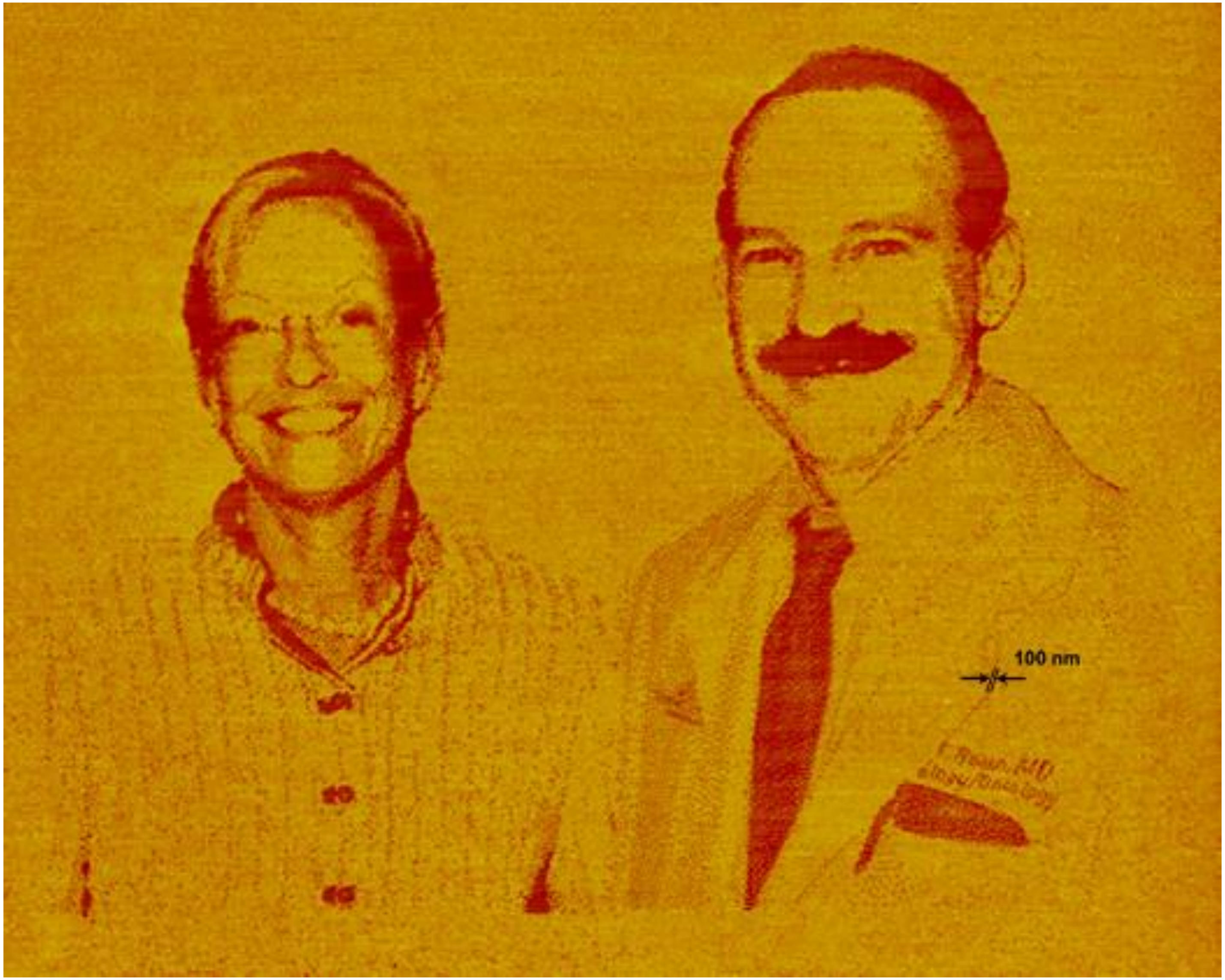
Dip-Pen Lithography



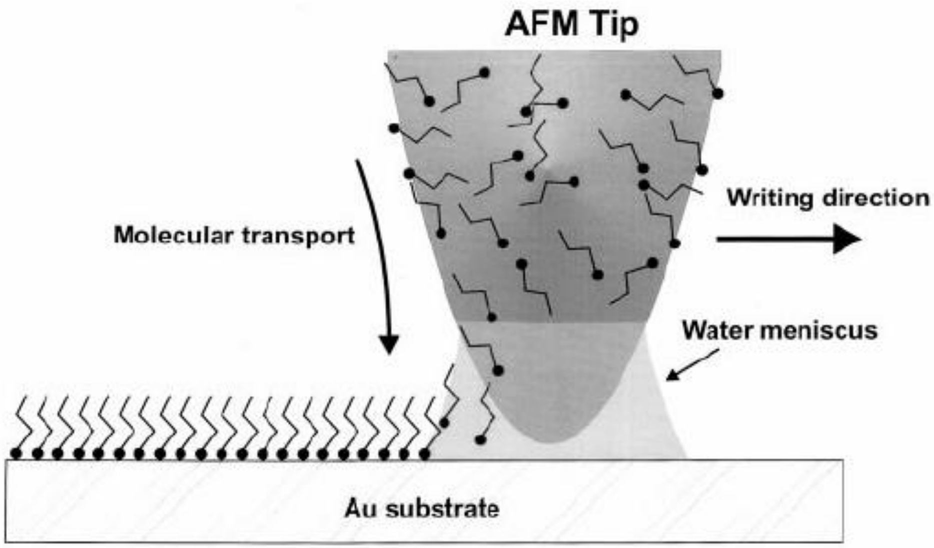
A Brief History of Writing Instruments

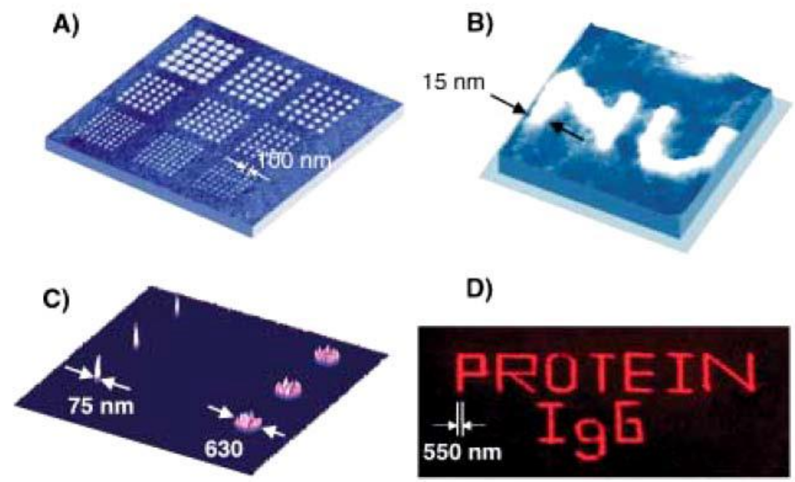
From Quills and Bamboos to fountain pens and brushes

M. Klein and Henry W. Wynne received US patent #68445 in 1867 for an ink chamber and delivery system in the handle of the fountain pen.

The ink is fed to the nib through a "feed" via a combination of gravity and capillary action.

Nanoscale Fountain Pen - Dip Pen Nanolithography(DPN)





Dip-pen nanolithography (DPN) is a new scanning-probe based directwriting tool for generating such surface-patterned chemical functionality on the sub-100 nm length-scale, and it is a technique that is accessible to any researcher who can use an atomic force microscope (a scanning probe technique).

(*Science* **283**, 661, 1999)

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The Family of Scanning Probe Techniques

The basic idea: local probe

- Probe of small size measures a property in a confined region
- Size of probe determines resolution
- Current, force, E- and B-field, temperature, acoustic waves, light intensity, …
- Create an image, cross-section, spectrum, force curve, topography, …

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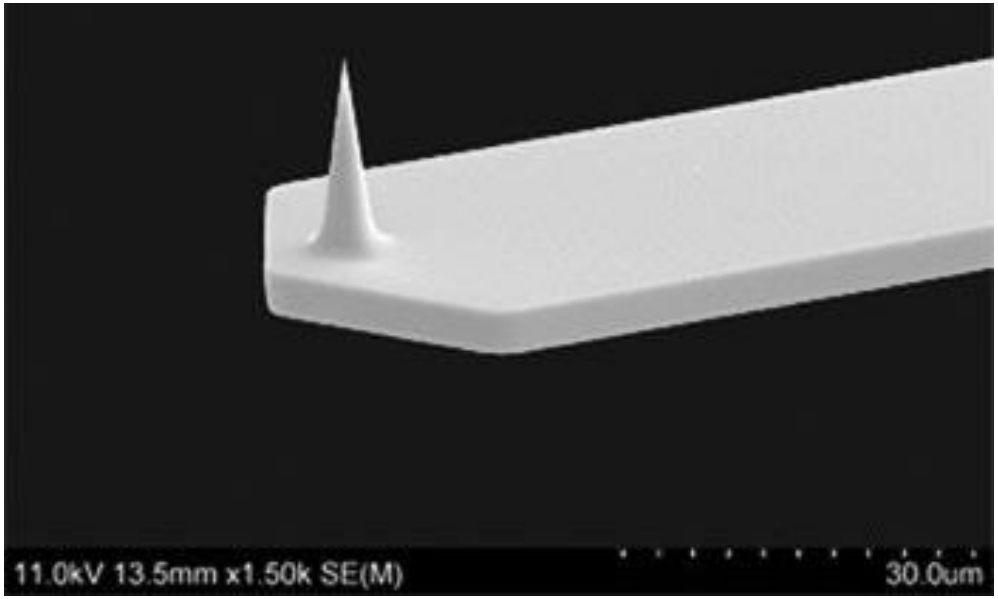
The Challenge: Nanoscopic Resolution!

- Have the smallest possible probe! --> Nanofabrication
- Don't break it!
- Control the tip/sample position with nanoscopic resolution in a macroscopic instrument
- A necessity: Probe provides position feedback!
- Enemies: thermal drifts, vibration, acoustic & electric noise



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Various DPN Ink-Substrate Combinations

Ink	Substrate	Notes
Alkylthiols (e.g. ODT and MHA)	Au	15 nm resolution with sharp tips on single crystal surfaces, <50 nm on polycrystalline surfaces
Ferrocenylthiols	Au	redox active nanostructures
Silazanes	SiO_x, GaAs	patterning on oxides
Proteins	Au, SiO_x	both direct write and indirect assembly
Conjugated polymers	SiO_x	polymer deposition verified spectroscopically and electrochemically
DNA	Au, SiO_x	sensitive to humidity and tip-silanization conditions
Fluorescent dyes	SiO_x	luminescent patterns
Sols	SiO_x	solid-state features
Metal salts	Si, Ge	electrochemical and electroless deposition
Colloidal particles	SiO_x	viscous solution patterned from tip
Alkynes	Si	C–Si bond formation
Alkoxysilanes	SiO_x	humidity control important
ROMP materials	SiO_x	combinatorial polymer brush arrays

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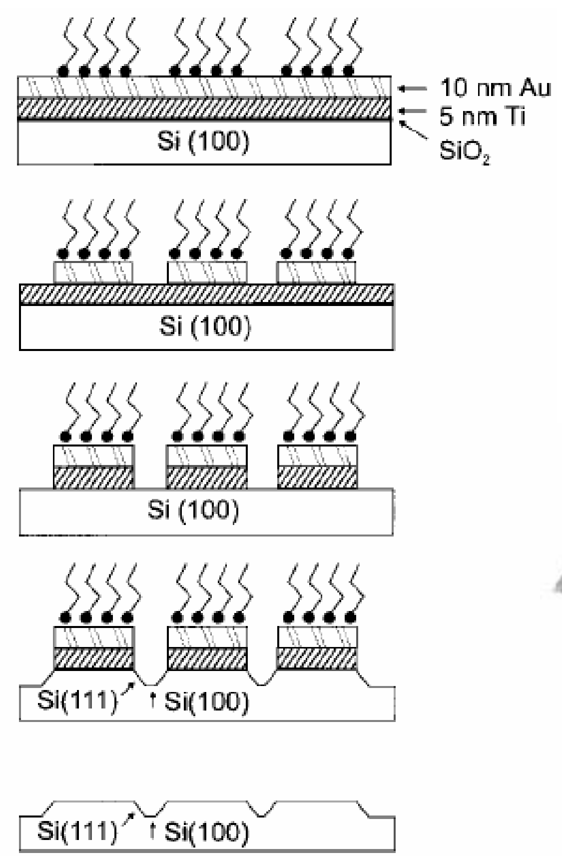
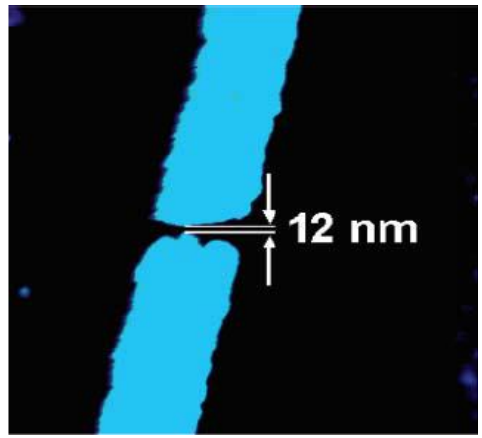
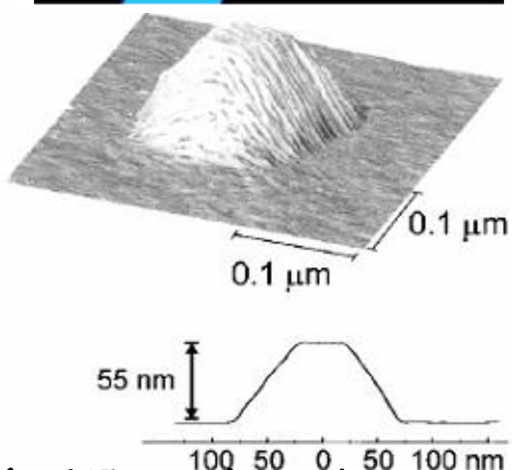
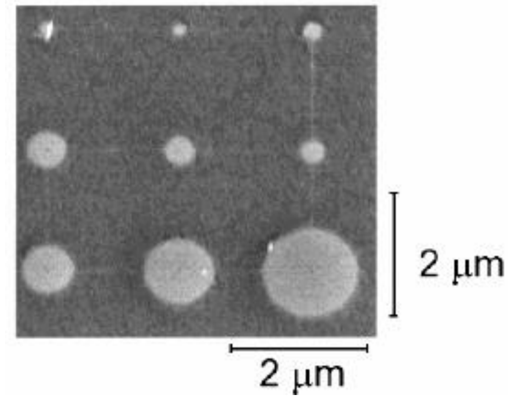
(*Angew. Chem. Int. Ed.* **43**, 30, 2004)

Various DPN Ink-Substrate Combinations

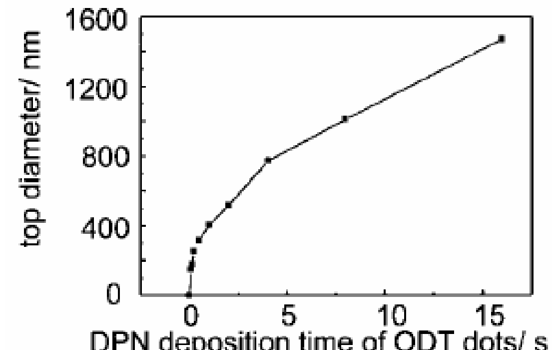








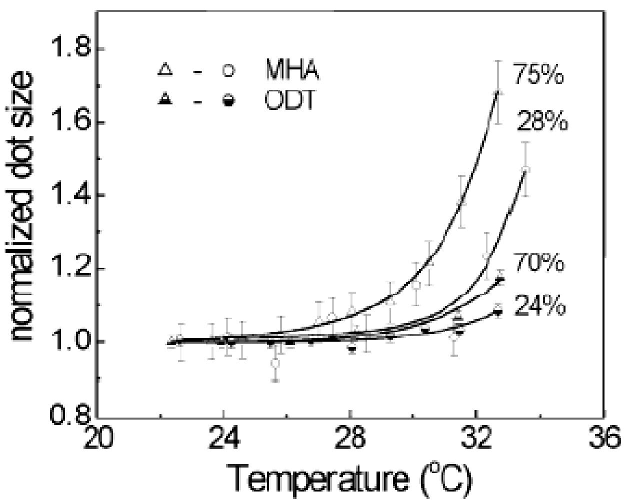
Diffusion of Ink determines resolution.

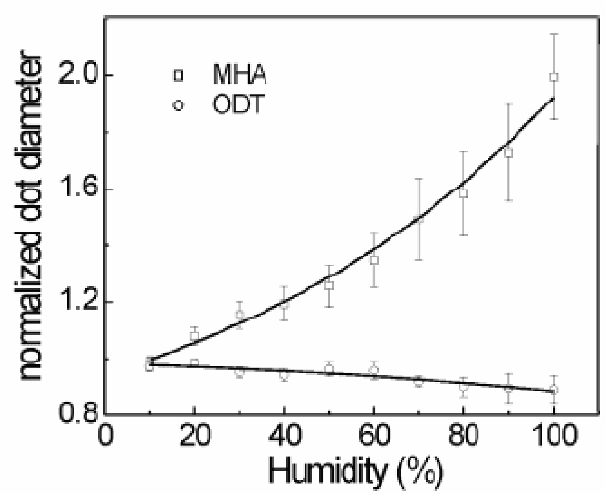


- Resolution (~15 nm) is better than μCP (~35 nm).
- But low throughput due to serial writing process.

(Adv. Mater. **12**, 1600, 2000*)*

Humidity & Temp. Affect Resolution





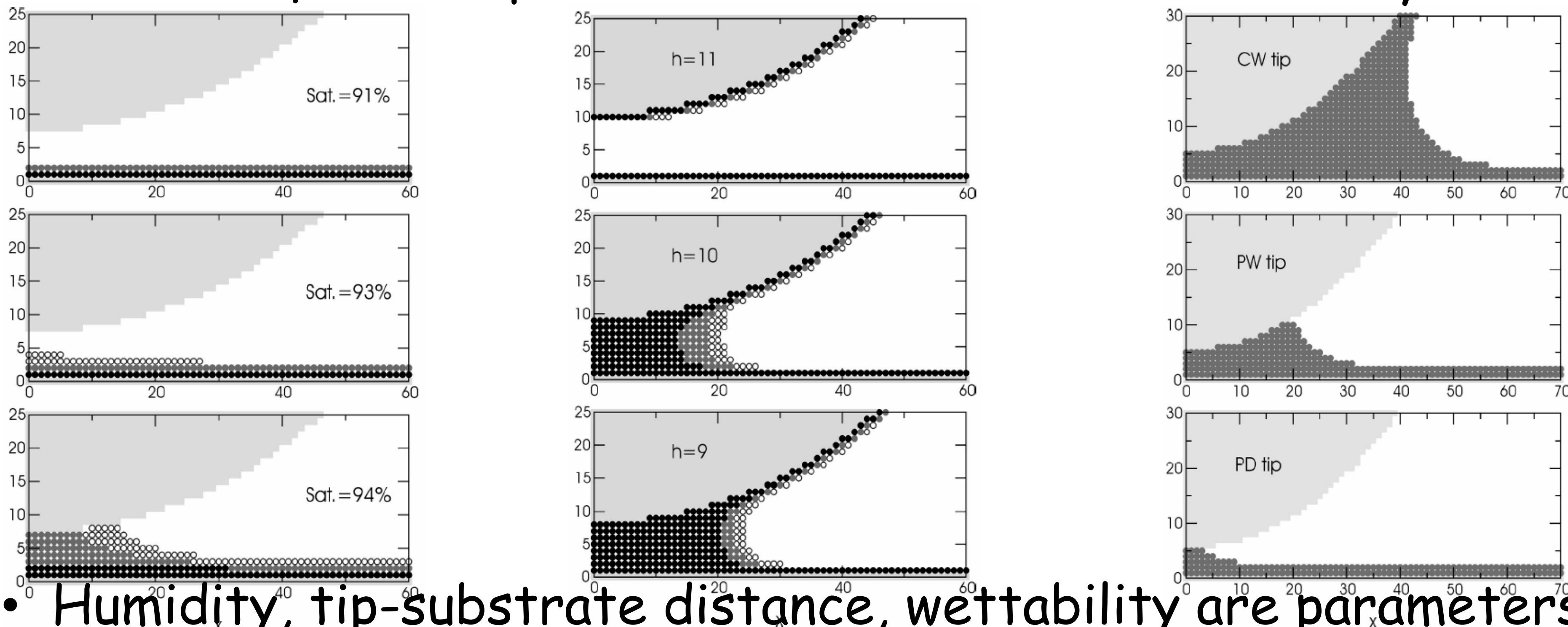
- Ink solubility is a key factor in determining temperature and humidity dependence of growth rate.
- Increase in the deposition rate with increasing temperature.
- Different solubilities of the molecules on the Au substrates influence SAM growth rates.

AFM in a glove box

(*J. Phys. Chem. B* **107**, 751, 2003)

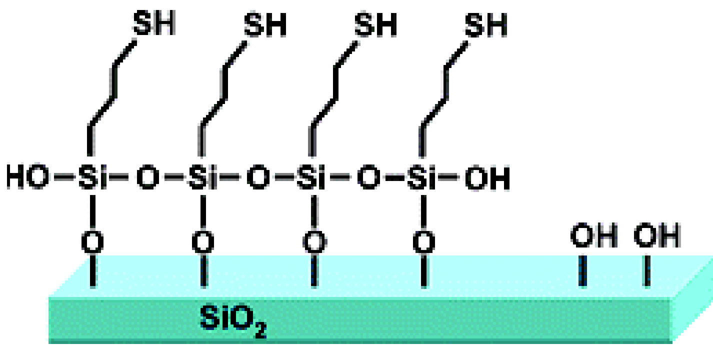
Monte Carlo Simulation of Meniscus Formation

Humidity | Tip-Substrate Distance | Wettability of Tip



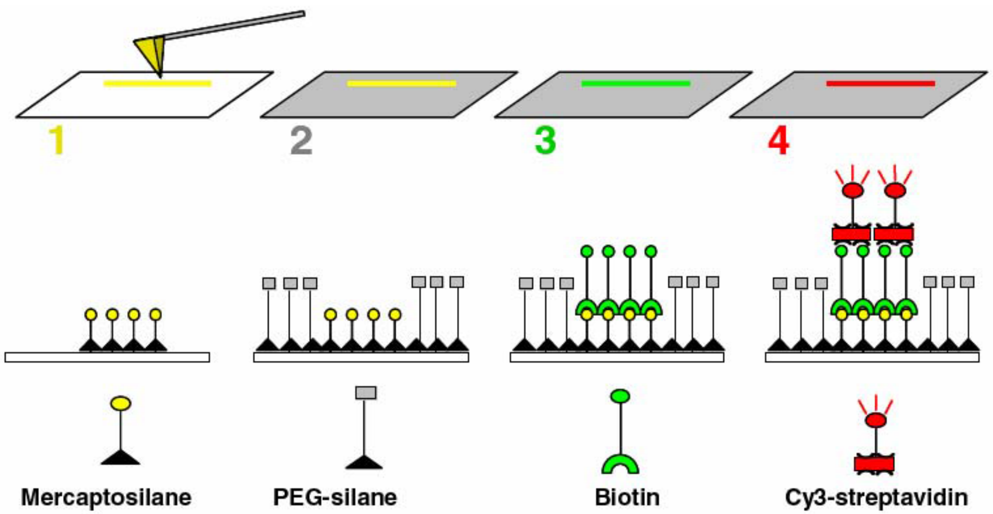
- Humidity, tip-substrate distance, wettability are parameters.
- A complete simulation requires models which combine the thermodynamics of meniscus formation with the dynamic effects of ink desorption, transport through the meniscus, and self-assembly.(*J. Chem. Phys.* **116**, 3875, 2002)

DPN on Glass

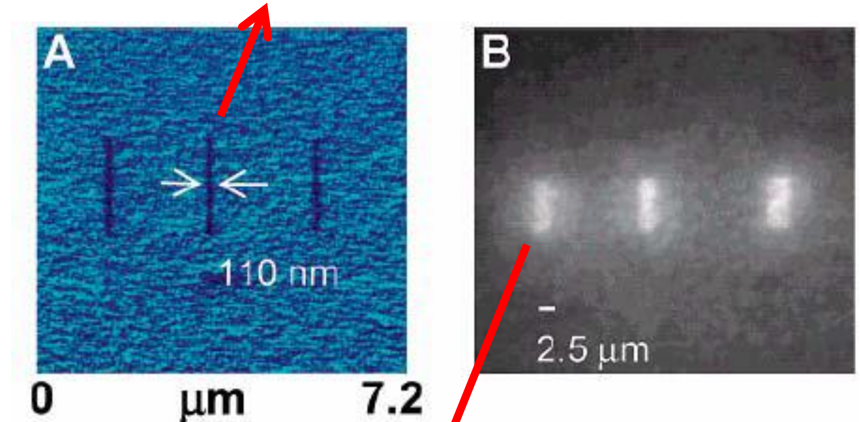


(*J. Am. Chem. Soc.* **125**, 12096, 2003)

- Silane is evaporated onto the AFM tip under anhydrous conditions.
- Humidity need to be kept low to prevent prepolymerization of silane.



Mercaptosilane lines



Fluorescent biotinst-reptavidin lines

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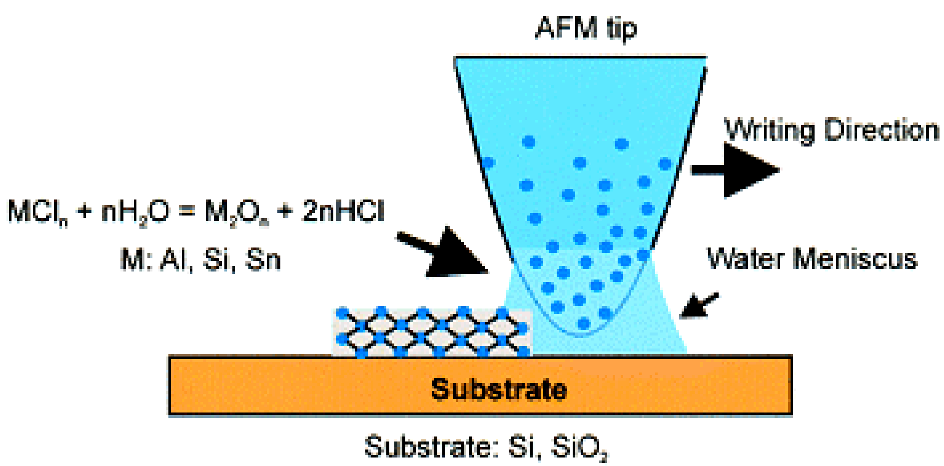
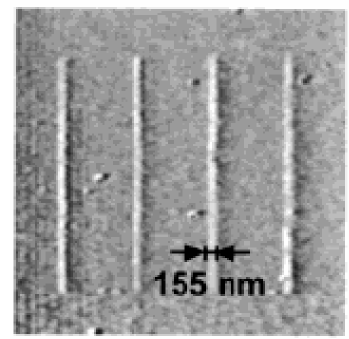
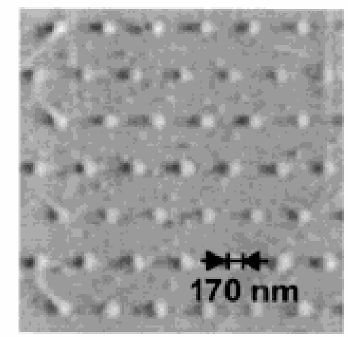
Sol-Gel DPN



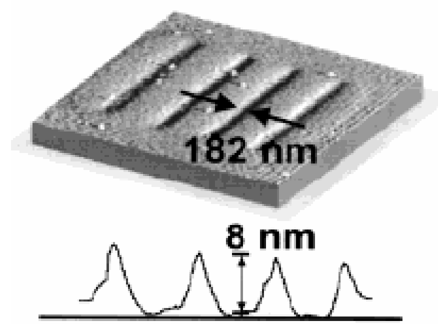


Tin Oxide

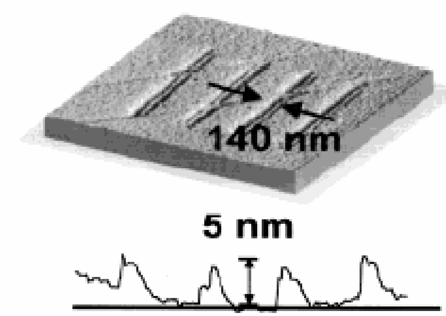


Aluminum Oxide

- Delivery of metal oxide sol-gel precursors using AFM tips.
- Atmospheric moisture and the water meniscus serve to hydrolyze the sol-gel precursors.



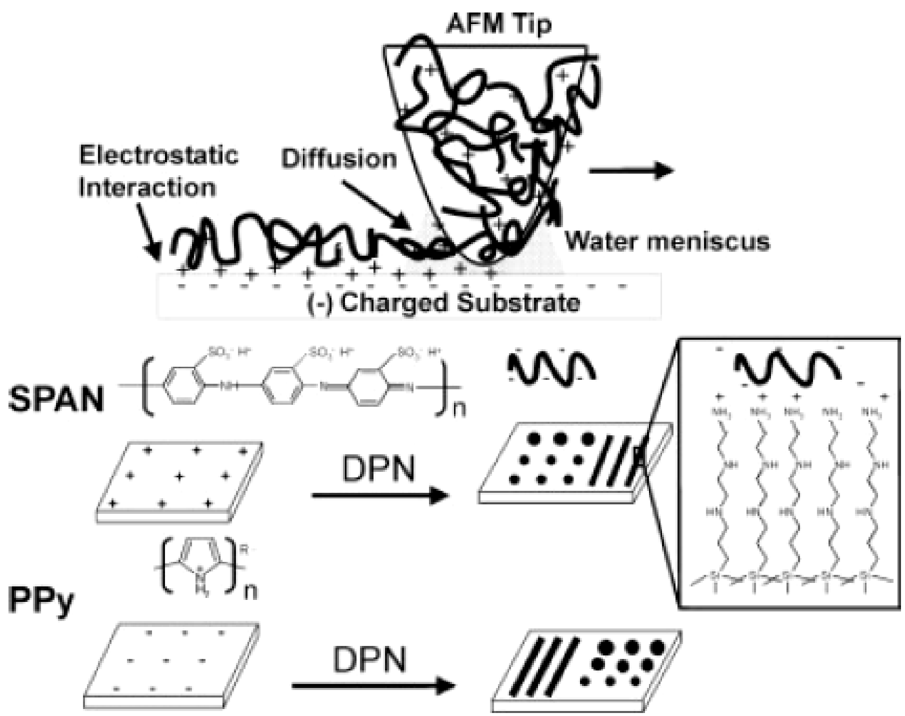
Silica -Initial

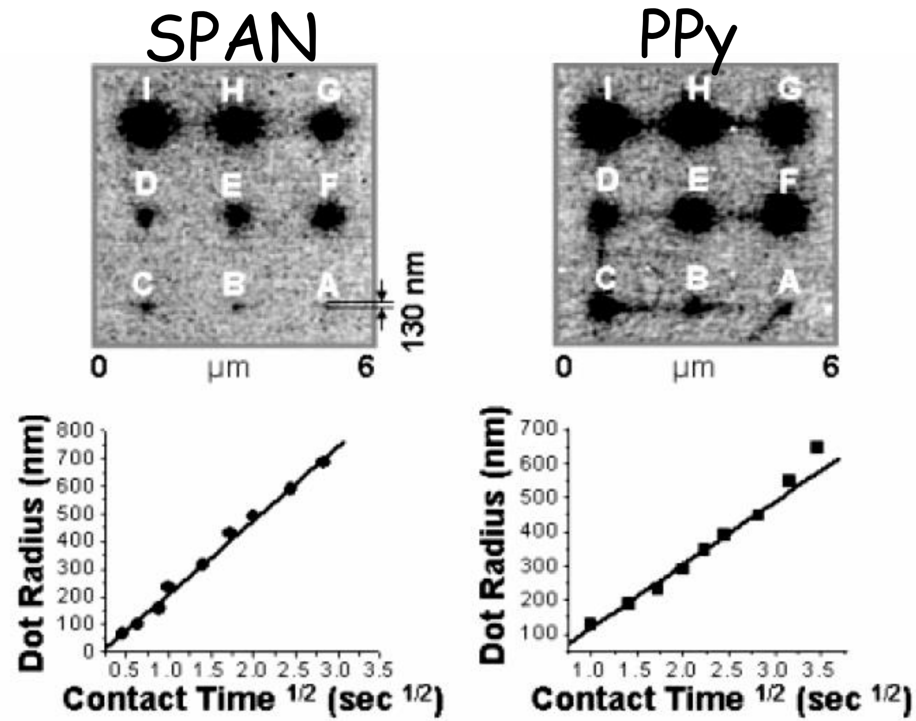


Silica -Heated

(*J. Am. Chem. Soc.* **124**, 1560, 2002)

Electrostatic DPN

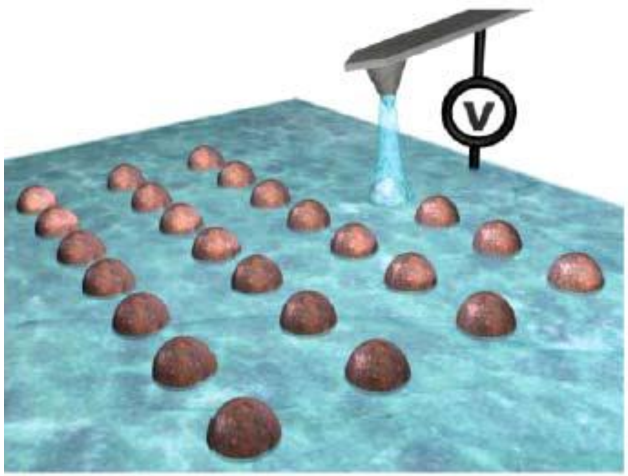


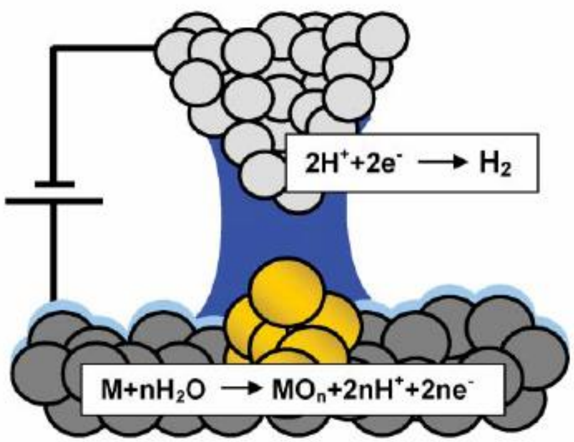


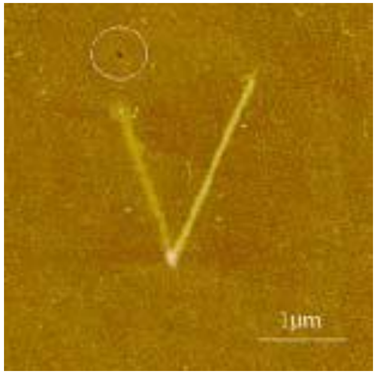
- The smallest feature size is ~130 nm compared to 15 nm resolution using small molecule inks.
- Meniscus-driven transport of water-soluble polymers leads to fast diffusion and pattern smearing.

(*Adv. Mater.* **14**, 1474, 2002)

Electrochemical DPN (E-DPN)

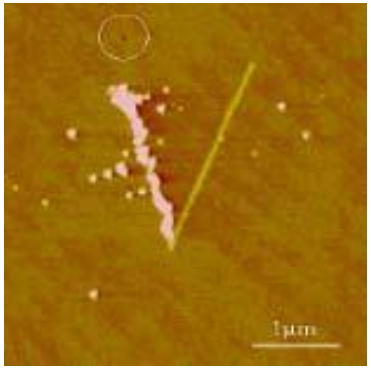






Electrodeposition of Pt (+4V)

$$PtCl_6^{2-} + 4e \rightarrow Pt + 6Cl^-$$

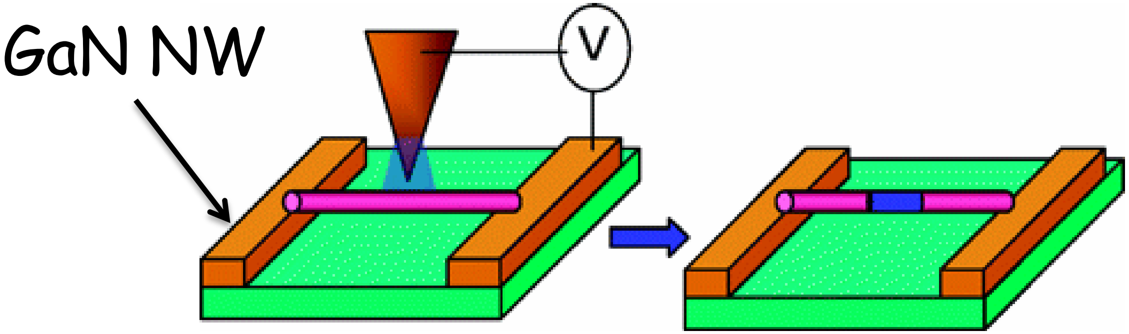


Elecxtrooxidation of Si (-10V)

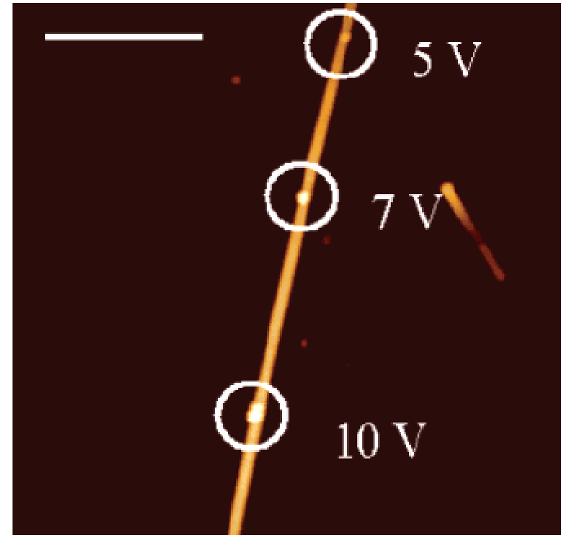
- Water meniscus between AFM tip and surface as a reaction vessel.
- Nanoelectronic devices with sections made of different metals or semiconductors.

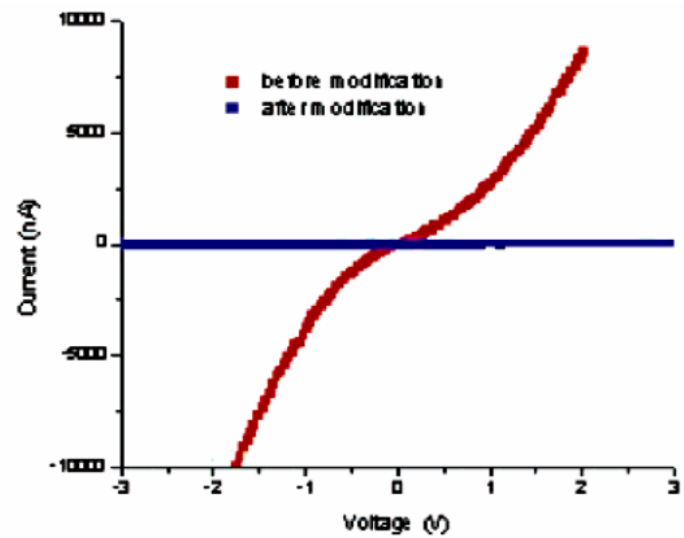
(J. Am. Chem. Soc. **123**, 2105, 2001)

Nanoscale Writing on Nanowires



$$2GaN + 6OH^{-} + 6h^{+} \rightarrow Ga_2O_3 + 3H_2O + N_2$$

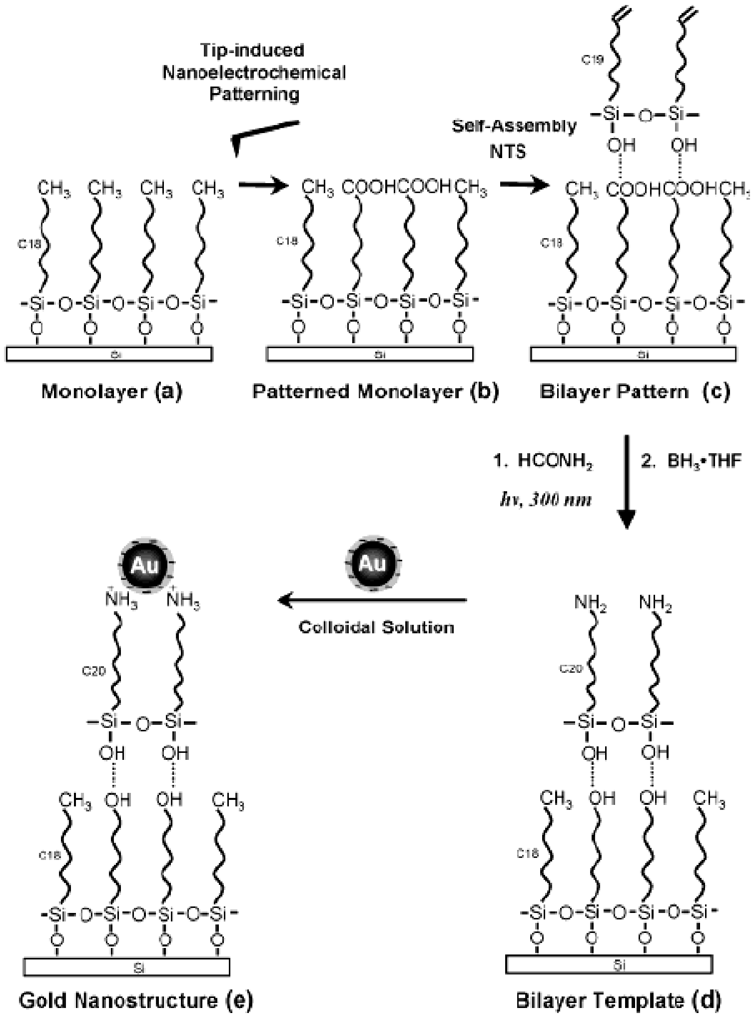


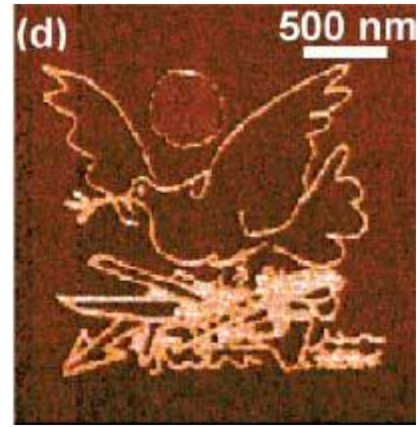


- GaN/GaO heterostructures formed via a reaction with tip-applied KOH ink.
- A convenient means to deliver chemicals to specific locations on an existing nanostruture to perform chemical and structural modification.

(*J. Am. Chem. Soc.* **1256** 6409, 2004)

SAMs Nano-Electrochemistry



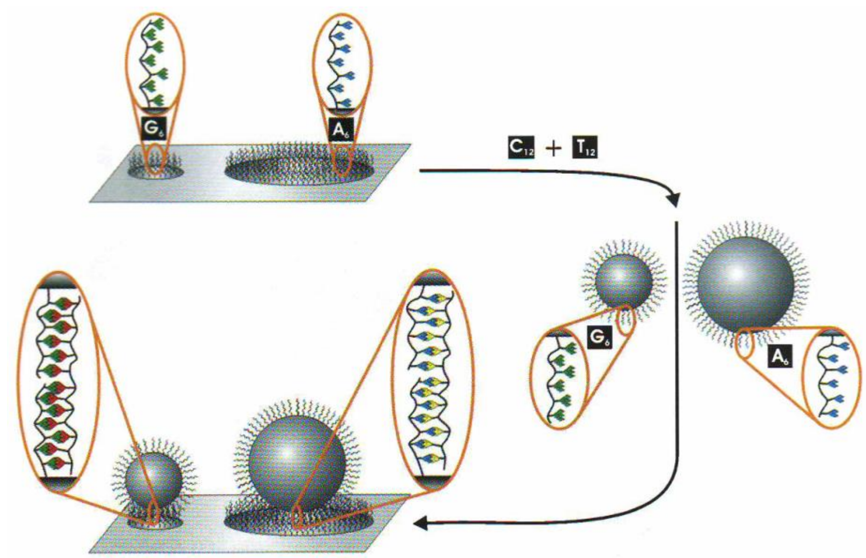


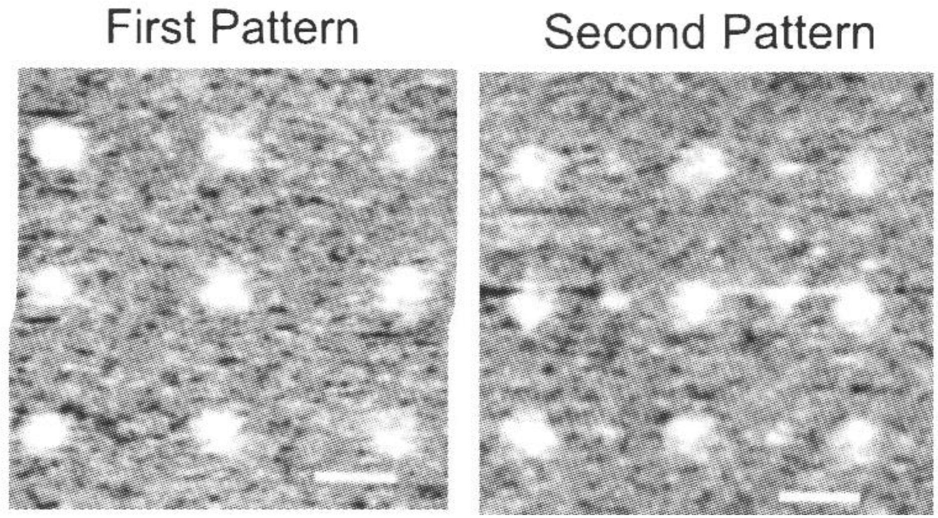
Picasso's World Without Weapons

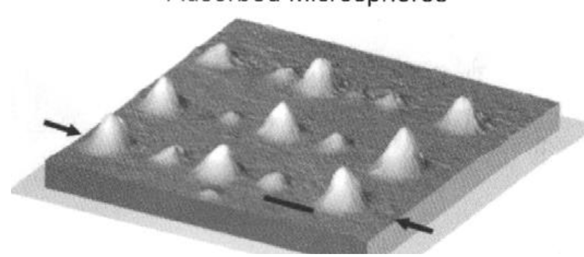
- Fine-tuning (sub-nanometer) of single molecule overlayers suggests interesting possibilities for the advancement of a 3D chemical nanofabrication methodology.

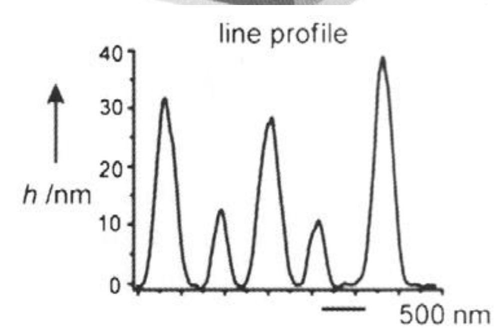
(*Nano Lett.* **4**, 845, 2004)

Writing Molecular Recognition









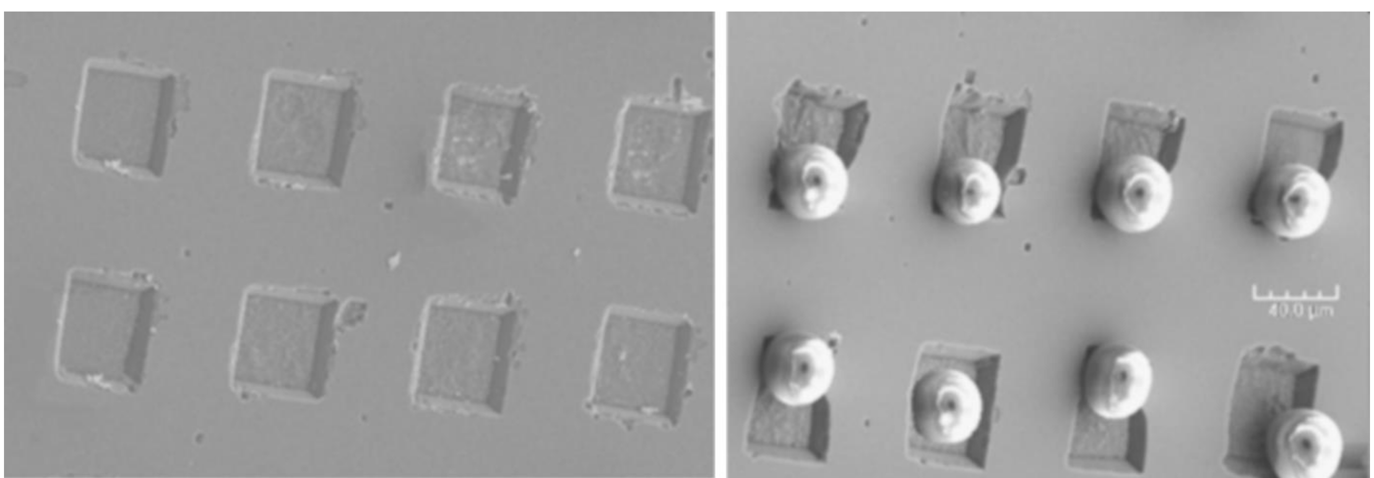
Orthogonal Assembly: using well-known specificity of T-A and C-G nucleotide base pairing in DNA to guide nanoscale building blocks functionized with a particular DNA strand to complementary DNA surface sites.

(*Angew. Chem. Int. Ed.* **40**, 3071, 2001)

Applications for DPN

We focus on four of four key applications:

- Biomolecular micro- and nanoarrays
- Controlling bio-recognition processes from the molecular to the cellular level
- Building nanostructured materials with DPN: templates for orthogonal assembly
- DPN-patterned etch resists



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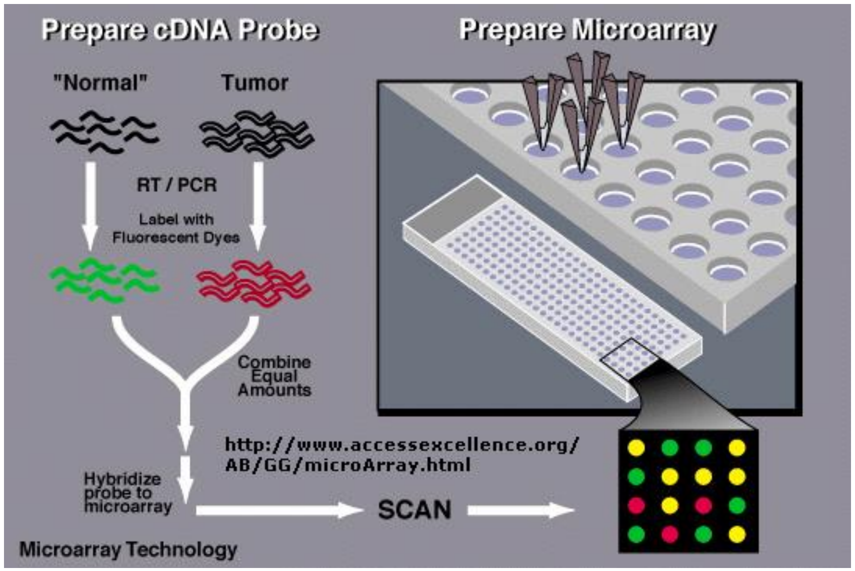
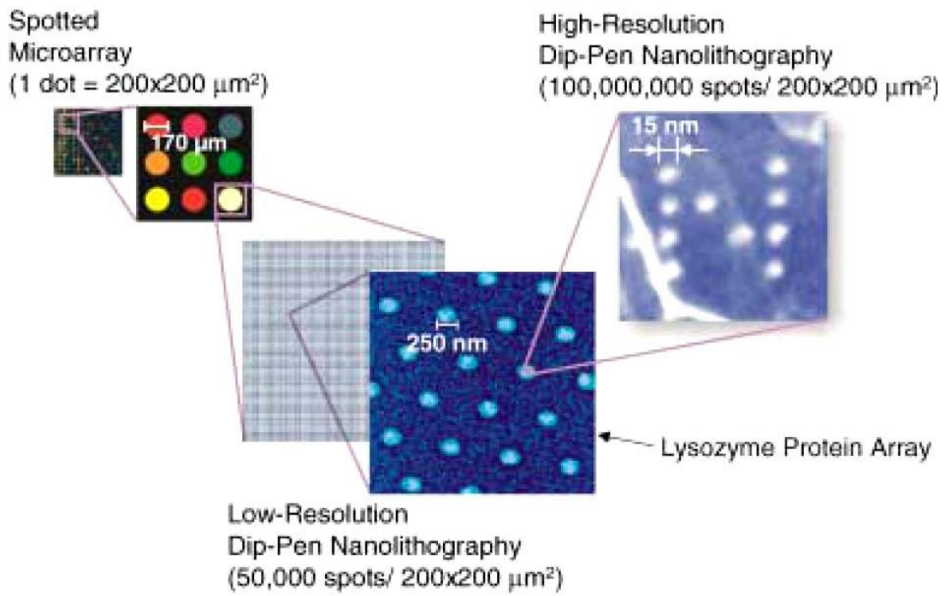
DPN for Biomolecular Array Fabrication

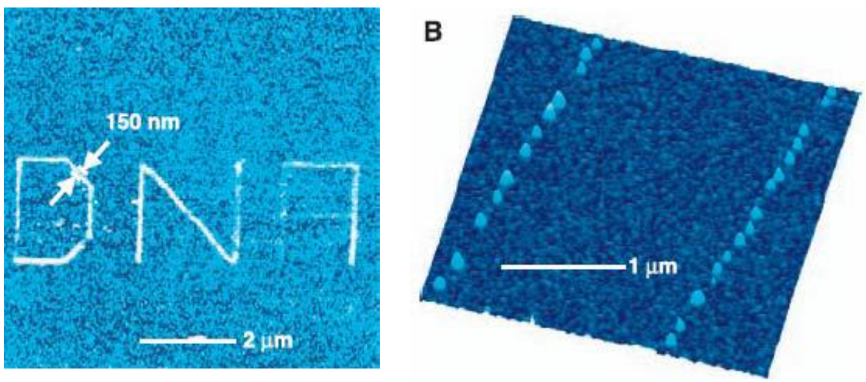


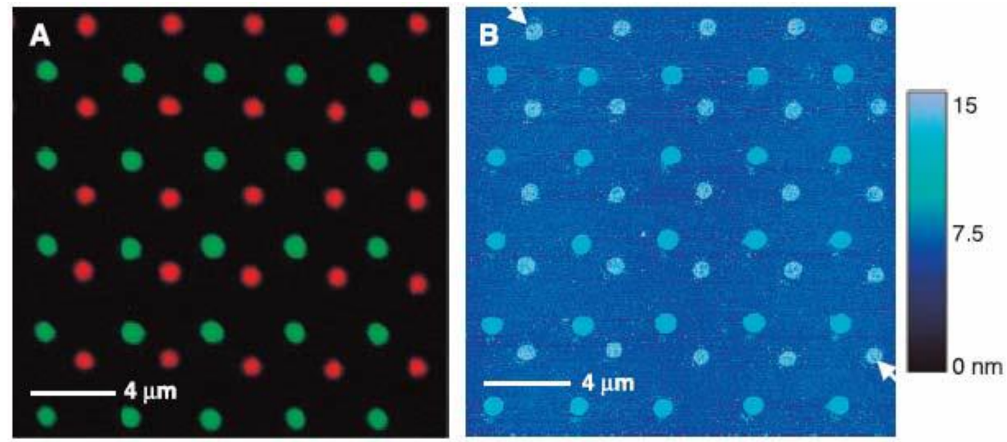


- As a direct-write technique, DPN is particularly well-suited for patterning biological molecules on surfaces.
- DPN provides 10,000 to 100,000,000-fold increase in density.
- To screen an entire human genome for single-nucleotide polymorphism: State-of-the-art chips (20 μm features): a car space in a parking lot DPN (150 nm features): $2x2\ cm^2$ chip

DNA Nanoarrays

Thiol-end oligonucleotides on Au





Oligonucleotide-modified Au nanoparticles bound to a high-resolution DNA line by base pairing in the presence of complementary linking DNA.

- Hexanethiol-oligonucleotide on Au and acrylamide-oligonucleotide on glass.
- Nanoparticle labels are particularly promising tags for nanoscale detection.

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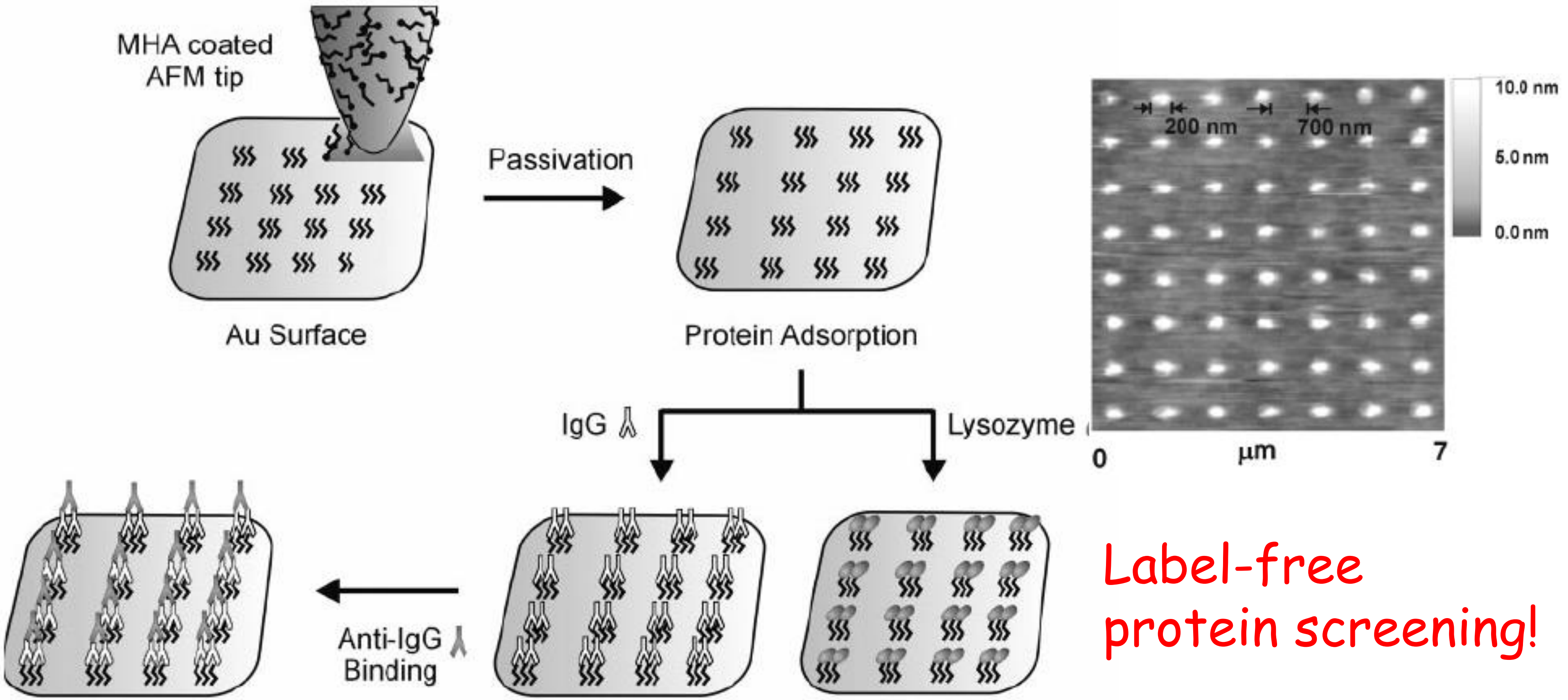
(*Science* **296**, 1836, 2002)

Protein Nanoarrays



Label-free protein screening!

(*Science* **295**, 1702, 2002)

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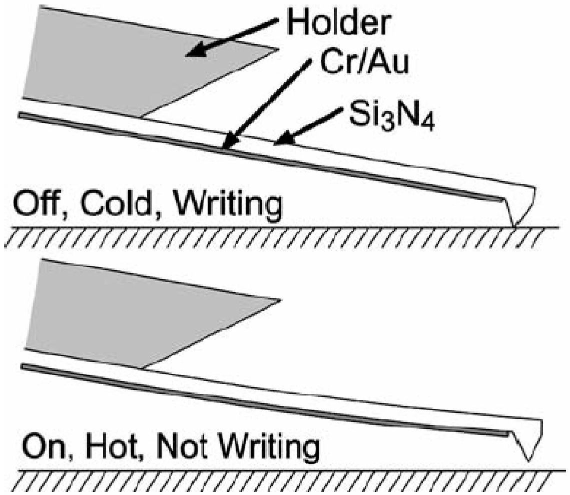
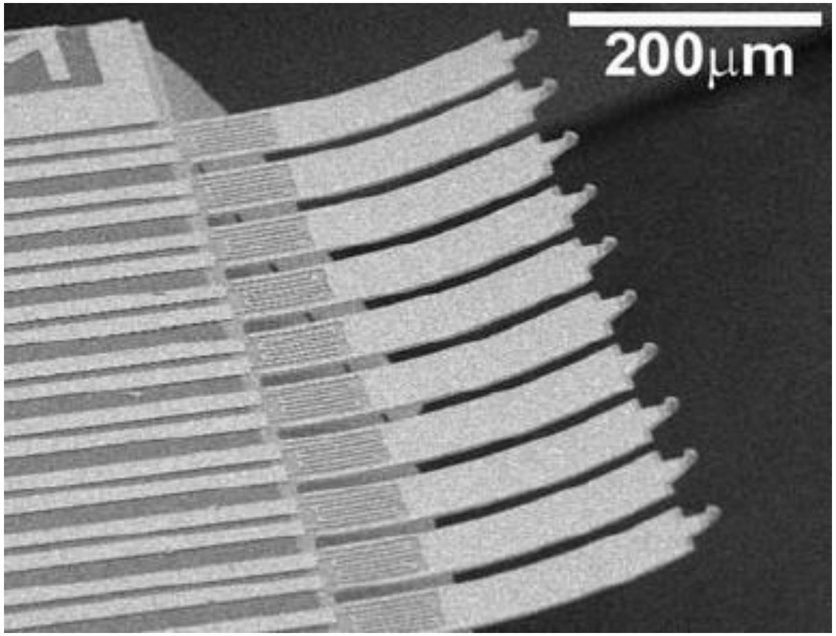
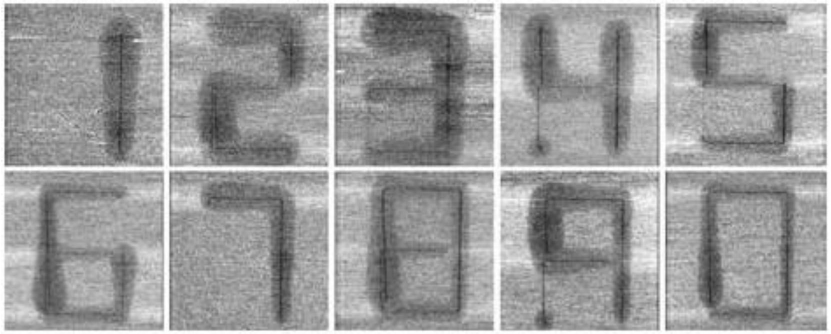
Nanoplotters

Bimorph Actuated DPN Probe





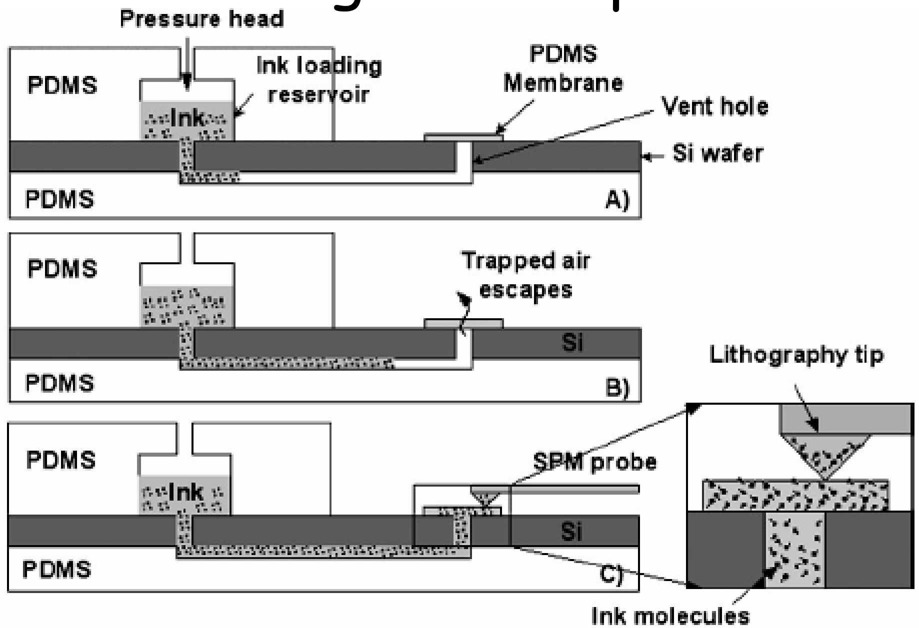


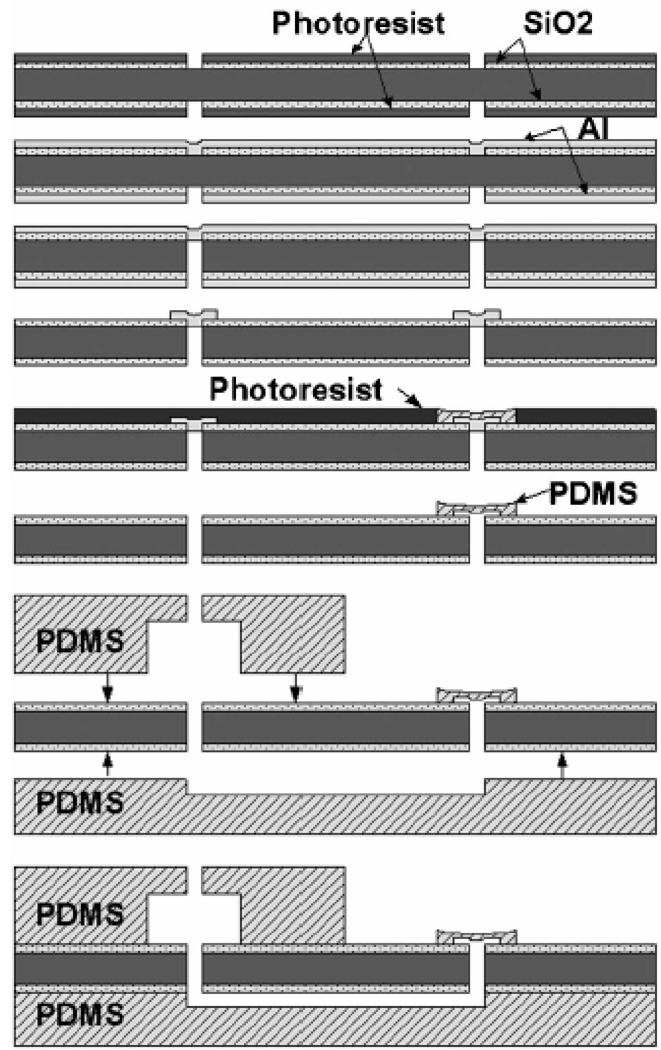
- Parallel DPN to compensate slow serial low throughput.
- The probes are actuated by passing DC current through a heater embedded in the probe base.

(*Appl. Phys. Lett.* **84**, 789, 2004)

Nanoblotters

Inking AFM Tips



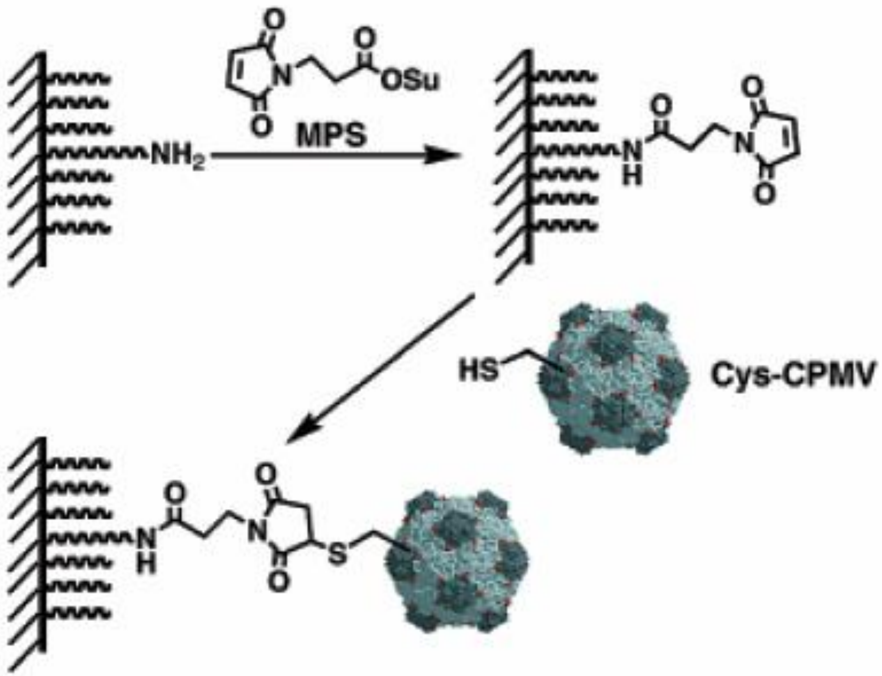


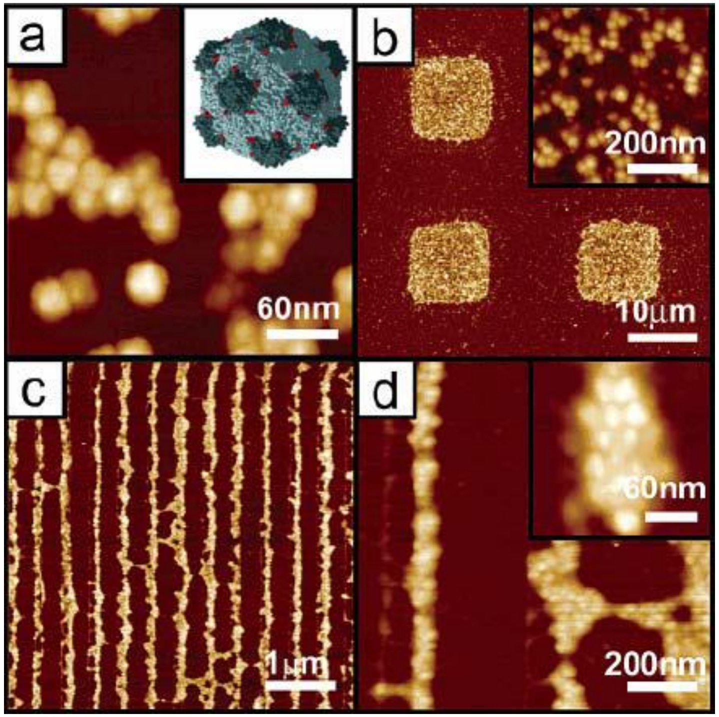
- A microfluidic chip for parallel and multiplexed addressing multiple tips.
- Thin PDMS membranes were used as ink pads to reduce evaporation of the ink and contamination.

(*Appl. Phys. Lett.* 85, 136, 2004)

Controlling Biorecognition Process

Functionalized alkanethiols as the linkers, and genetically modified cow pea mosaic virus (Cys-CPMV) as the adsorbate.

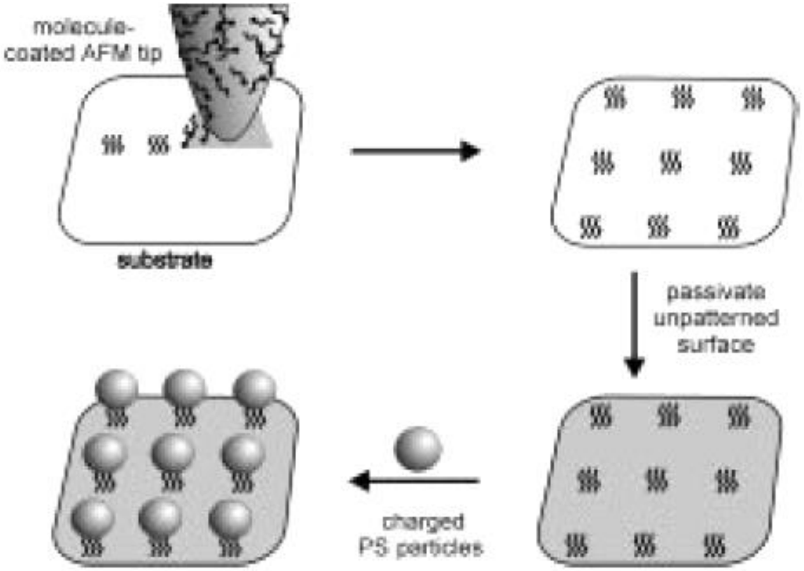




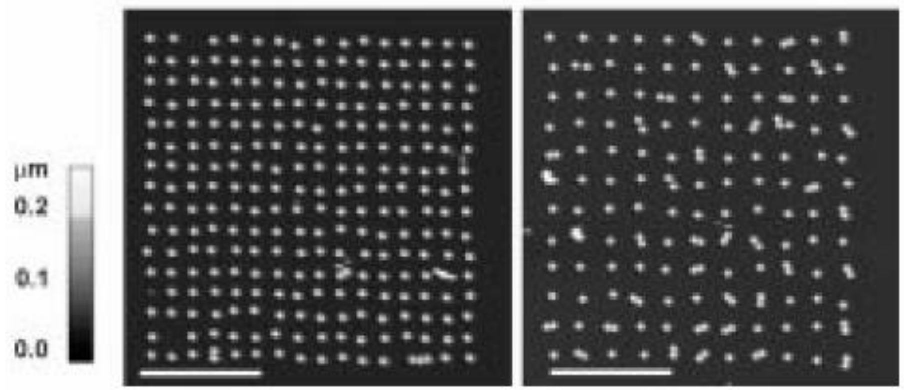
These nanometric templates are used to investigate the role of inter-virion interactions on assembly morphology and kinetics.

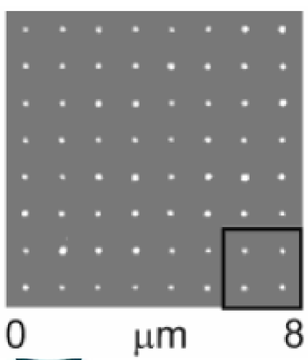
(*J. Am. Chem. Soc.* **125**, 6848, 2003)

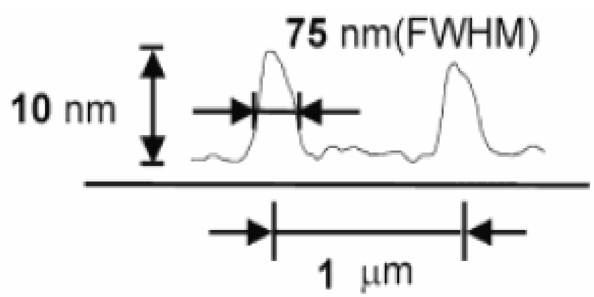
Templates for Orthogonal Assembly



190 nm Amidine-polystyrene Particles (positive charge)





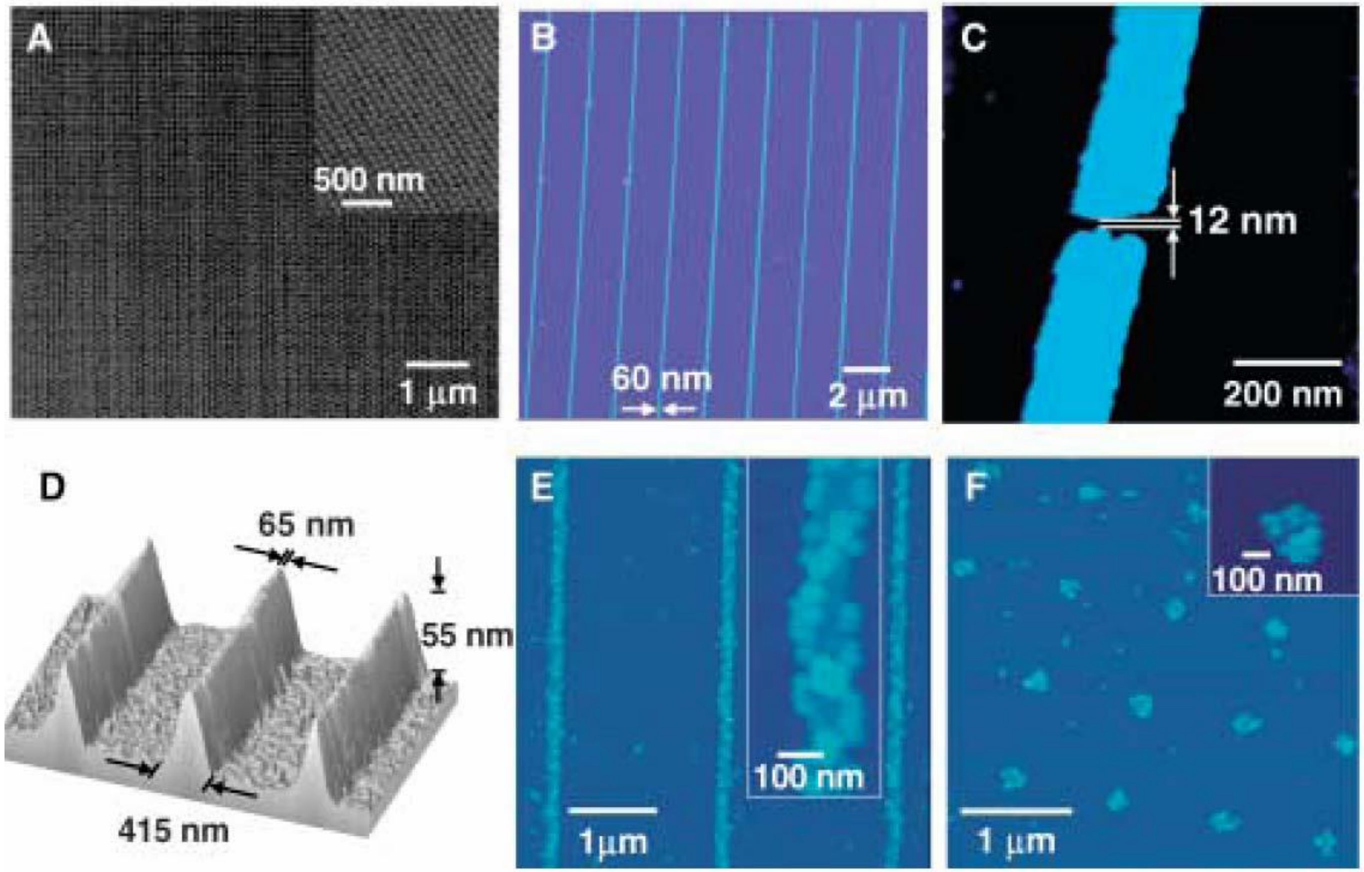


Iron Oxide Nanoparticles

Outside of biology, the orthogonal assembly of particles is of interest in fields ranging from colloidal crystallization to magnetic information storage.

(*Adv. Mater.* **14**, 231, 2002)

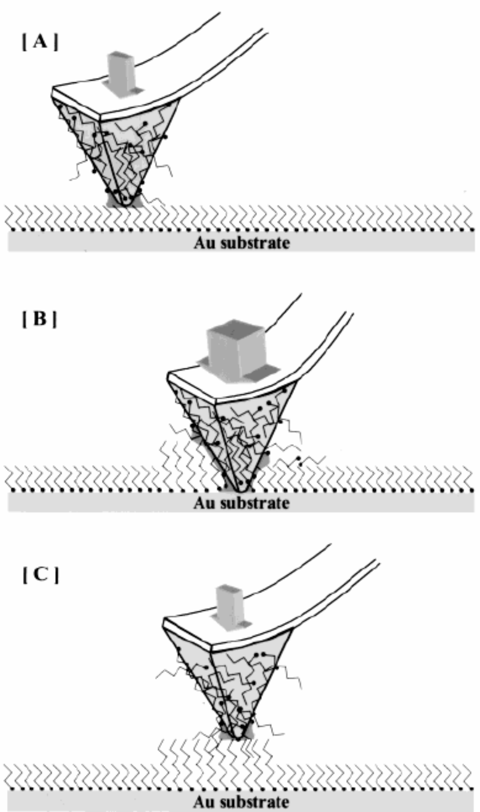
DPN Patterned Etch Resists



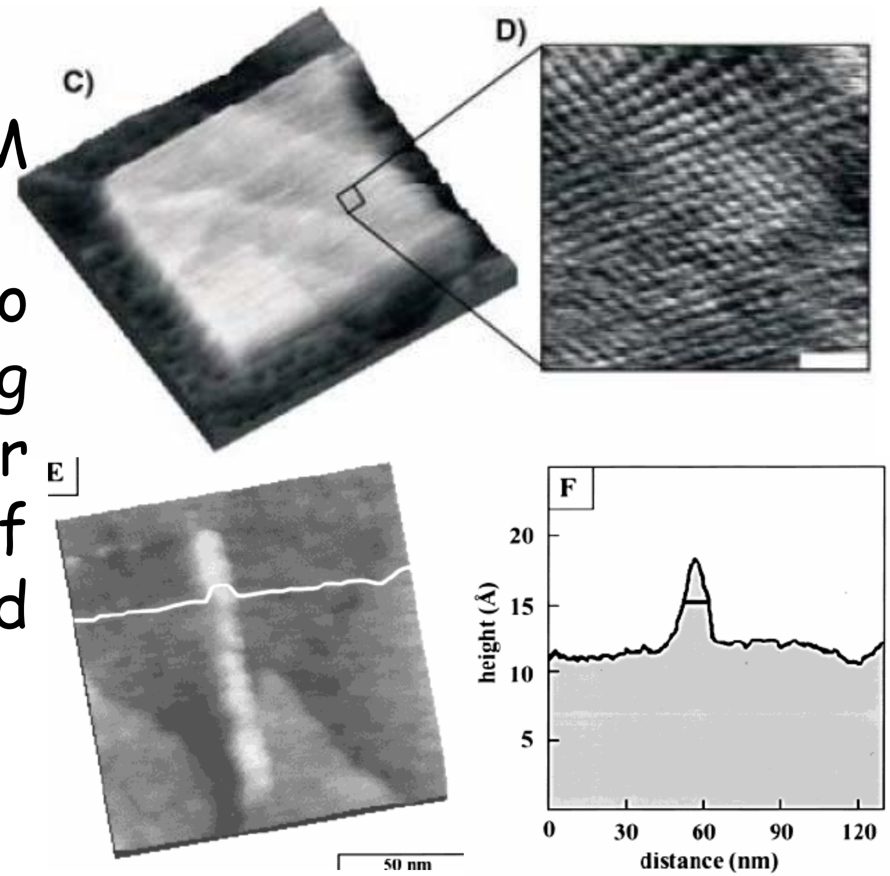
DPN-patterned etch resist provide a straightforward way of creating arrays of inorganic nanostructures (e.g. Au, Ag, Pd) on a semiconducting or insulating surface.

Beyond DPN: DPN-Nanograting Combination

Nanopen-Reader-Writer (NPRW)



A bulk SAM passivation layer to inhibit writing except under conditions of high applied force



$CF_{12}C_2$-thiol in C_{10}-thiol on Au

(*Langmuir* **16**, 3006, 2000)

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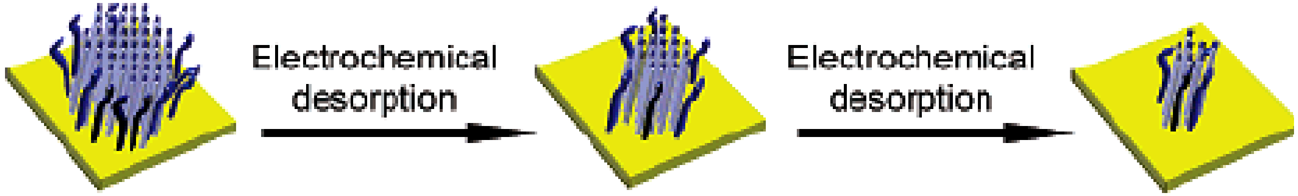
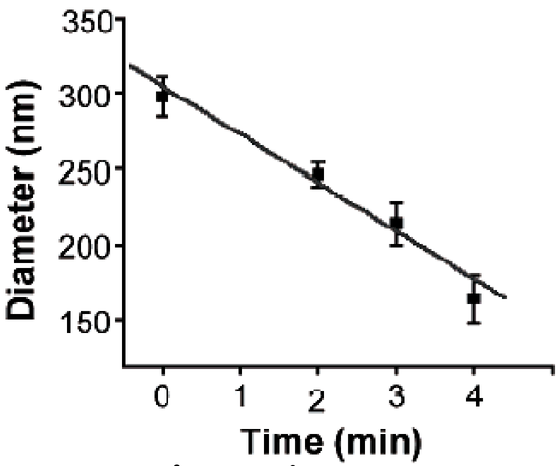
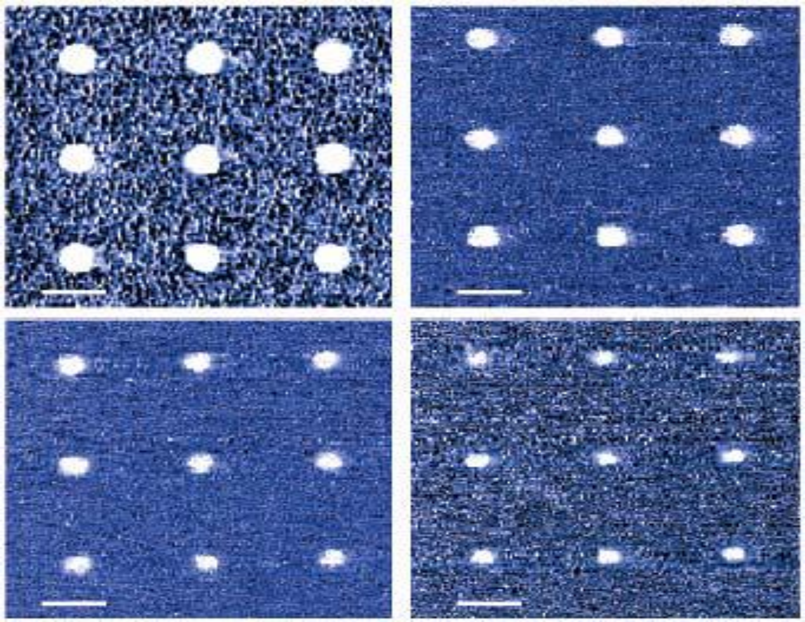
National ChungHsing University

Electrochemical Witting Nanostructures







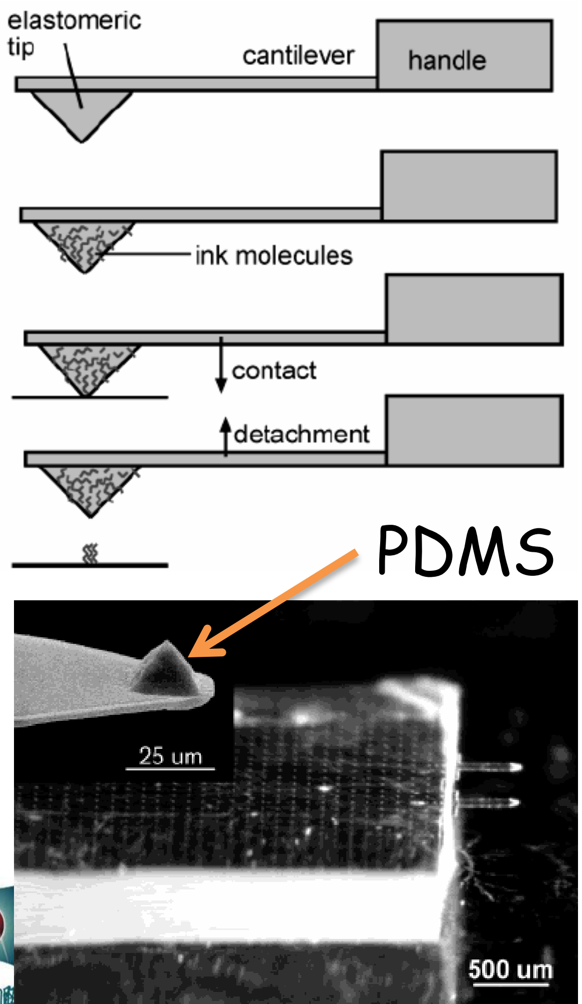
MHA dot array showing desorption at -750 mV as a function of time

- Electrochemical desorption of the peripheries of organic SAM.
- Free volume surrounding SAM and the greater ion accessibility to edge sites facilitate this process.

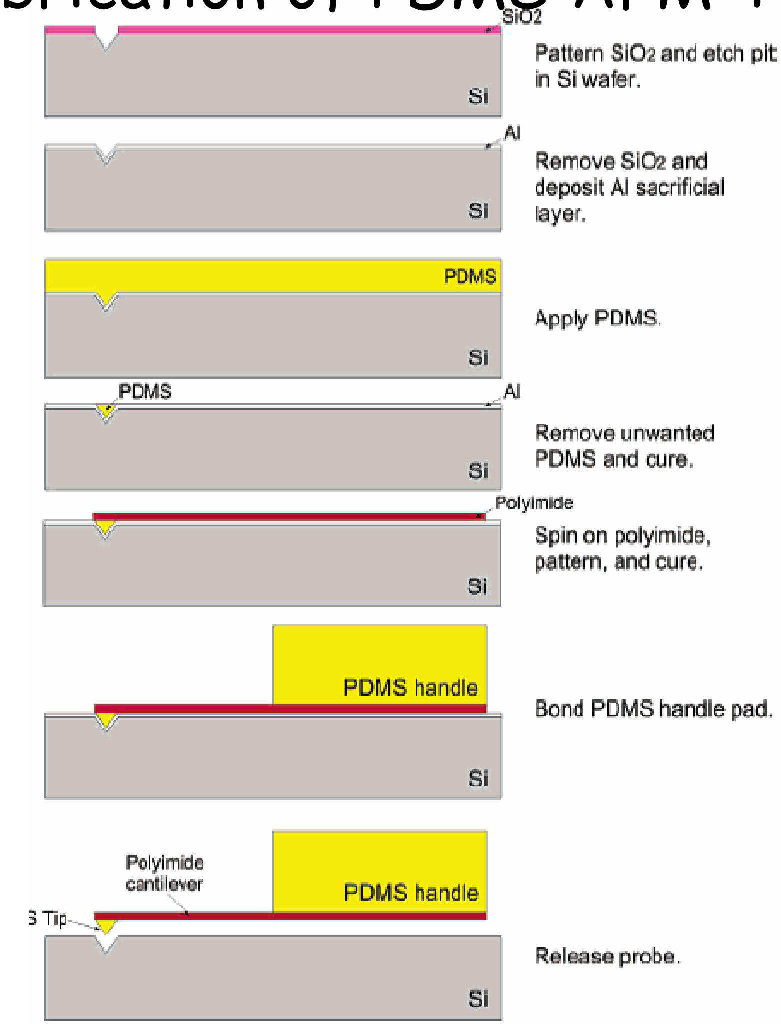
(*Nano Lett.* **2**, 1389, 2002)

Scanning Probe Contact Printing (SP-CP)

SP-CP

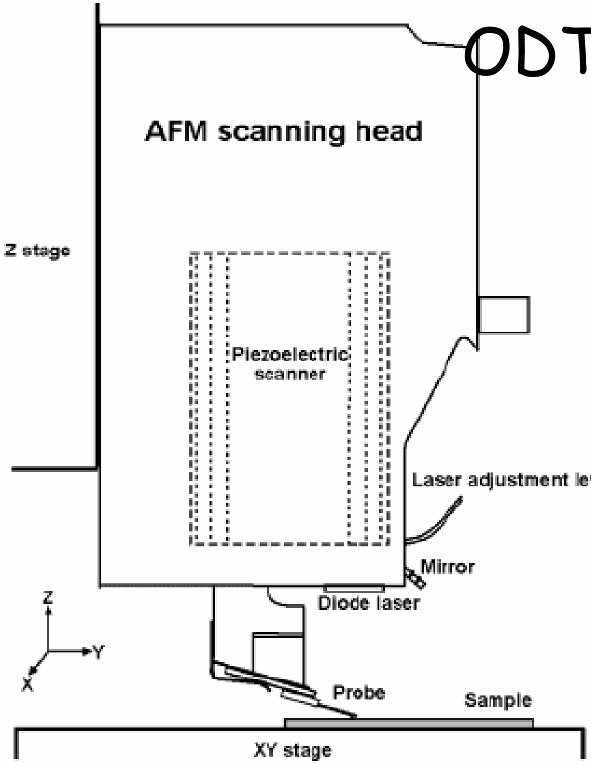


Fabrication of PDMS AFM Tips



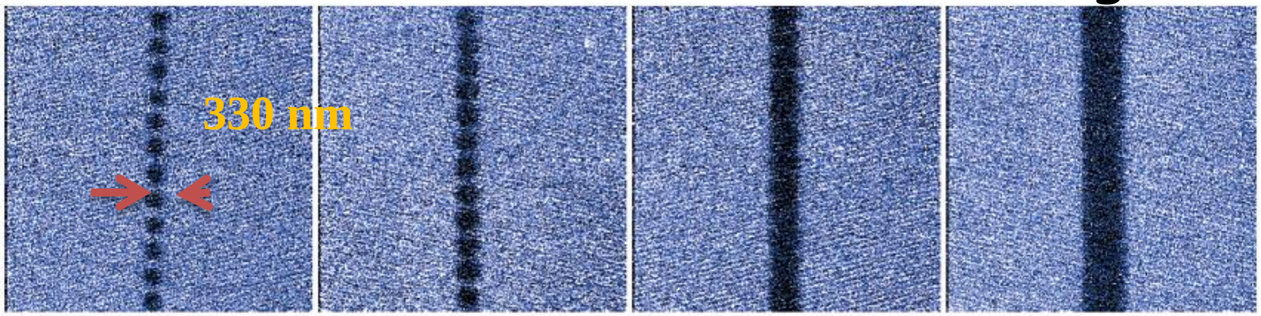
(*Langmuir* **19**, 8951, 2003)

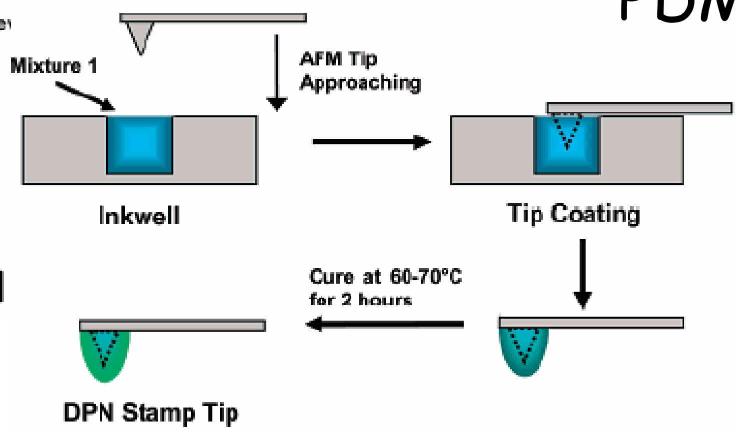
SP-CP and Beyond



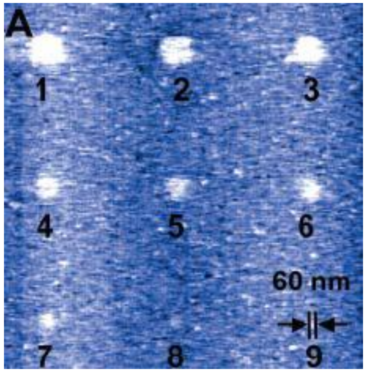
SP-CP Setup

ODT Lines Printed with Different Printing Time





PDMS Stamp Tip



- Soft PDMS tips allow easy absorption of inks.
- PDMS coated tip has better resolution than pure PDMS tip.

(Langmuir **19**, 8951, 2003; Nano Lett. **4**, 1469, 2004)

Summary of DPN

Advantages:

- High resolution (15 nm – sub-100 nm)
- Good registration
- Direct write capability (multiple inks)
- Biological compatible

Disadvantages:

- Serial process – low throughput
- Limited substrates and inks