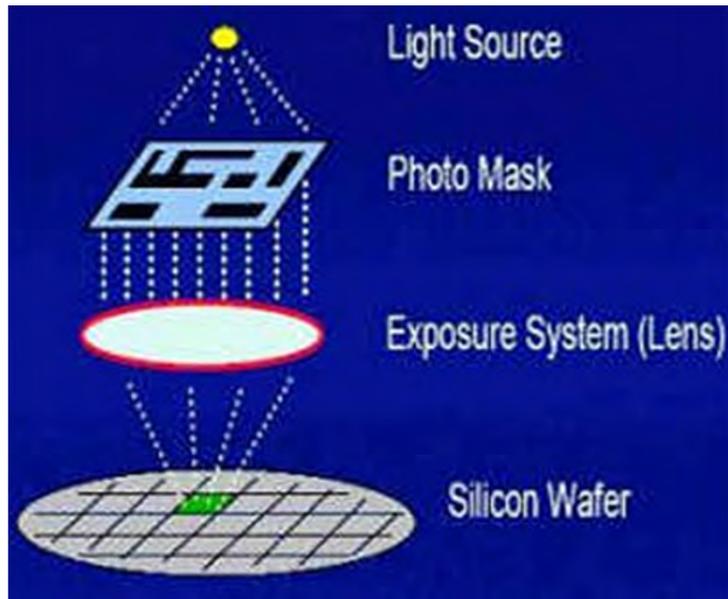
Diagrams illustrating the concepts underlying the use of alkanethiol SAMs as monolayer photoresists on gold. (A) The self-assembled monolayer is formed providing a protective coating for the gold. (B) The SAM is photolyzed in air generating alkyldisulfonates in the regions exposed to UV radiation. (C) The alkyldisulfonates can be rinsed off of the surface with distilled water exposing the gold for subsequent processing.



Scanning electron microscopy images of the sample patterned as described in the text. Light areas were protected from UV exposure by the grid type mask. Dark areas are where the gold has been removed by the acid etching step. (A) A 33 μm marker is shown in the lower right of the image. The gold lines are ~5-6 μm across, replicating the mask dimensions. (B) This higher resolution image shows the edge of a gold line providing an indication of the scale of the damage at the edge of a line. A 1.0 μm marker is shown in the lower right of the image.

J. Huang, D.A. Dahlgren, J. C. Hemminger, Langmuir, 1994, V. 10 (3), 626-628





$$R(\text{解析度}) \propto \frac{\lambda}{(NA)} \dots\dots\dots (1)$$

$$DOF(\text{聚焦深度}) \propto \frac{\lambda}{(NA)^2} \dots\dots\dots (2)$$

**Proximity and Contact Printing**

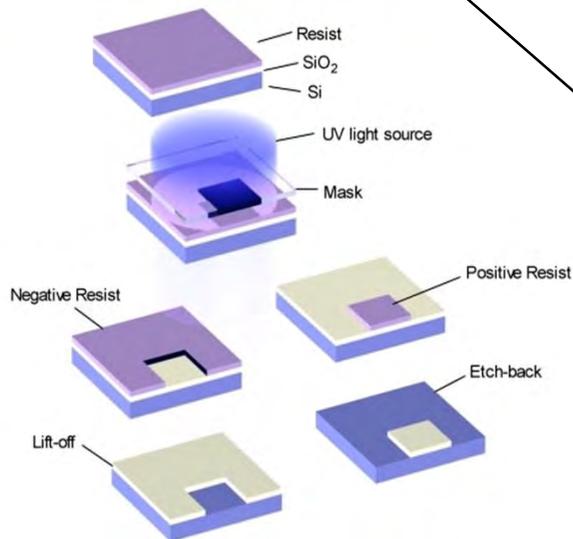
Resolution =  $\sqrt{\lambda \{\text{gap between mask and resist} + \text{resist thickness}\}}$

where  $\lambda$  is the wavelength of the illuminating radiation

**Projection Printing**

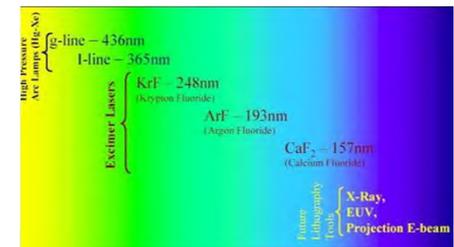
Resolution =  $\{K_a * \lambda\} / \{NA\}$  ; Depth of Focus =  $\{K_b * \lambda\} / \{NA^2\}$

where  $K_a$  is process constant ~ 0.75  
 $K_b$  is a process constant ~ 0.5  
 NA is the numerical aperture of the optical system

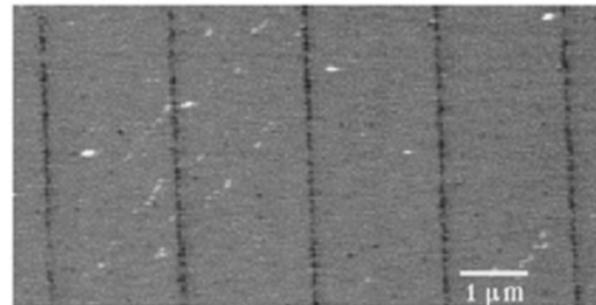
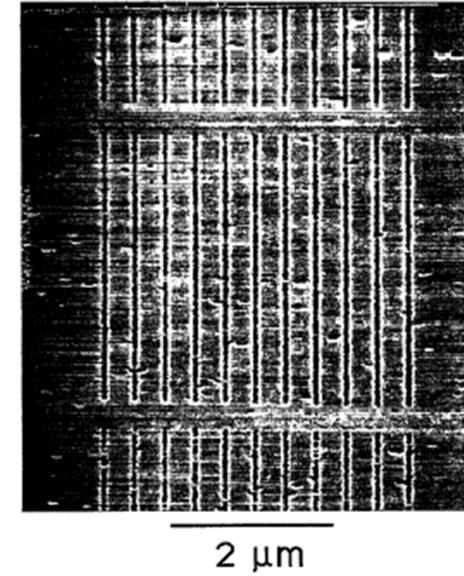
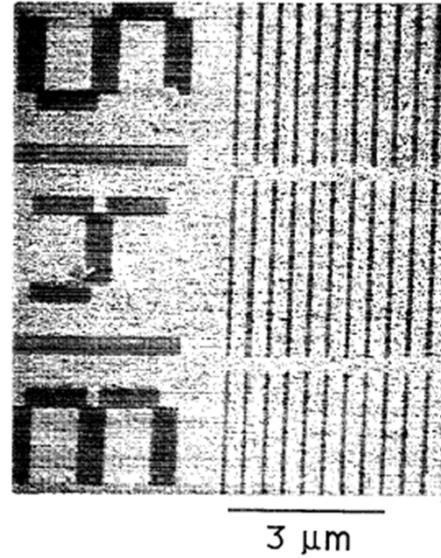
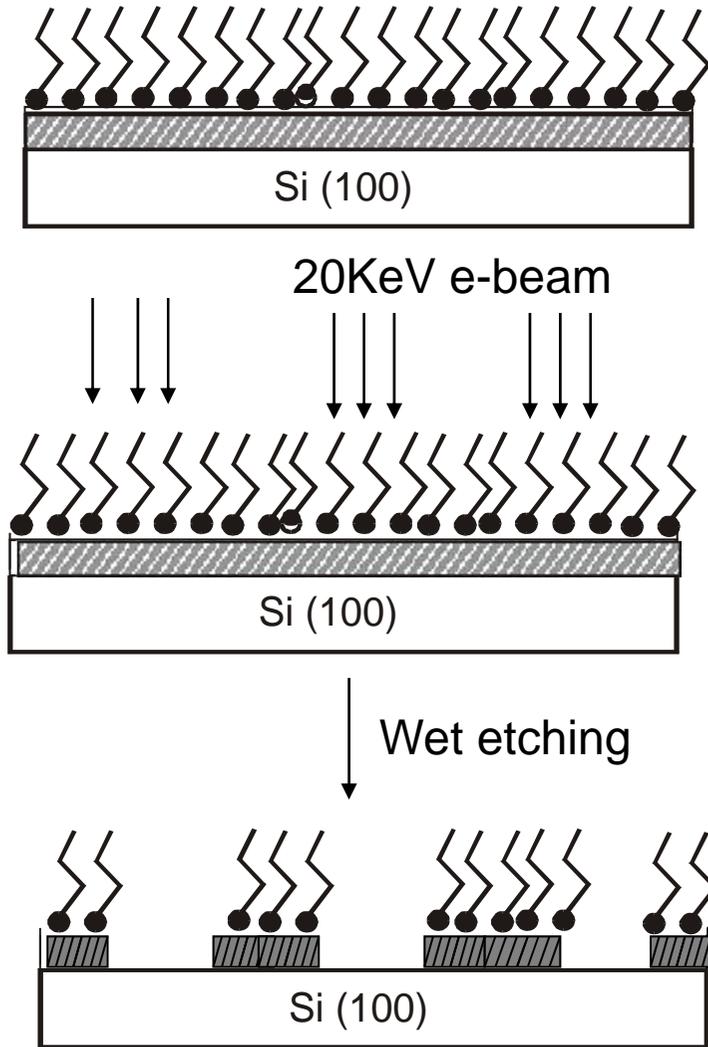


The shorter the wavelength, the better the resolution

The shorter the wavelength, the smaller the DOF



With e-beam as light source, monolayer as resist



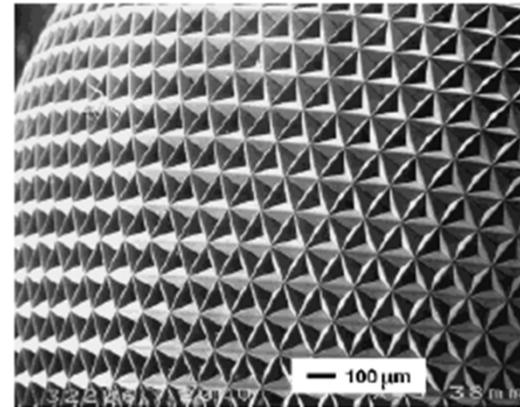
*Allara et al. APL 1996*

Resolution ~5-6 nm

# Soft lithography

## Top ten advancements in material science

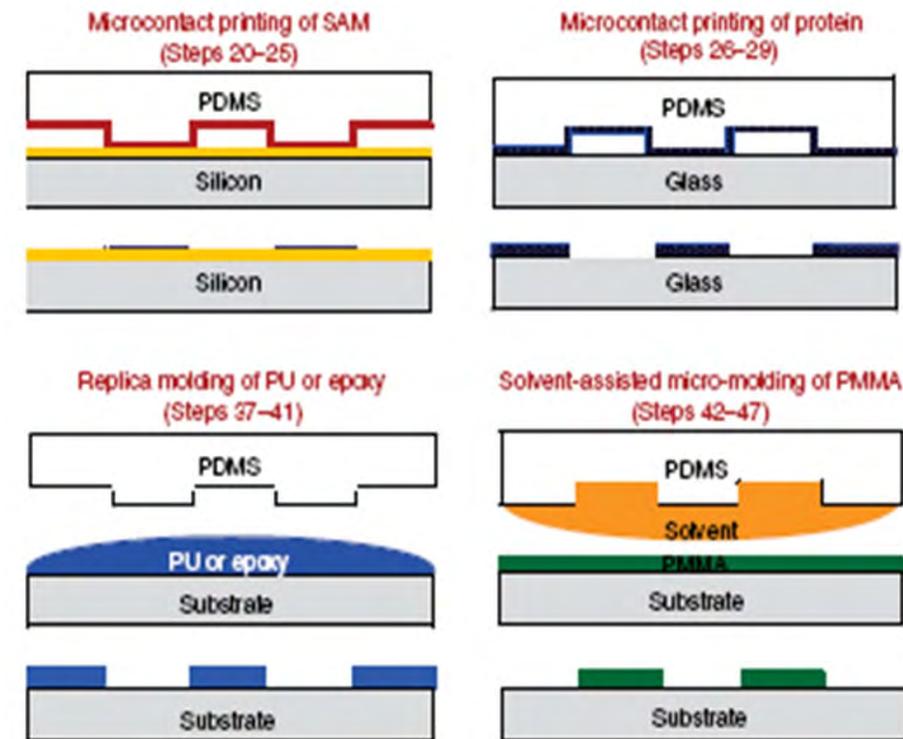
- 1. International Technology Roadmap for Semiconductors.
  - 2. Scanning probe microscopes
  - 3. Giant magnetoresistive effect
  - 4. Semiconductor lasers and LEDs
  - 5. National Nanotechnology Initiative
  - 6. Carbon fiber-reinforced plastics
  - 7. Materials for Li ion batteries
  - 8. Carbon nanotubes
  - 9. **Soft lithography**
  - 10. Metamaterials
- Materials Today* 11, 40 (2008)



Microstructure on a curved surface

Use of elastomeric mold of PDMS with low surface energy allows easy separation

- Replica molding (REM)
- Micro transfer molding ( $\mu$ TM)
- Micromolding in capillaries (MIMIC)
- Solvent assisted micromolding (SAMIM)

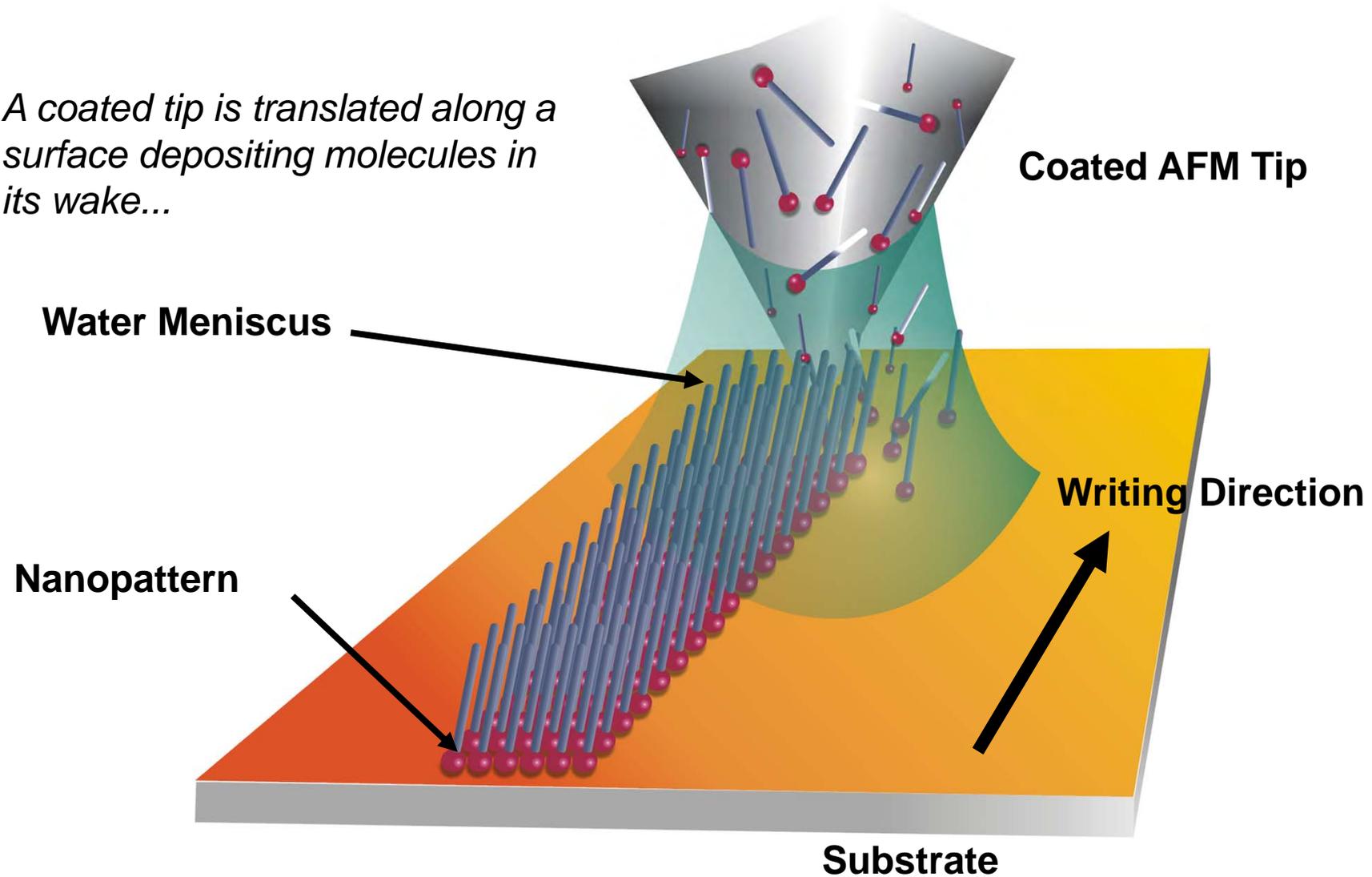


Whitesides, et al. *Angew. Chem.* 37, 550(1998)

*Nature Protocols* 2010, 5, 491.

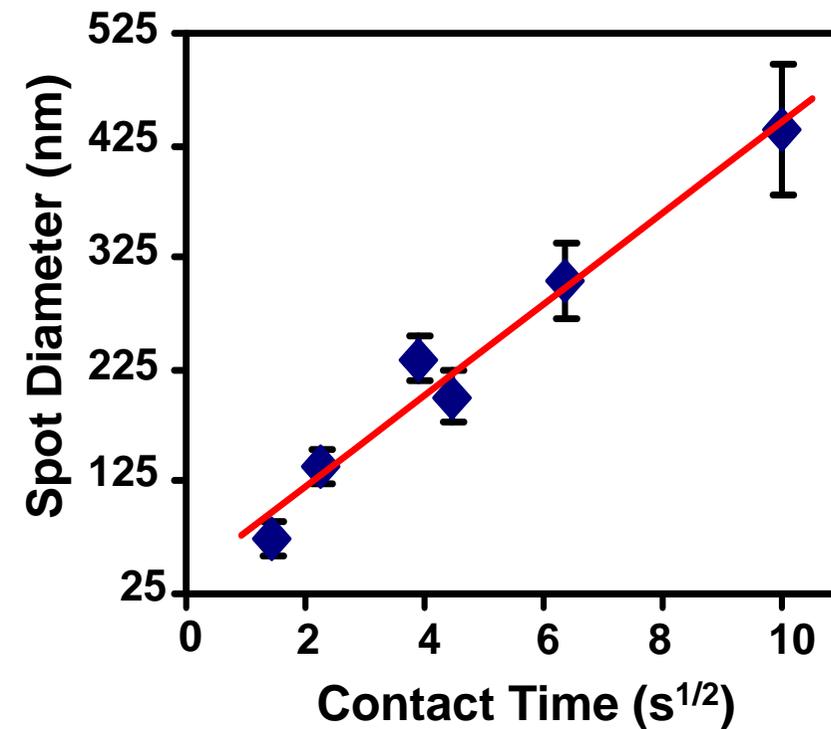
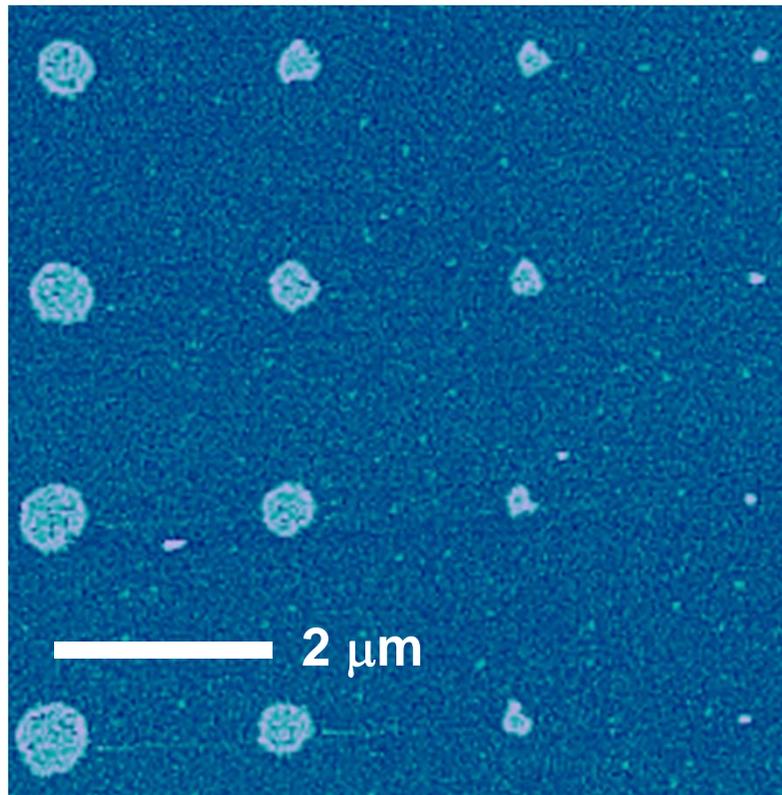
# Dip Pen Nanolithography

*A coated tip is translated along a surface depositing molecules in its wake...*



# Pattern Size Control with DPN

- ❖ Area of the Final Patterns 🔔 Contact Time between Tip and Sample

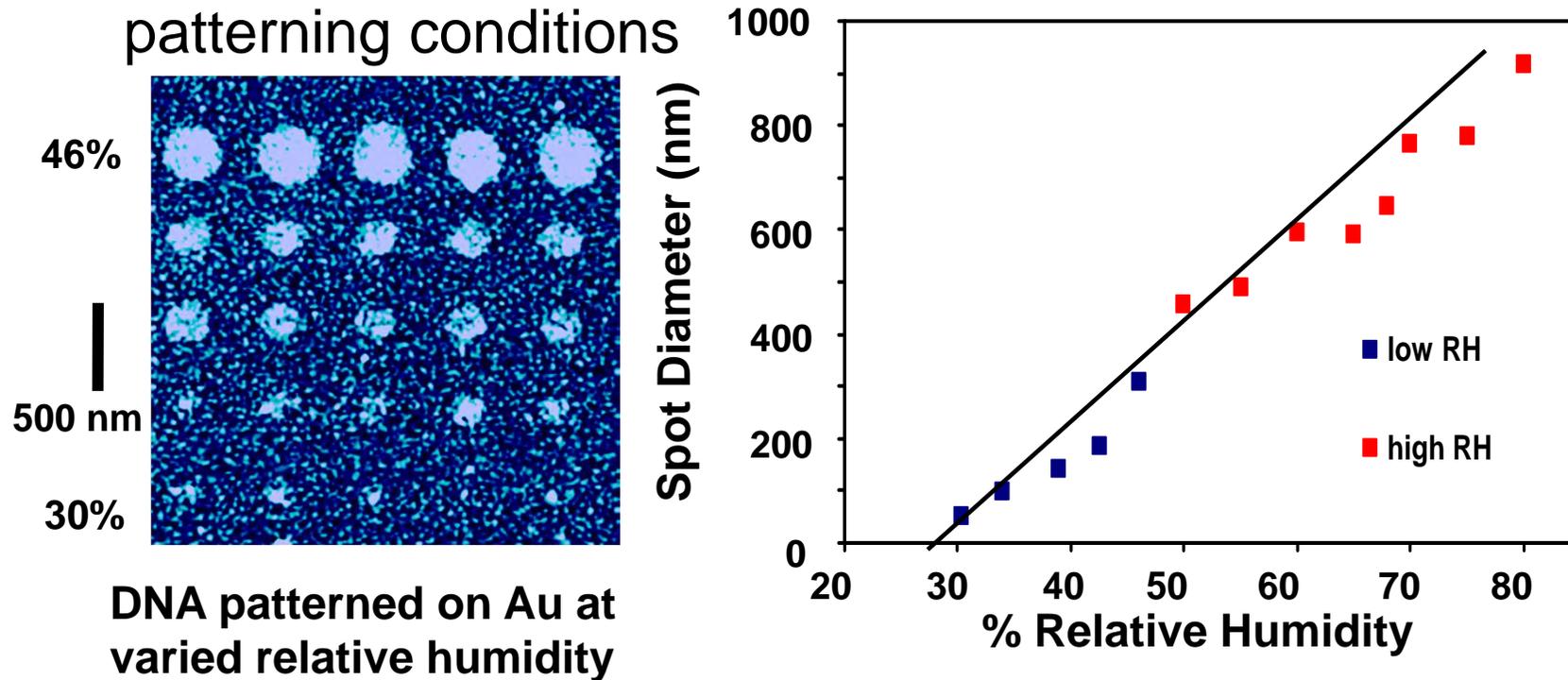


DNA patterned on gold w/ nanoparticle labels

Demers, L. M. et al. *Science* 298, 1836-1838 (2002).

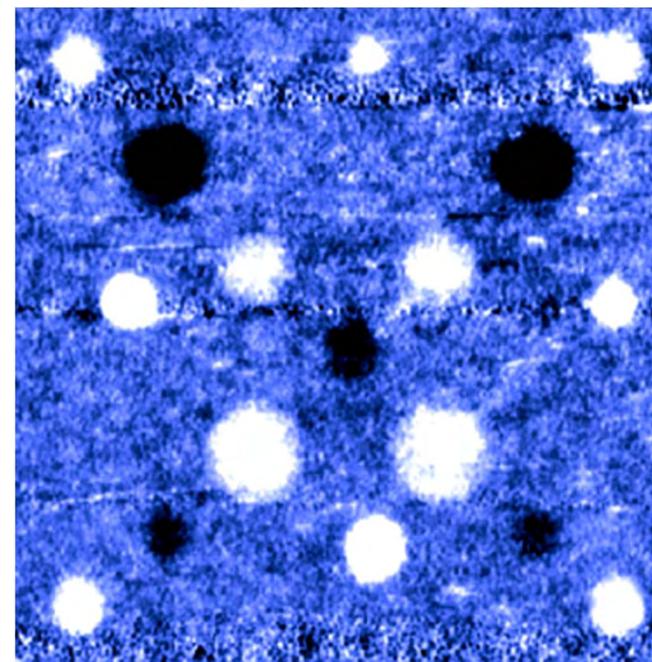
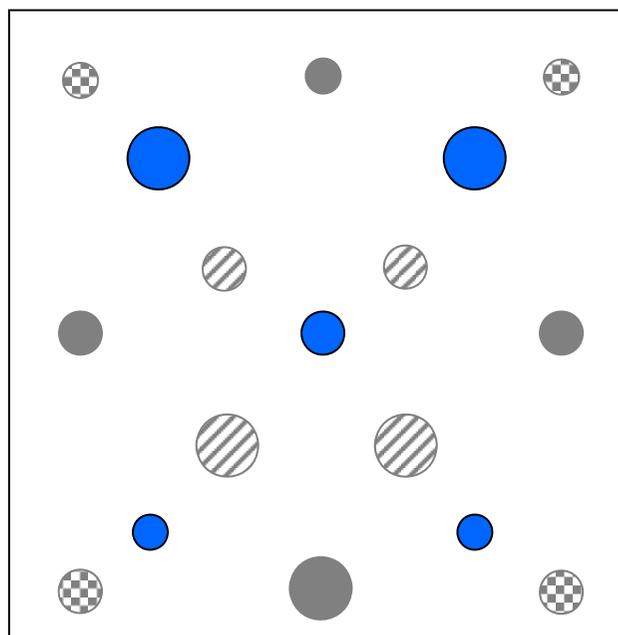
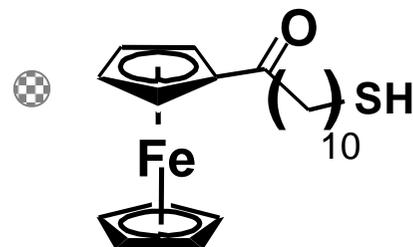
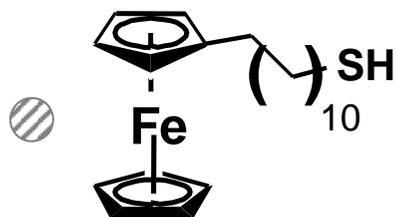
# Effect of Temperature and Humidity

- Control over relative humidity and temperature enables precise calibration of feature size
- E-Chamber provides software control over ambient patterning conditions



Demers, L. M. et al. *Science* 298, 1836-1838 (2002).

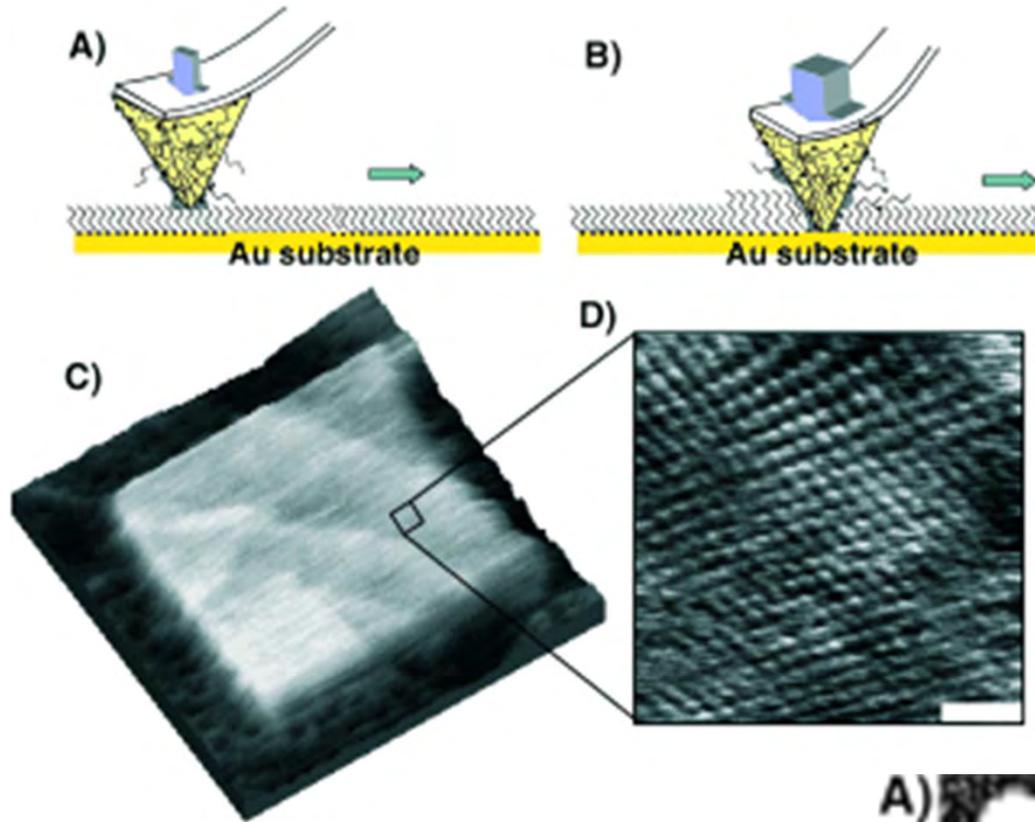
# Combinatorial Study Using Multiple Nanostructures Made of Different Inks



0  $\mu\text{m}$  5.2

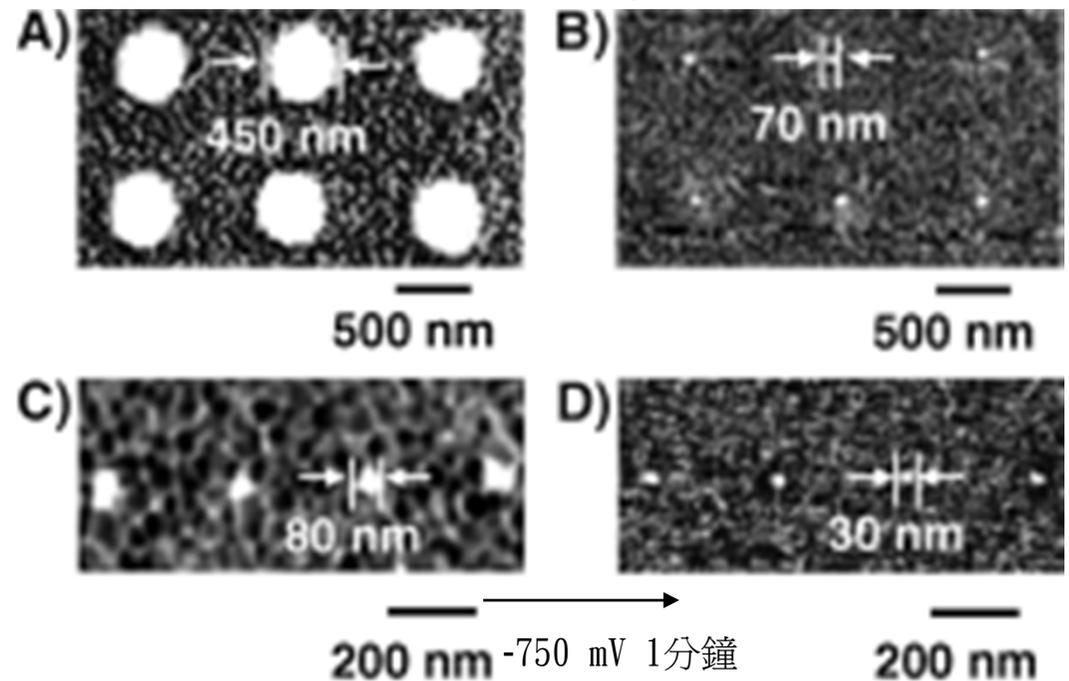
Ivanisevic, A. et al *J. Am. Chem. Soc.* 124, 11997-12001 (2002).

How to shrink further?



Adsorption of a layer of short chain SAM to prevent diffusion, exchange with long chain SAM.

-750 mV 6 min

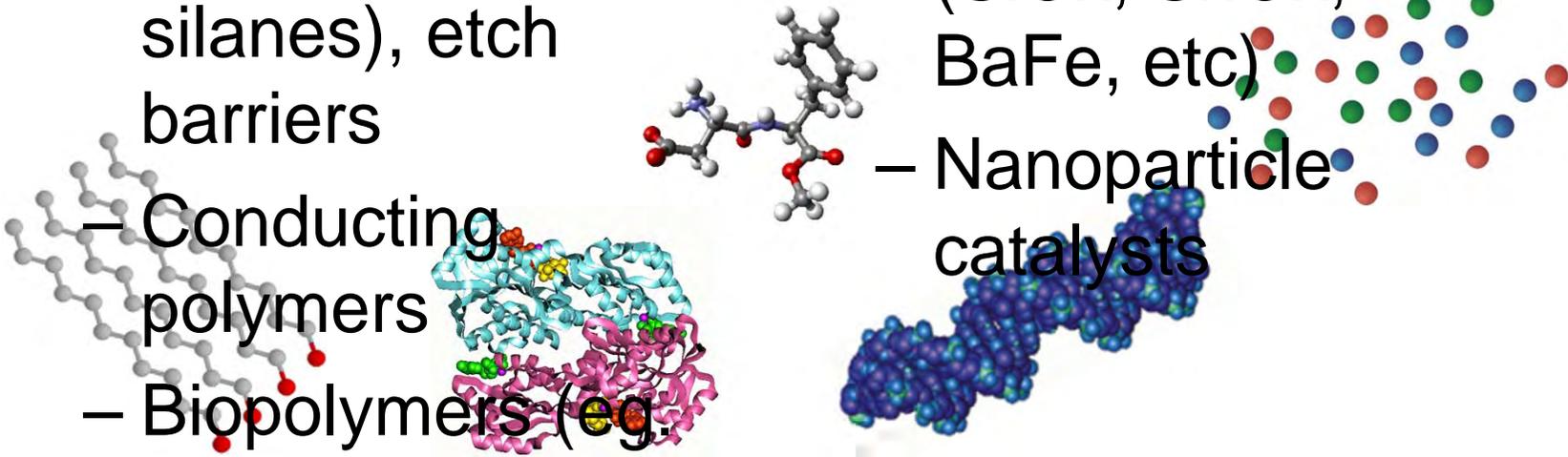


Trim the edge by electrochemistry

-750 mV 1分鐘

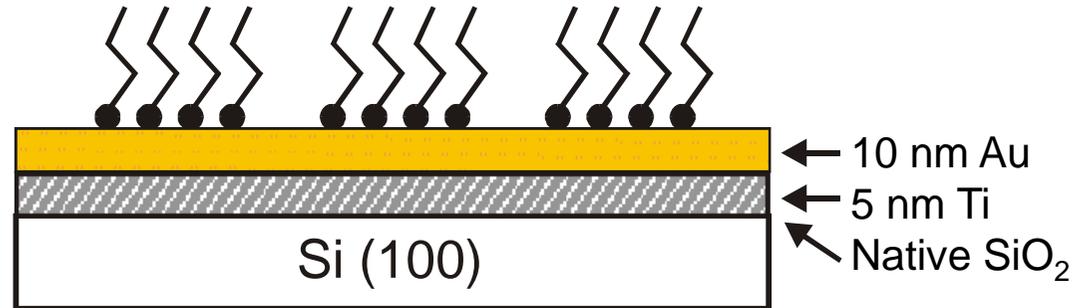
# DPN Inks

- Soft Materials
  - Small functional molecules
  - SAMs (e.g. alkanethiols, silanes), etch barriers
  - Conducting polymers
  - Biopolymers (eg. DNA, proteins, peptides)
- Hard Materials
  - Metal inks
  - Sol precursor inorganic inks (SiOx, SnOx, BaFe, etc)
  - Nanoparticle catalysts

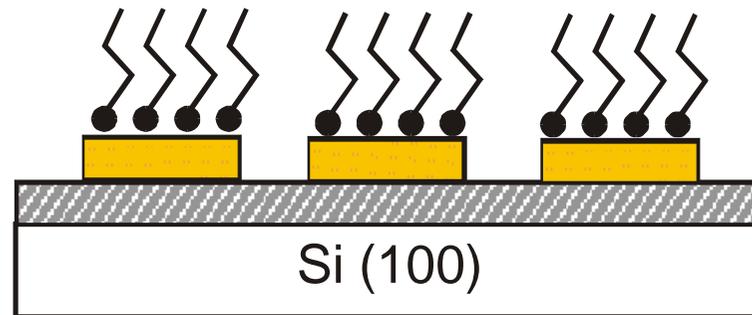


# Etch Barriers for Solid-State Nanostructures

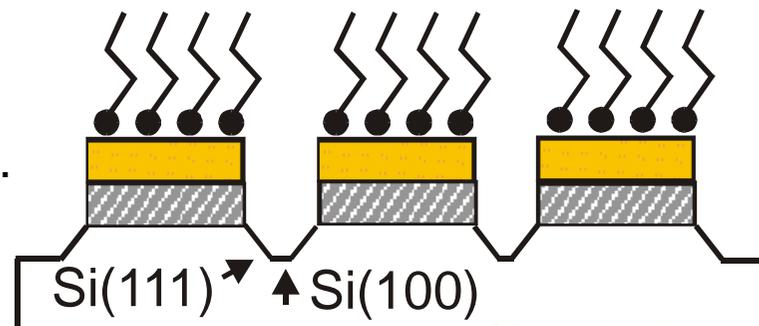
1. "Write" regions of octadecanethiol (ODT) on Au thin film.



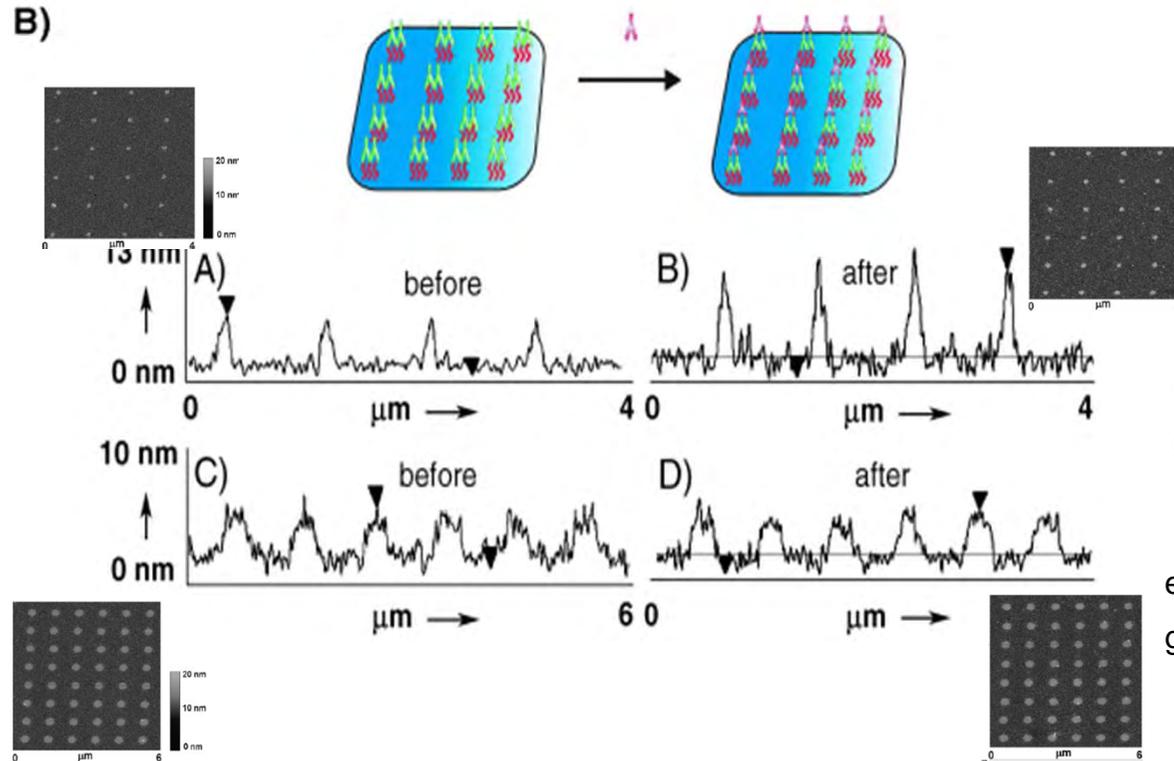
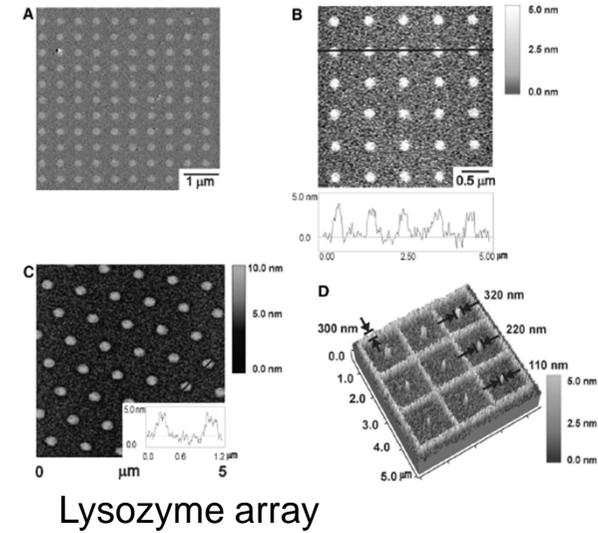
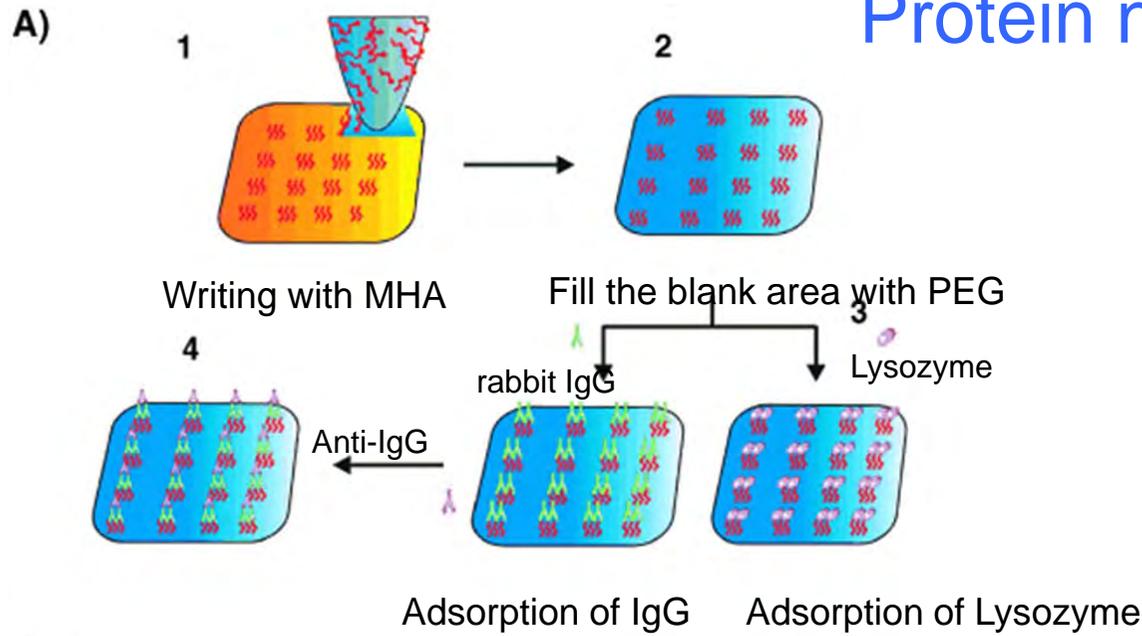
2. Selectively etch Au using wet chemical etchant (ferri/ferrocyanide 2-5 min).



3. Remove Ti and SiO<sub>2</sub>, etch Si, and passivate Si surface.



# Protein nanoarrays by DPN



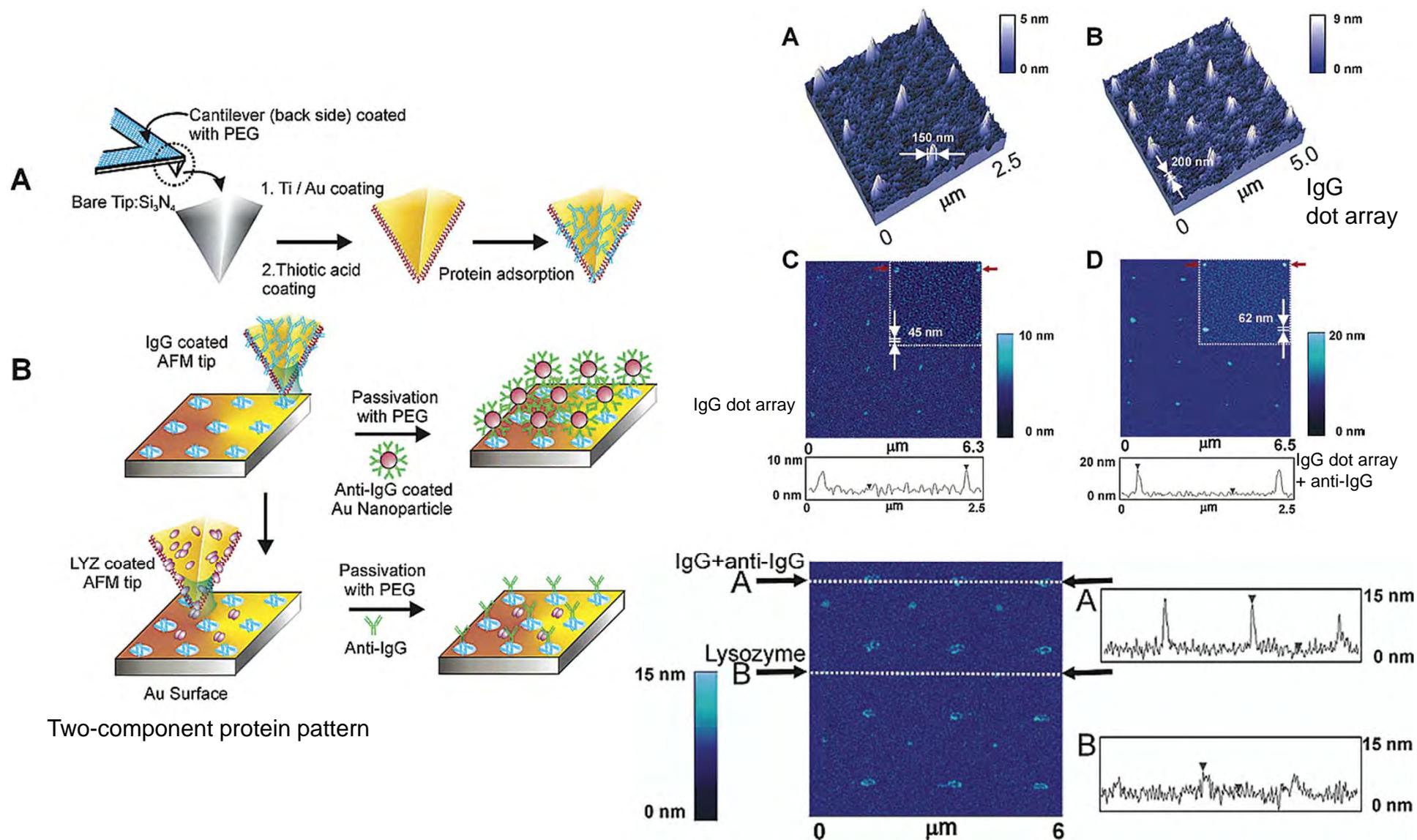
No non-specific binding!!

exp. to a mixture of lysozyme, retronectin, goat/sheep anti-IgG human IgG and rabbit anti-IgG

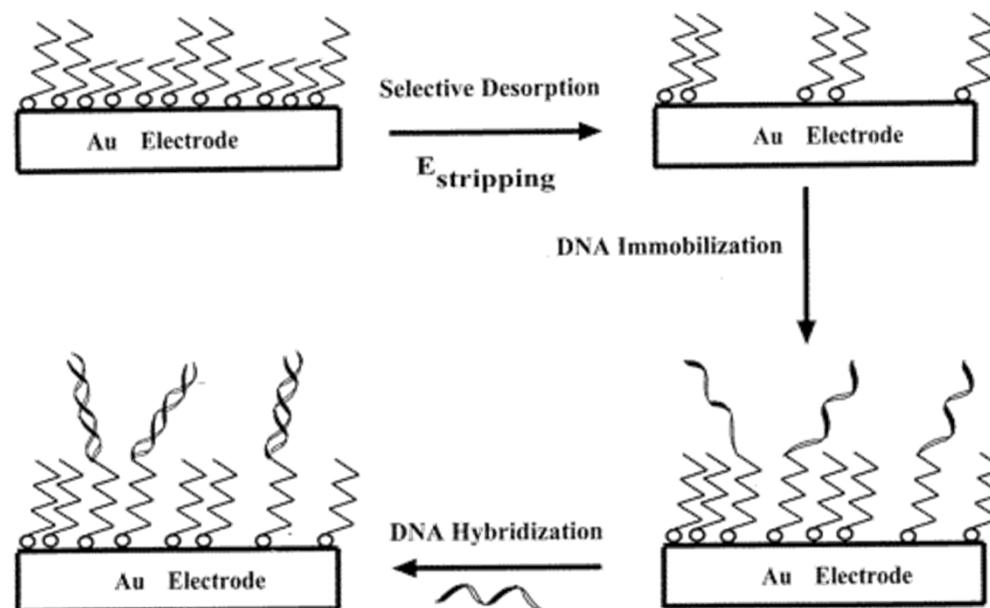
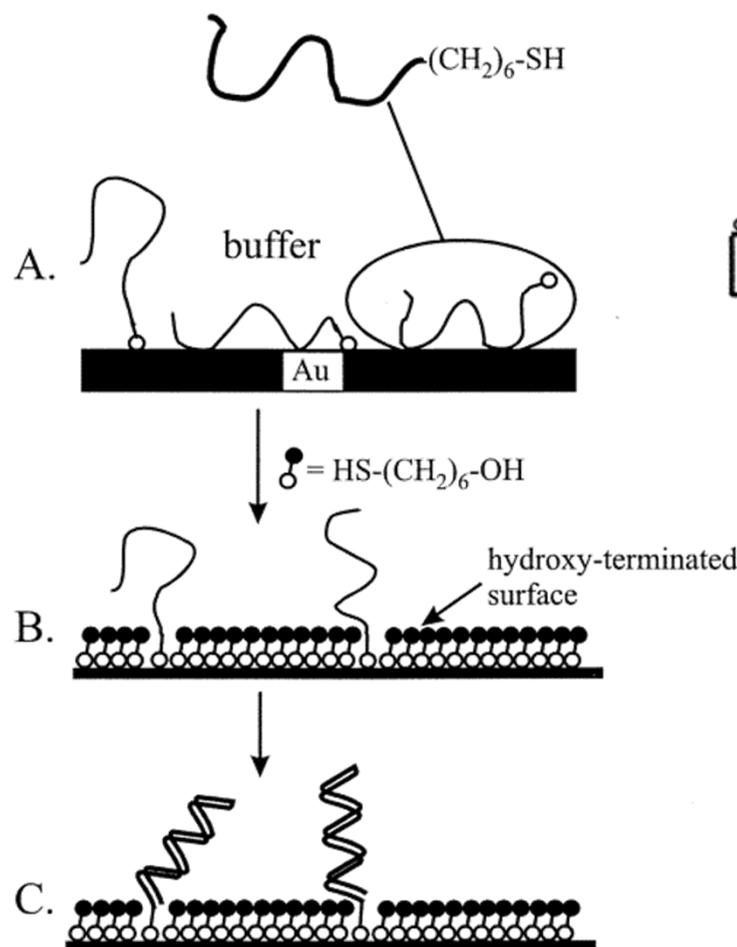
exp. to a mixture of lysozyme, retronectin, goat/sheep anti-IgG human IgG

Mirkin et al *Science* **295**, 1702 (2002)

# Direct writing of protein array



Selective desorption of an alkanethiol in a mixed SAM for subsequent oligonucleotide immobilization and hybridization.

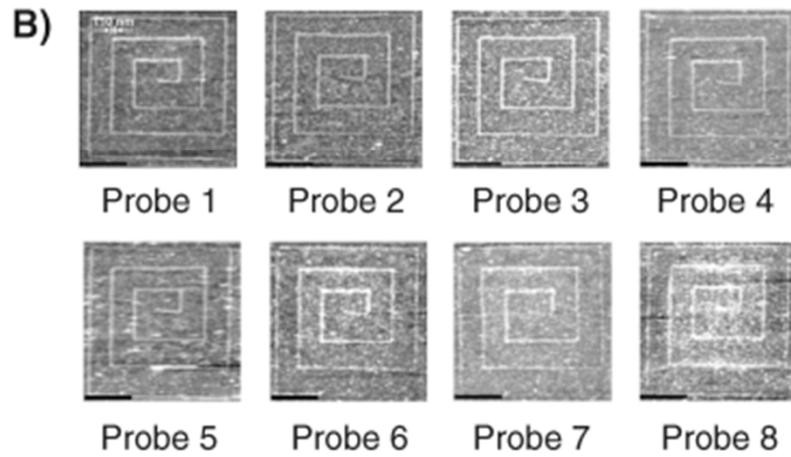
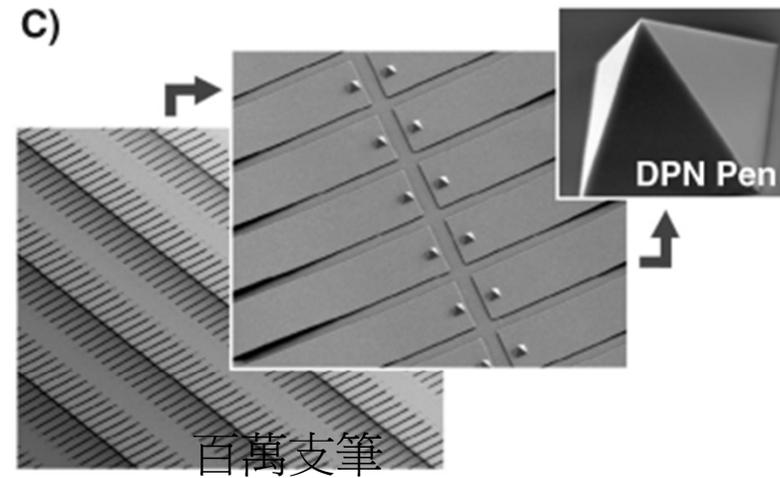
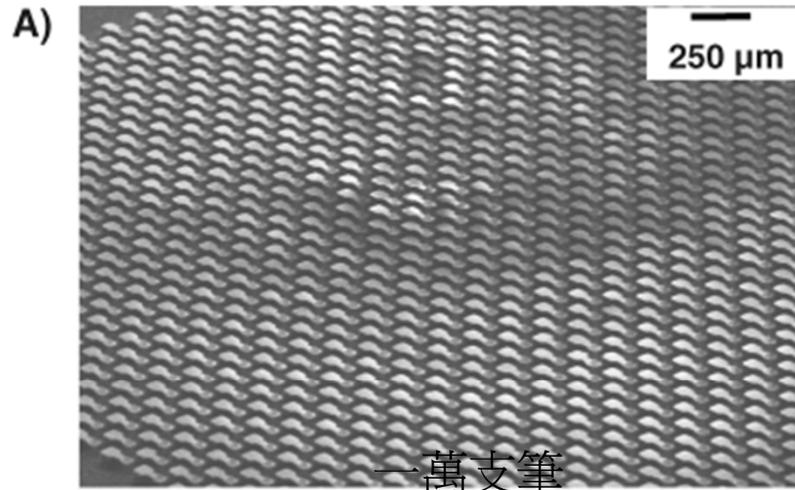


Langmuir, 2001, V. 17 (24), P.7637

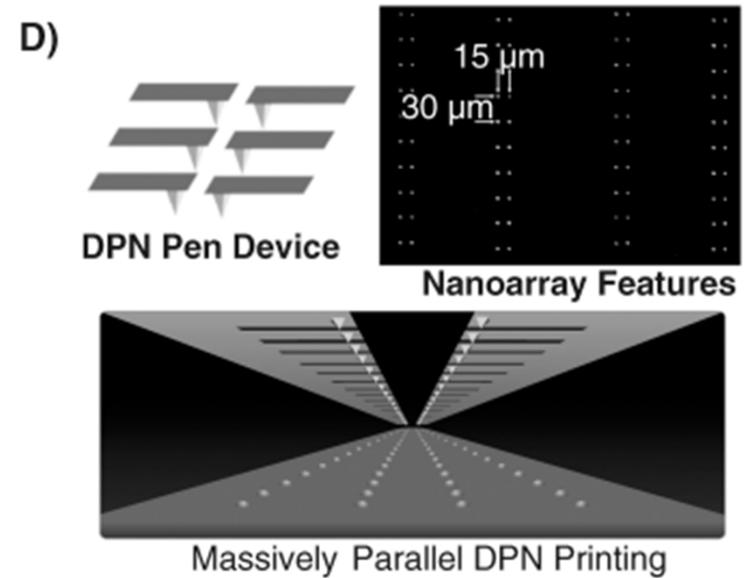
(A) Single-stranded DNA (HS-ssDNA) which adsorbs to the gold substrate through the thiol end group as well as through backbone/substrate contacts. A multitude of adsorption states exists. (B) After the formation of a mercaptohexanol (MCH) monolayer that prevents contacts between the DNA backbone and the substrate, the HS-ssDNA is left attached by the thiol end. (C) The end-tethered HS-ssDNA after hybridization to complementary oligonucleotides.

*J. Am. Chem. Soc.* **120**, 9788(1998)

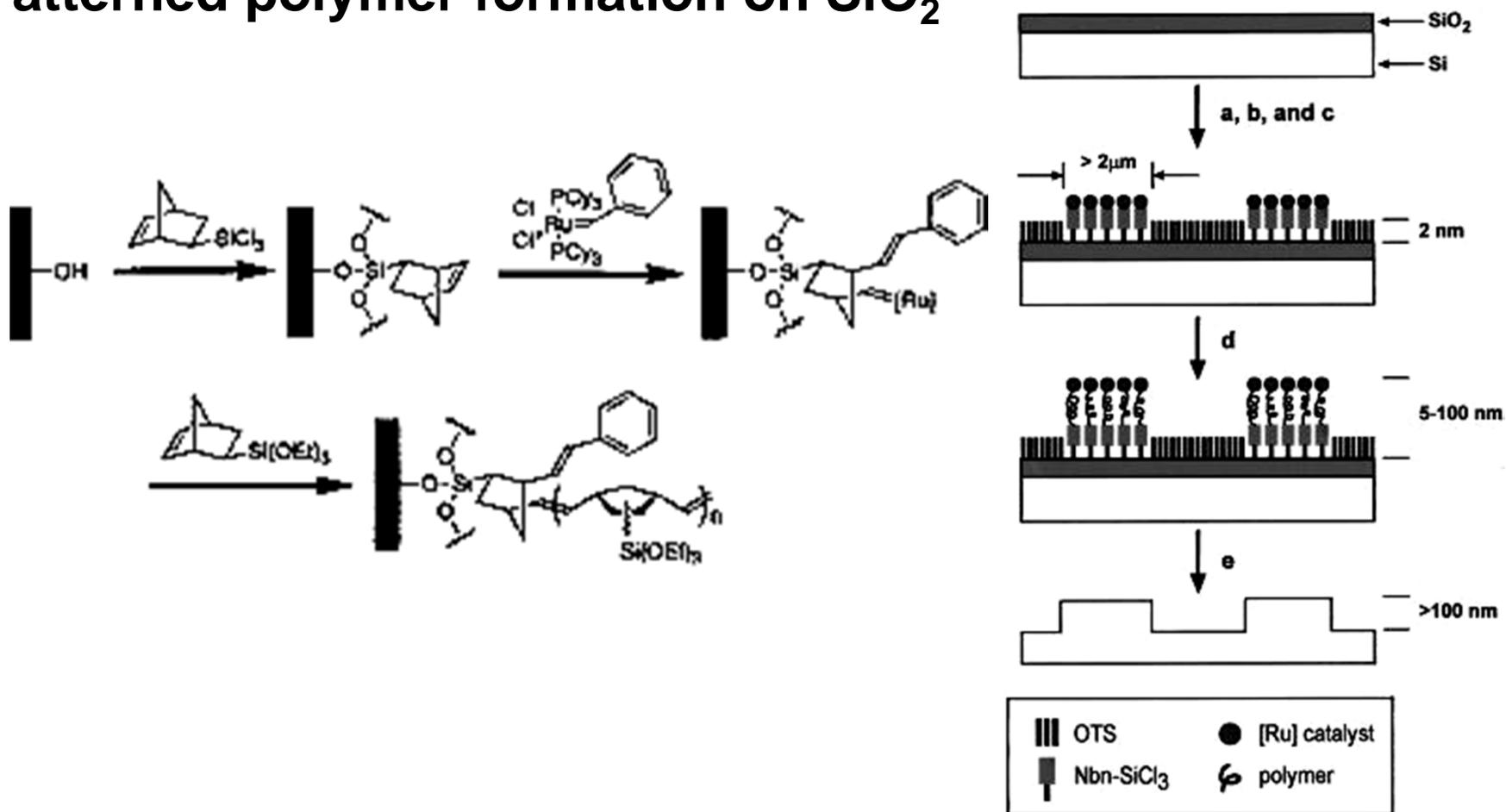
# How to mass produce?



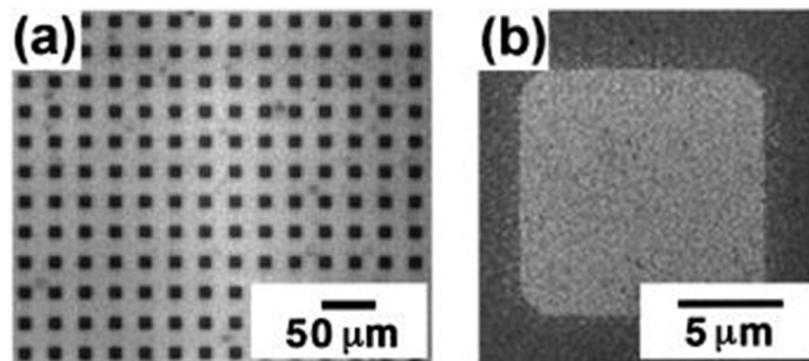
32 pens writing simultaneously



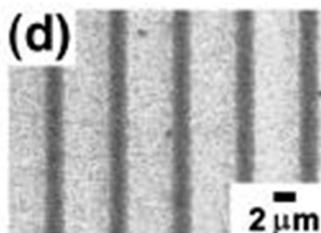
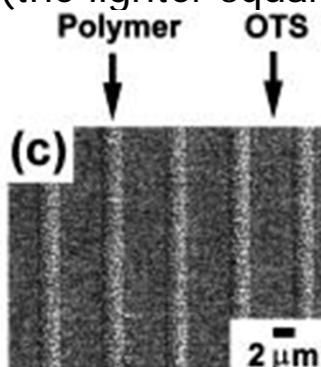
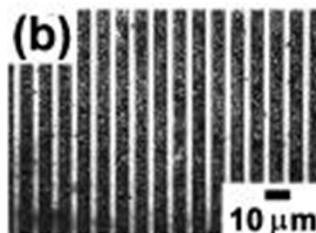
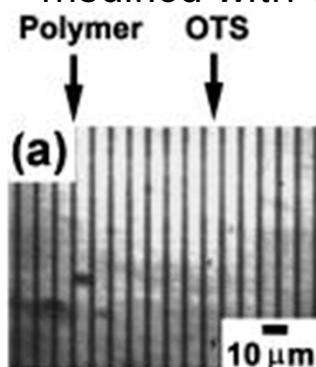
# Patterned polymer formation on SiO<sub>2</sub>



Patterned polymer formation by  $\mu$ CP, activation, and ring-opening metathesis polymerization on the surface of SiO<sub>2</sub>/Si. No order or structure is implied by the representation of the OTS (octadecyltrichlorosilane), norbornene-terminated SAM, [Ru] catalyst [(Cy<sub>3</sub>P)<sub>2</sub>Cl<sub>2</sub>Ru = CHPh, Cy = cyclohexyl], and polymer.

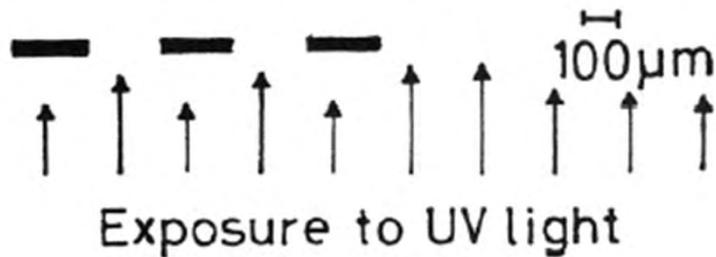
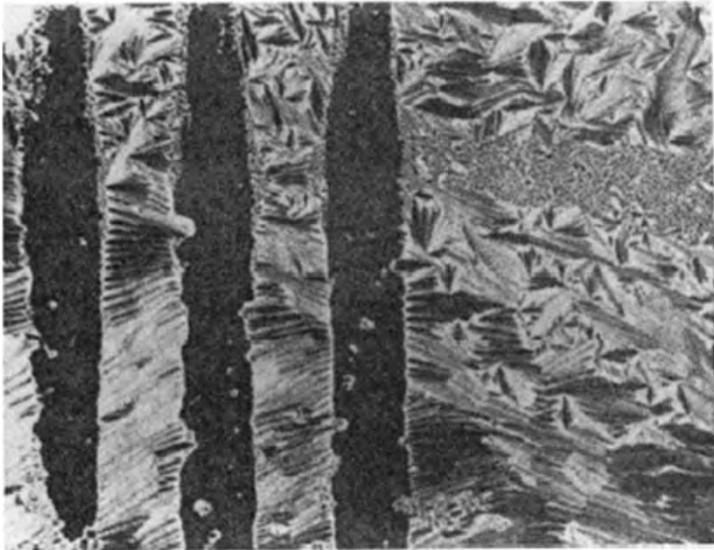


(a) Optical micrograph of the patterned poly[Nbn-(OEt)3] film (50 nm) on the surface of SiO<sub>2</sub>/Si. A uniform polymer film covers the surface except inside the 10 μm×10 μm squares, where OTS had been printed by μCP. (b) Scanning electron microscopy shows well-defined boundary (with edge roughness <300 nm) between the polymer (dark region) and the area modified with OTS (the lighter square).

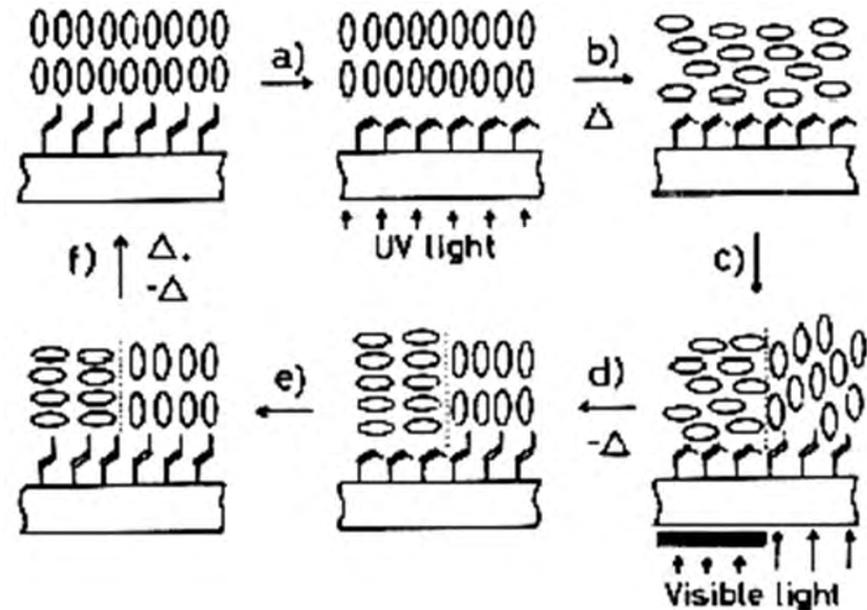


(a) Optical micrograph of 2-μm-wide lines of patterned poly [Nbn-Si(OEt)<sub>3</sub>] film generated by polymerization from surface before RIE (thickness ~10 nm). (c) Optical micrograph of the sample after RIE with SF<sub>6</sub> for 3 min at 30 W in a parallel-plate etcher. (b) SEM micrograph of the sample before RIE [same sample as shown in (a)]. (d) SEM micrograph of the sample after RIE.

# Aligning liquid crystal molecules



Polarized photomicrograph of a cell of 8  $\mu$ m thickness exposed to UV through a 200- $\mu$ m lines and spaces photomask.



Schematic representation of an erasable optical information storage using a photoresponsive smectic LC cell: (a) initialization by UV exposure in the smectic phase; (b) heat above  $T_{SN}$  to cause planar alignment in the nematic phase; (c) subsequent writing-in with visible light in the nematic phase; (d) rapid cooling down for fixation; (e) memory storage below  $T_{SN}$ ; (f) erasure by heating.

## Anisotropic conductivity in the monolayer

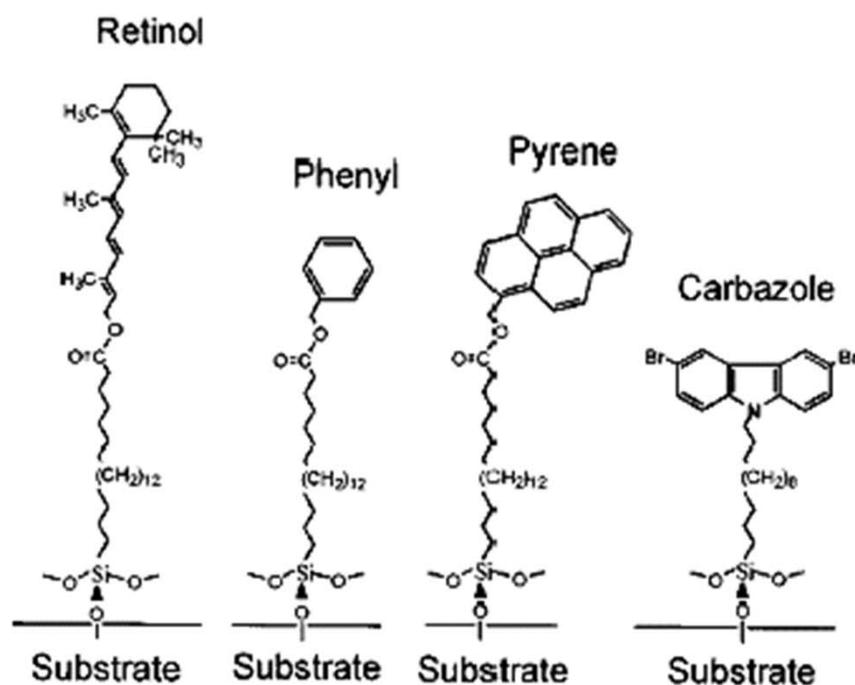
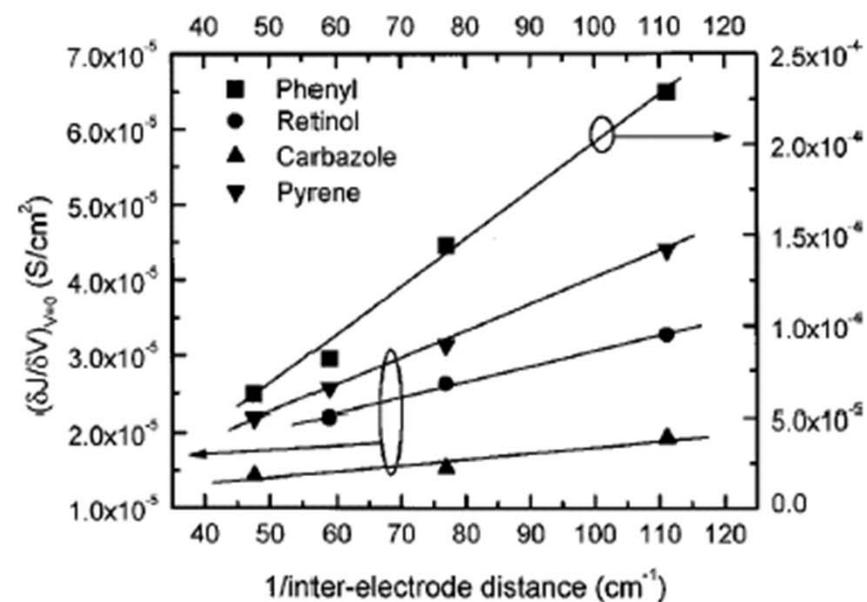


FIG. 1. Schematic representation of the chemical structures of the four monomolecular organic heterostructures.



# Transistor using a single monolayer

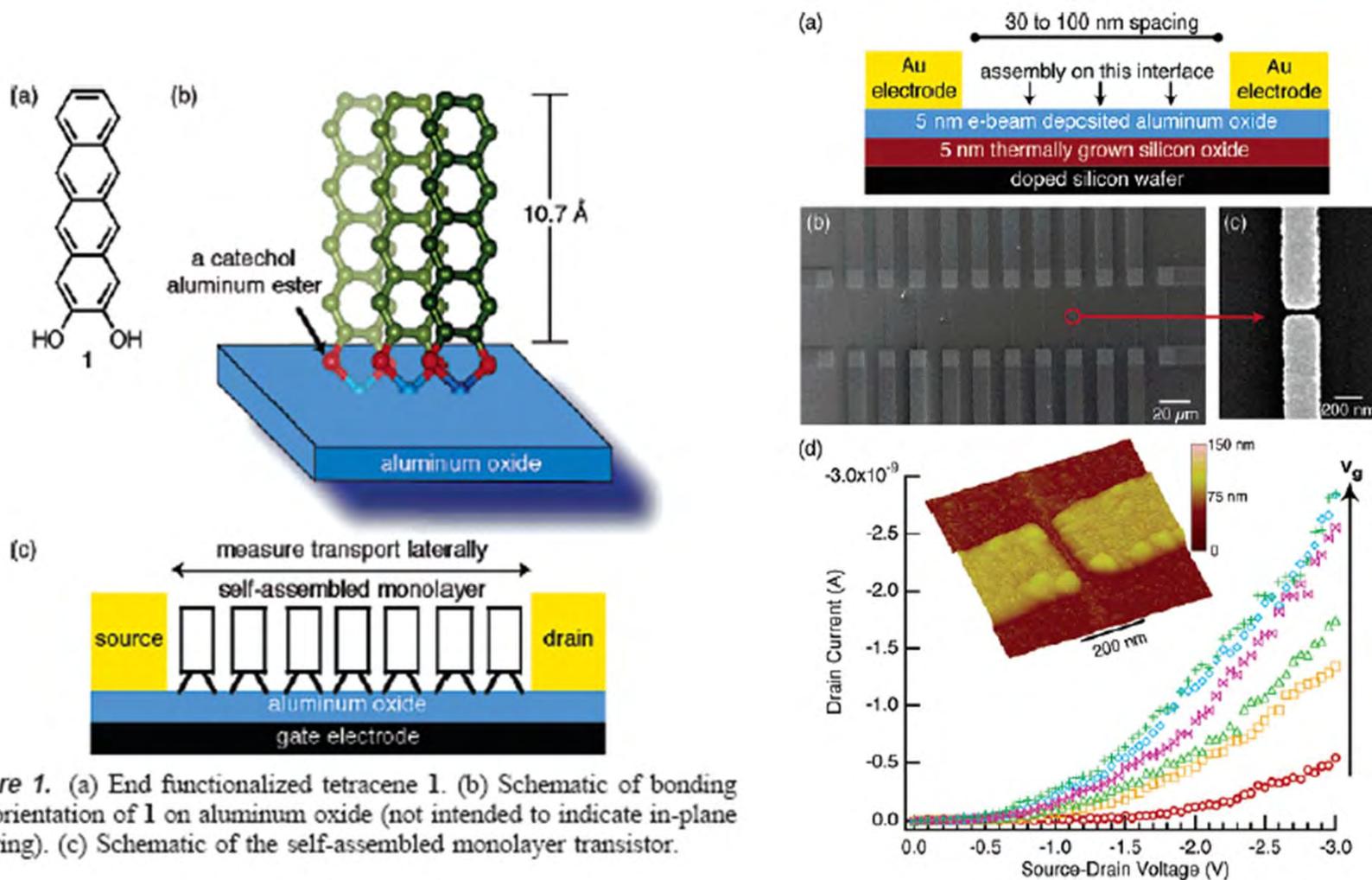
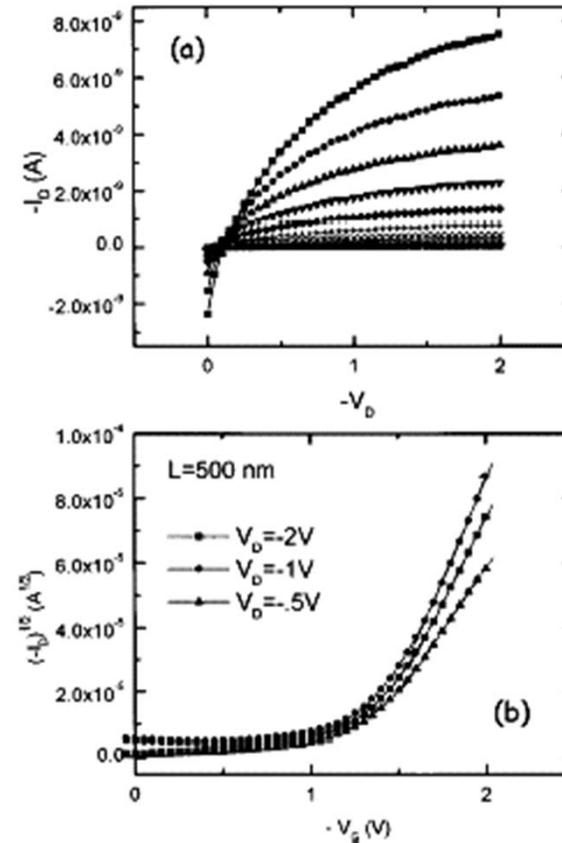
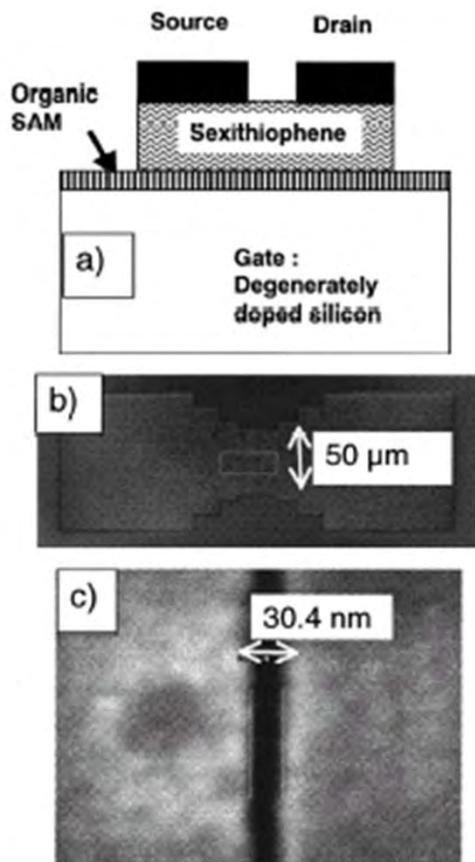


Figure 1. (a) End functionalized tetracene 1. (b) Schematic of bonding and orientation of 1 on aluminum oxide (not intended to indicate in-plane ordering). (c) Schematic of the self-assembled monolayer transistor.

## Low-voltage, 30 nm channel length, organic transistors with a self-assembled monolayer as gate insulating films

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Output current–voltage ( $I_D$ – $V_D$ ) and transfer  $I_D^{1/2}$ – $V_G$  characteristics of a 500 nm channel length OTFT ( $V_G$  from 22 V, top curve, to 20.7 V, step 0.1 V!).

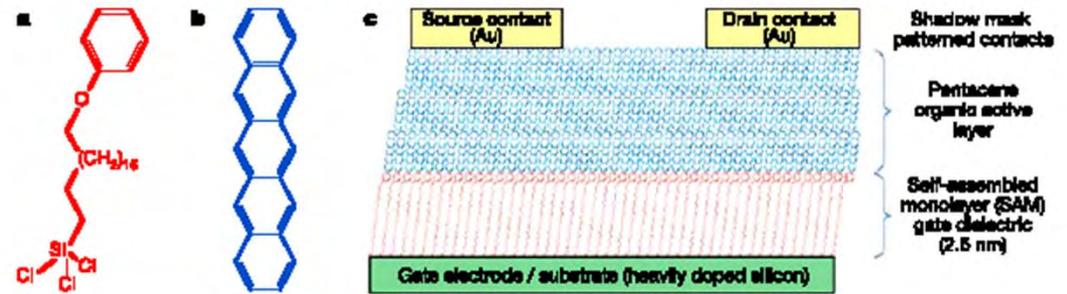
# Low-voltage organic transistors with an amorphous molecular gate dielectric

Marcus Halik<sup>1</sup>, Hagen Klauk<sup>1</sup>, Ute Zschieschang<sup>1</sup>, Günter Schmitt<sup>1</sup>, Christine Dehm<sup>1</sup>, Markus Schütz<sup>2</sup>, Steffen Maisch<sup>2</sup>, Franz Effenl<sup>1</sup>, Markus Brunnbauer<sup>3</sup> & Francesco Stellacci<sup>3</sup>

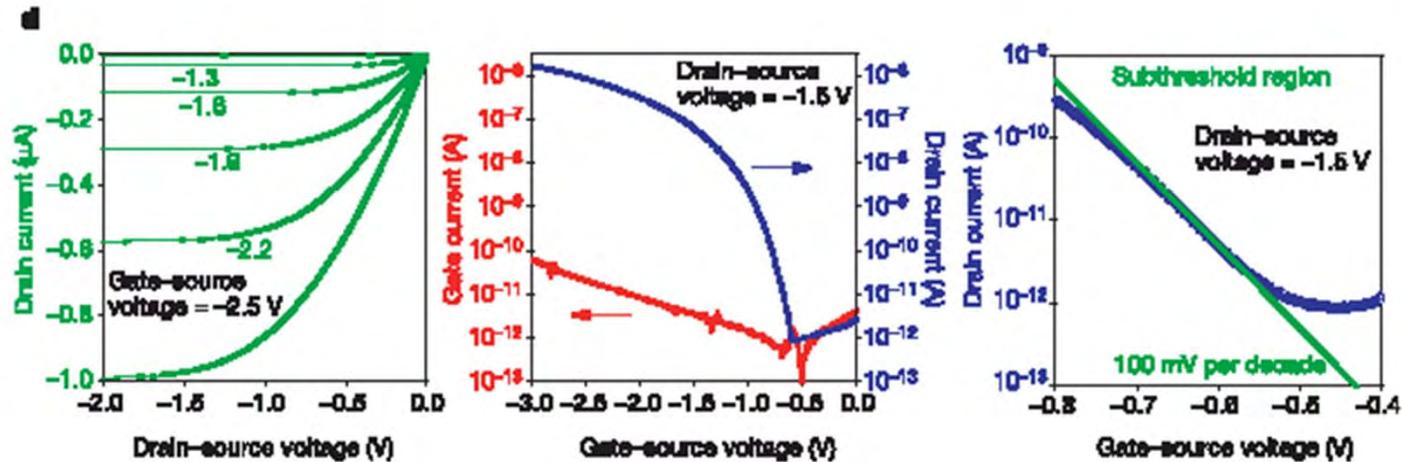
<sup>1</sup>Infinion Technologies AG, New Memory Platforms, Materials and Technology, Paul-Gossen-Straße 100, 91052 Erlangen, Germany

<sup>2</sup>University Stuttgart, Department of Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

<sup>3</sup>Massachusetts Institute of Technology, Department of Materials Science and Engineering, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA



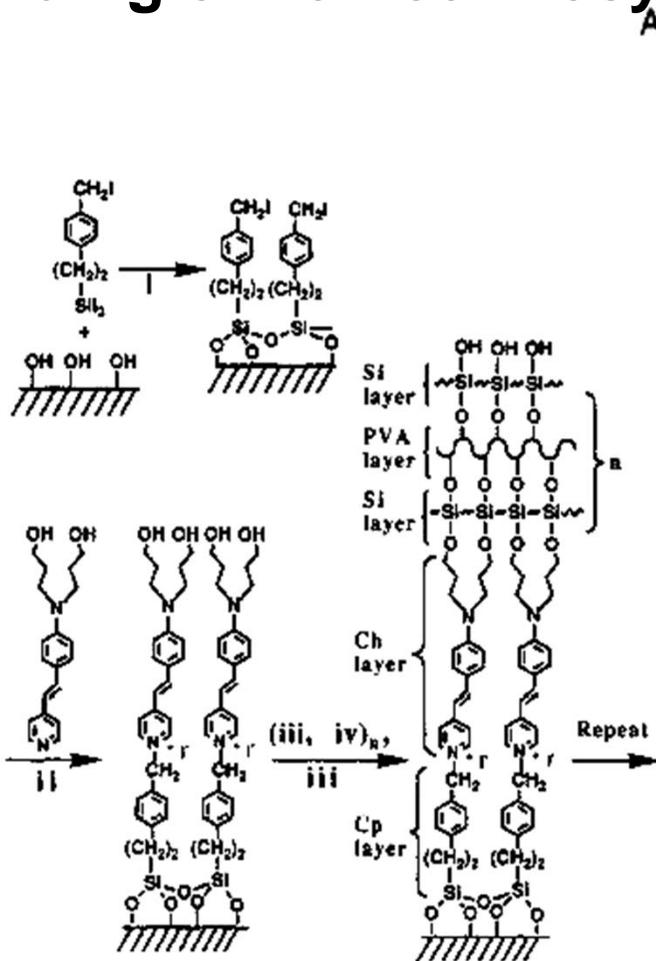
characteristics of a TFT fabricated as described above. The transistor shows a field-effect



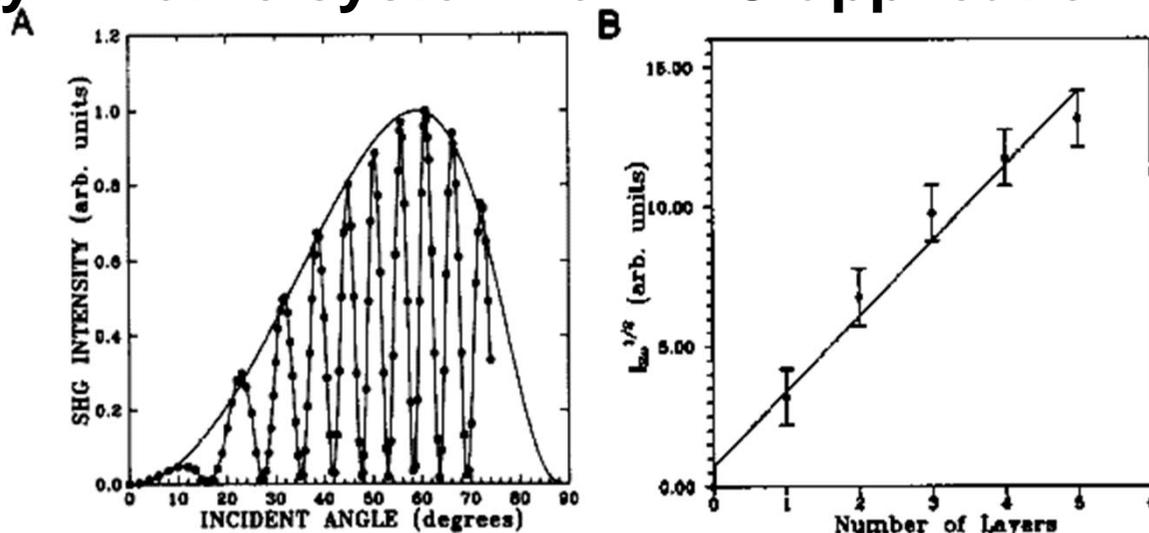
(18-phenoxyoctadecyl)trichlorosilane

Nature 2004

# Building of non-centrosymmetric system for NLO application

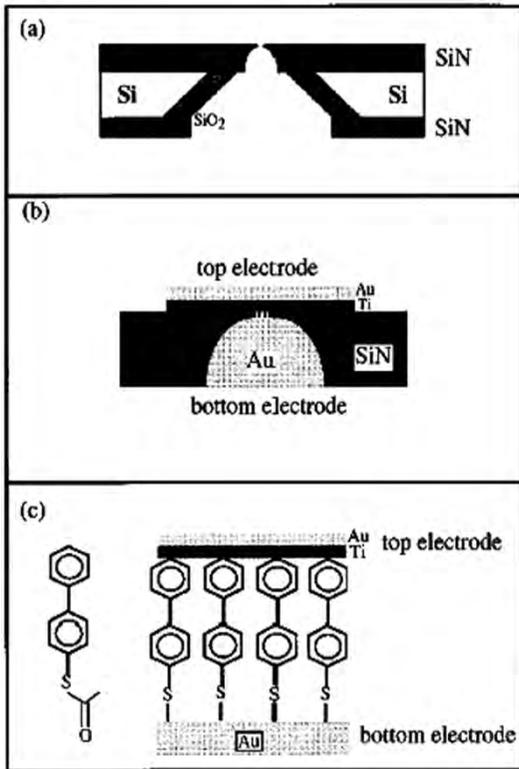


Conditions: (i) benzene, 25°C; (ii) reflux in n-PrOH; (iii) Cl<sub>3</sub>SiOSiCl<sub>2</sub>OSiCl<sub>3</sub> in THF; (iv) poly(vinyl alcohol) in DMSO.

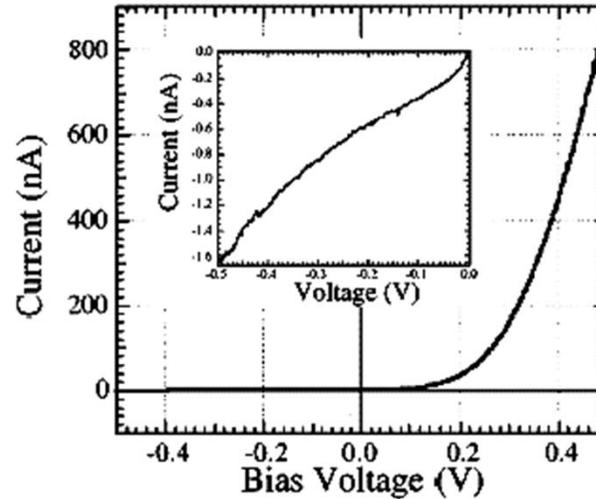


(A) SHG intensity as a function of fundamental beam incident angle from a glass slide having a self-assembled CpCh monolayer on either side. The interference pattern arises from the phase difference between the SHG waves generated at either side of the substrate during propagation of the fundamental wave. The solid envelope is a theoretical curve generated for  $\chi^{(2)}_{zzz}/\chi^{(2)}_{zyy}=3$ . (B) Plot of the square root of SHG intensity versus the number of chromophore layers in the multilayer superlattice. The straight line is the linear least-squares fit to the experimental data.

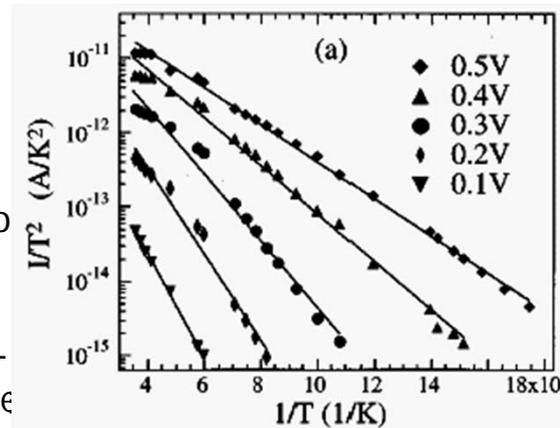
# Studying charge conduction through molecules



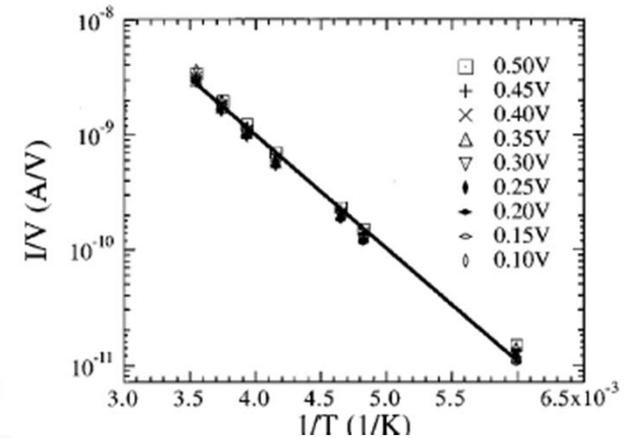
Fabrication of the heterostructure. (a) nano pore etched in suspended SiN membrane with a diameter about 300Å. (b) Au-Ti top electrode/SAM/ Au bottom electrode. (c) 4-thioacetyl biphenyl and detail diagram of the sandwich heterostructure.



$I$ - $V$  characteristics at r.t. Magnified view of the negative bias part in the inset.

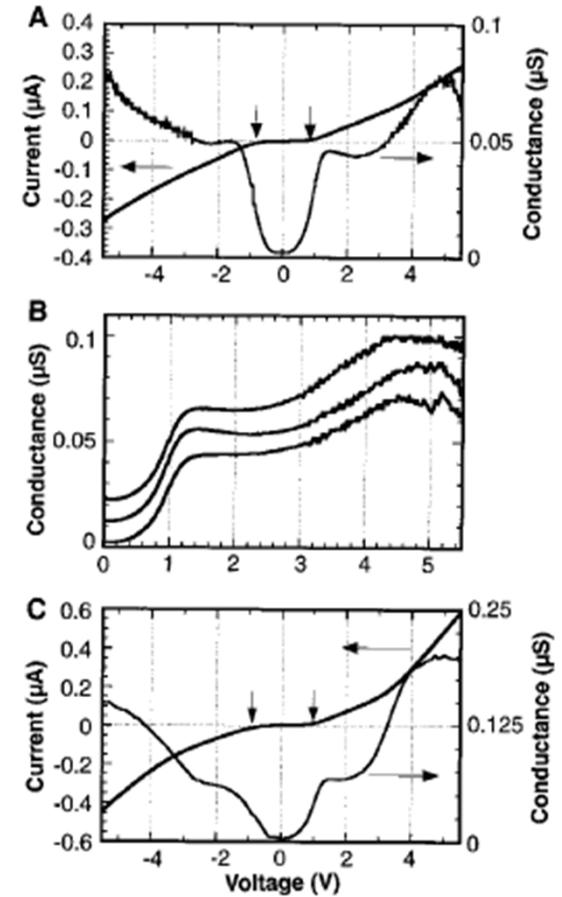
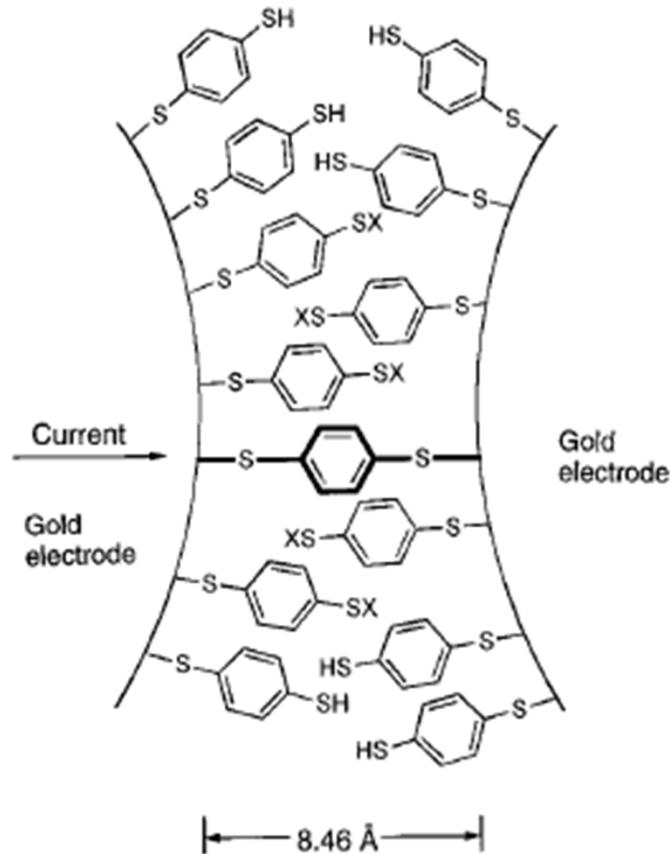
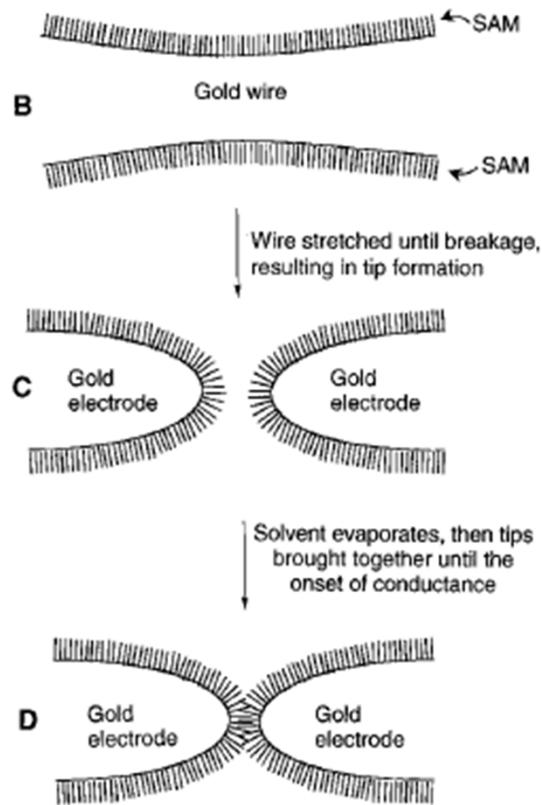


Plots of  $\ln(I/T^2)$  vs  $1/T$  for a series of positive bias voltages. The straight lines suggest thermionic injection of electrons from Au.

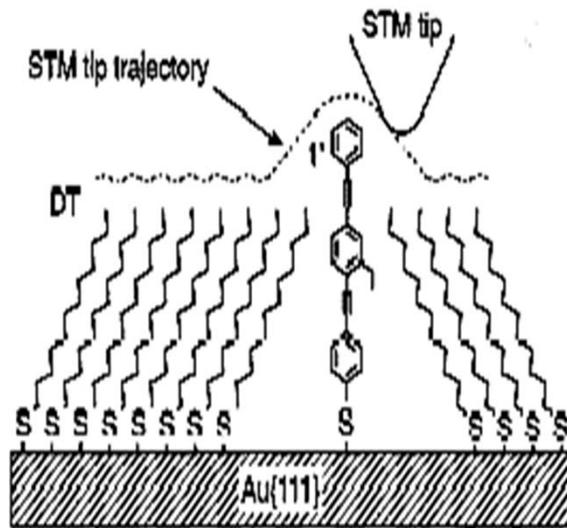


Plots of  $I/V$  vs  $1/T$  for a series of negative bias. The straight lines suggest hopping injection of electrons from Ti.

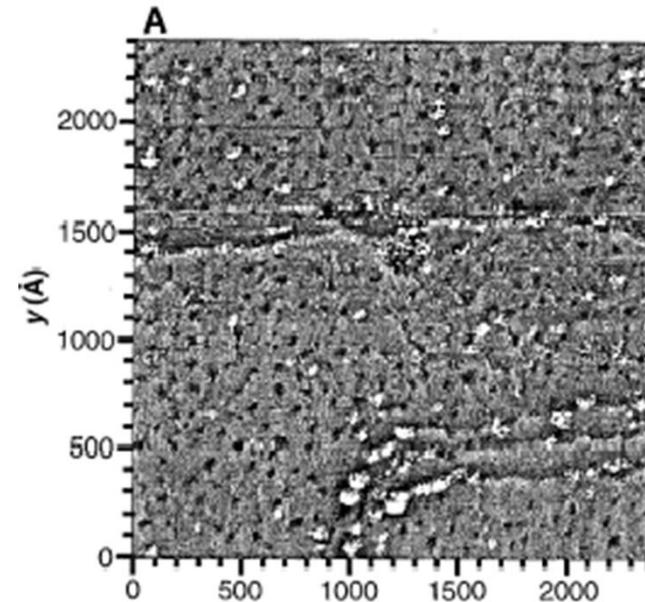
# Can a single molecule conduct?



# Measuring conductance through single molecular wires



A schematic representation of a DT and 1' SAM on Au{111}. The height that the 1' molecule extends above the DT film, if normal to the surface, is 7.3Å. The trajectory of the STM tip traces out a surface of constant current. The protruding 1' molecule "images" the end of the STM tip, resulting in a characteristic feature due largely to the shape of the end of the STM tip for each 1' molecule.



Constant-current STM topographs of an Au{111} surface covered by DT and 1' molecules (tip bias, 1.0V; tunneling current, 10pA.)

# Large On-Off Ratios and Negative Differential Resistance in a Molecular Electronic Device

**Fig. 1.** Schematics of device fabrication. (A) Cross section of a silicon wafer with a nanopore etched through a suspended silicon nitride membrane. (B) Au-SAM-Au junction in the pore area. (C) Blowup of (B) with **1c** sandwiched in the junction. (D) Scanning electron micrograph (SEM) of pyramid Si structure after unisotropic Si etching [that is, the bottom view of (A)]. (E) SEM of an etched nanopore through the silicon nitride membrane. (F) The active molecular compound **1c** and its precursors the free thiol **1b** and the thiol-protected system **1a**.

