Nanotechnology Breakthroughs of the Next 15 Years

2 – 5 years from now: 2010-2014

- Car tires that need air only once a year.
- Complete medical diagnostics on a single computer chip.
- Go-anywhere concentrators produce drinkable water from air.

5 – 10 years: 2014-2019

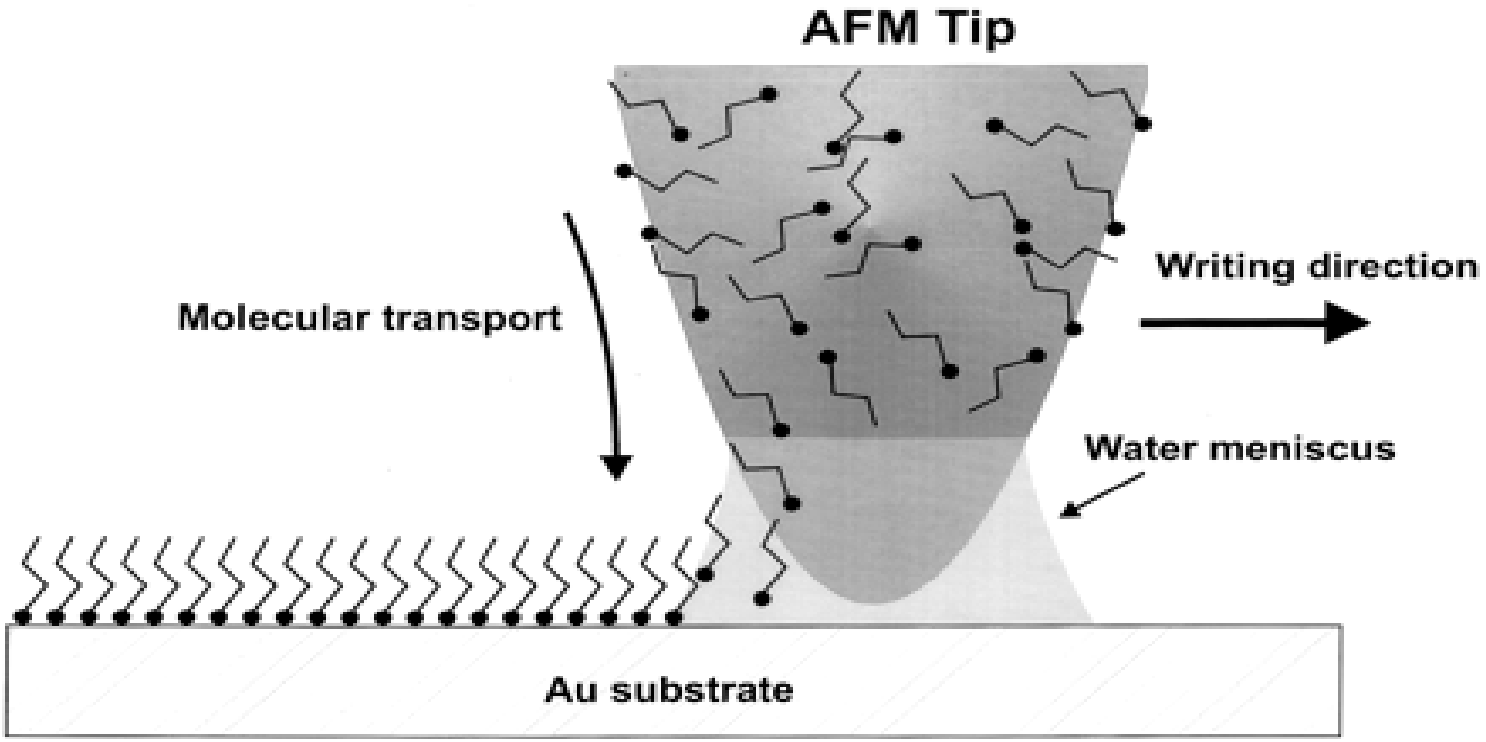
- Powerful computers you can wear or fold into your wallet.
- Drugs that turn AIDS and cancer into manageable conditions.
- Smart buildings that self-stabilize during earthquakes or bombings.

10 – 15 years: 2019-2024

- Artificial intelligence so sophisticated you can't tell if you're talking on the phone with a human or a machine.
- Paint-on computer and entertainment video displays.
- Elimination of invasive surgery, since bodies can be monitored and repaired almost totally from within.

The Future Trend Group, Feb. 13, 2009.

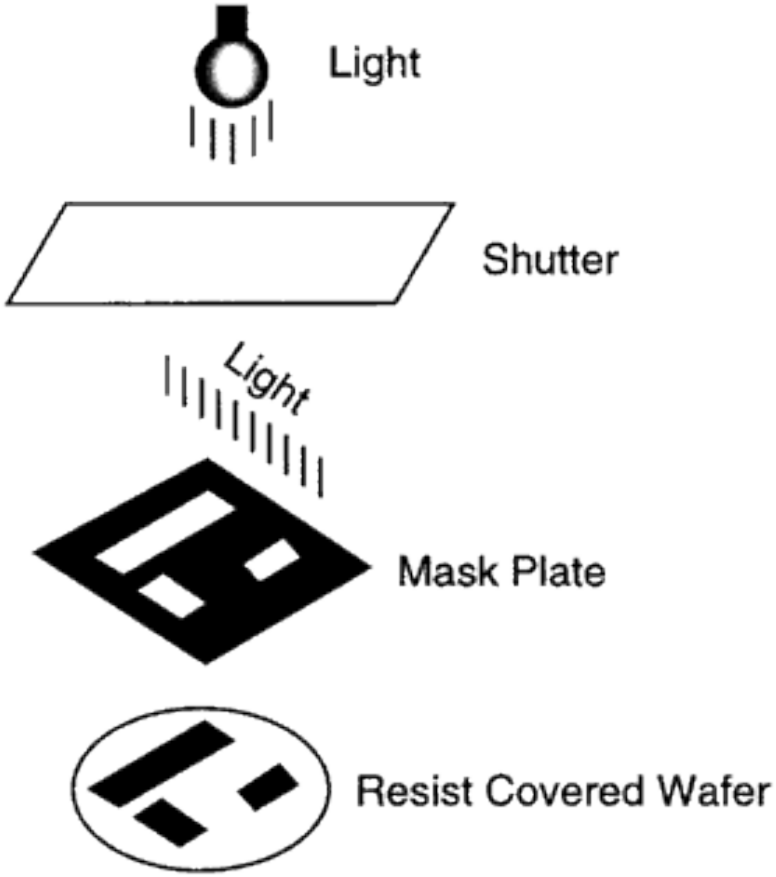
Lecture 5: Dip Pen Lithography based on SPM

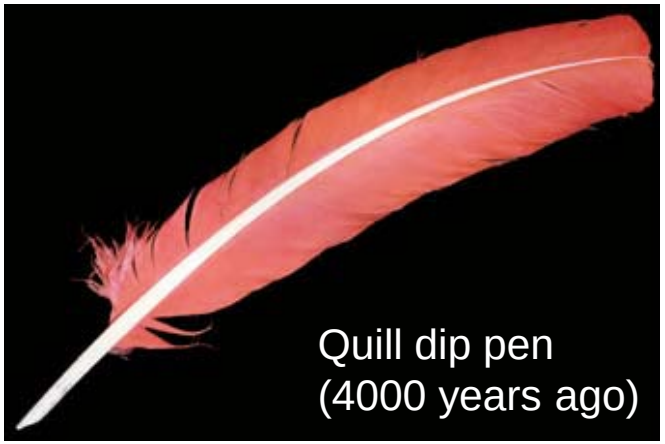


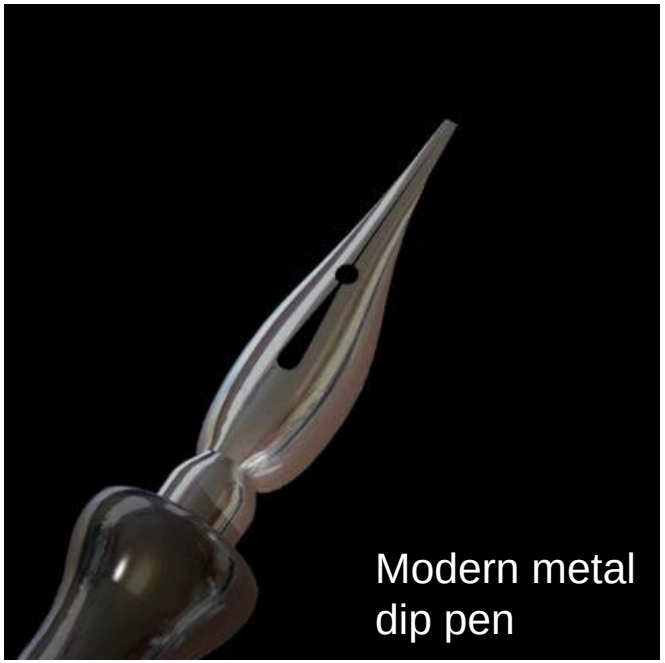
Schematic representation of DPN. A water meniscus forms between the AFM tip coated with ODT and the Au substrate. The size of the meniscus, which is controlled by relative humidity, affects the ODT transport rate, the effective tip-substrate contact area, and DPN resolution.

Science,1999,283,661-663

Photolithography & Dip Pens







Dip Pen Lithography based on SPM

- Lithographic methods are at the heart of modern-day microfabrication, nanotechnology, and molecular electronics.
- Conventional lithographic methods rely on patterning of a resistive film, followed by a chemical etch of the substrate.
- Dip-pen technology --- ink on a sharp object is transported to a paper substrate via capillary forces: approximately 4000 years old.
- These two concepts are related but disparate, with regard to scale and transport mechanism.
- dip-pen **nano**lithography (DPN) --- merging the two concepts, using an atomic force microscope (AFM) tip as a "**nib**", a solid-state substrate (in this case, Au) as "paper," and molecules with a chemical affinity for the solid-state substrate as "ink".
- Capillary transport of molecules from the AFM tip to the solid substrate is used in DPN to directly "write" patterns consisting of a relatively small collection of molecules in nanometer dimensions.

Science,1999,283,661-663

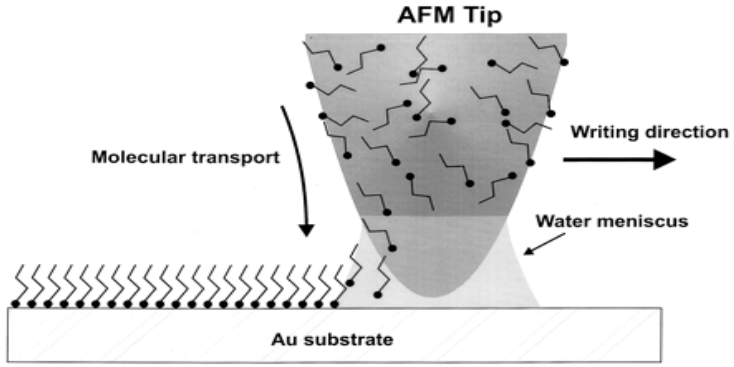
First example of DPN

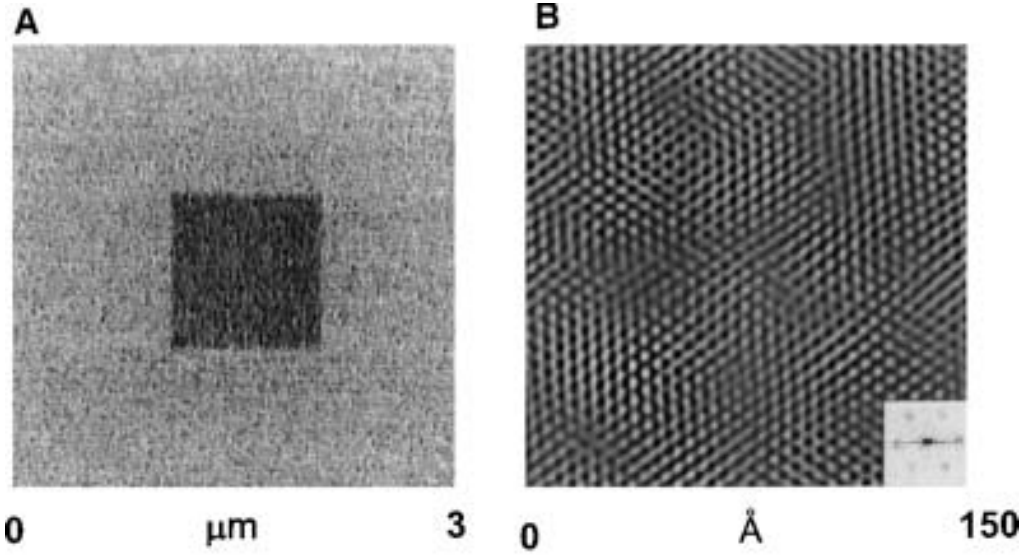
An atomic force microscope (AFM) tip is used to write alkanethiols with 30-nm line-width resolution on a gold thin film in a manner analogous to that of a dip pen. Molecules are delivered from the AFM tip to a solid substrate of interest via capillary transport, making DPN a potentially useful tool for creating and functionalizing nanoscale devices.

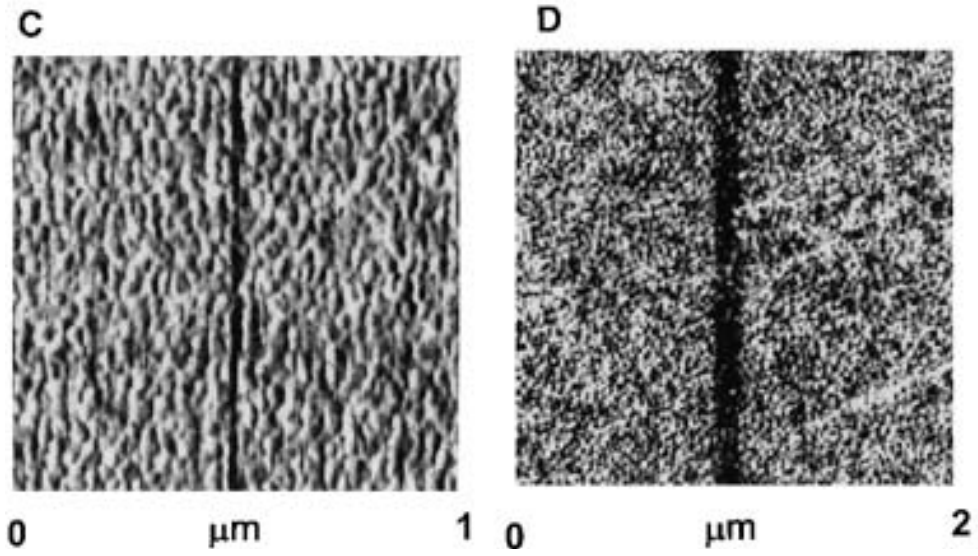
Science,1999,283,661-663

Patterning of ODT on gold: scanning

ODT







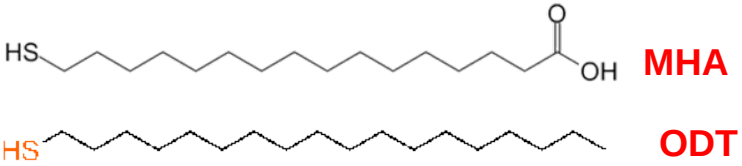
30 nm
34% humidity

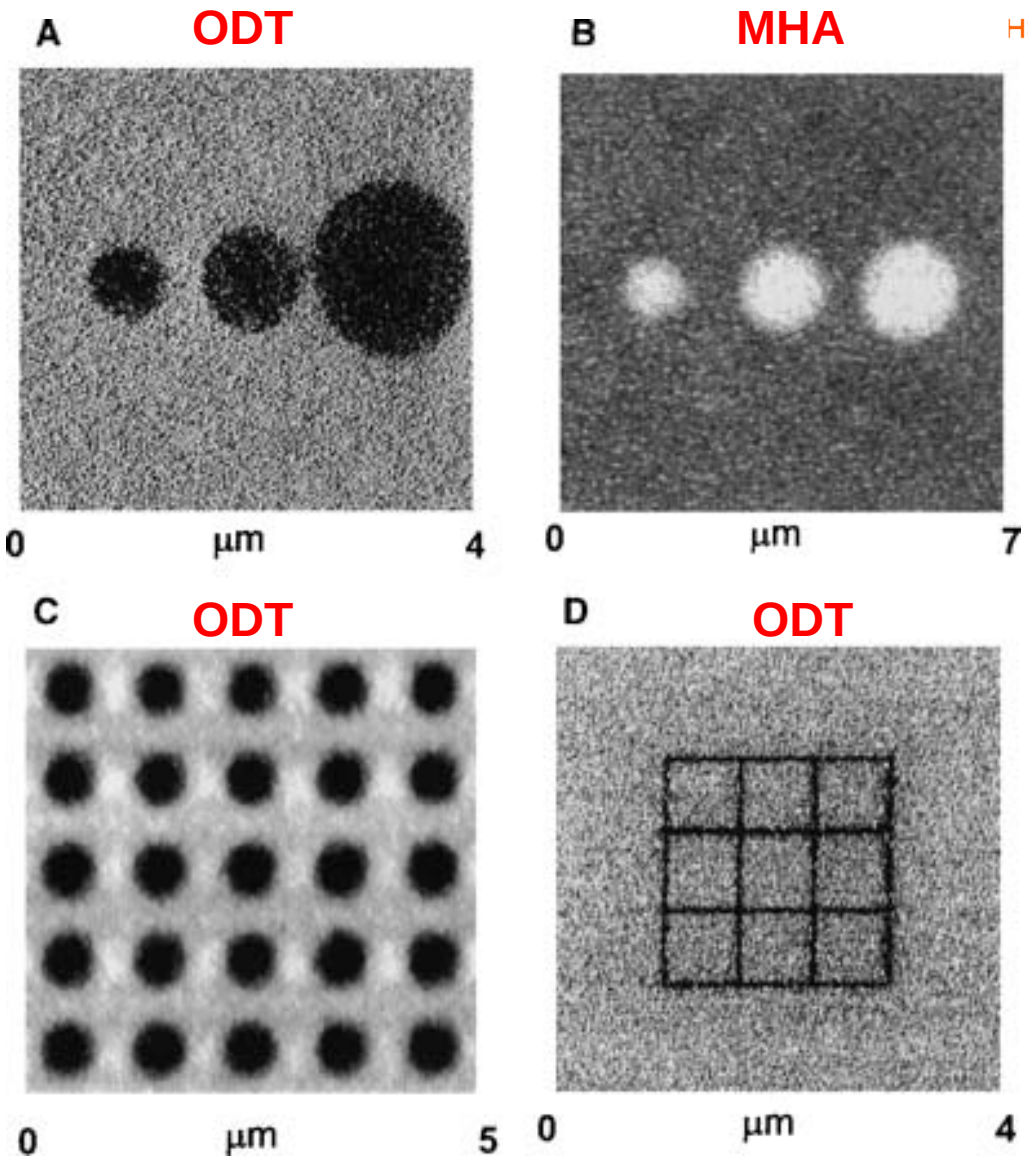
100 nm
42% humidity

(A) Lateral force image of a square of octadecanethiol **(ODT)** measuring 1 µm by 1 µm, deposited onto a Au substrate by DPN. This pattern was generated by scanning the 1-µm^2 area at a scan rate of 1 Hz for a period of 10 min at a relative humidity of 39%. Then the scan size was increased to 3 µm, and the scan rate was increased to 4 Hz while the image was recorded. The faster scan rate prevents ODT transport. (B) Lattice-resolved, lateral force image of an ODT SAM deposited onto Au(111)/mica by DPN. The image has been filtered with a fast Fourier transform (FFT), and the FFT of the raw data is shown in the lower right insert. The monolayer was generated by scanning a 1000 Å square area of the Au(111)/mica five times at a rate of 9 Hz at 39% relative humidity. (C) Lateral force image of a **30-nm-wide line** (3 µm long) deposited onto Au/mica by DPN. The line was generated by scanning the tip in a vertical line repeatedly for 5 min at a scan rate of 1 Hz. (D) Lateral force image of a **100-nm line** deposited on Au by DPN. The method of depositing this line is analogous to that used to generate the image in (C), but the writing time was 1.5 min. In all images, darker regions correspond to areas of relatively lower friction.

Science,1999,283,661-663

Patterning of ODT on gold: holding





(A) Lateral force image of an Au substrate after an AFM tip, which was coated with **ODT**, had been in contact with the substrate for **2, 4,** and **16 min** (left to right); the relative humidity was held constant at 45%, and the image was recorded at a scan rate of 4 Hz. (B) Lateral force image of dots of **16-mercaptohexadecanoic acid (MHA)** on a Au substrate. To generate the dots, an AFM tip coated with 16-mercaptohexadecanoic acid was held on the Au substrate for **10, 20,** and **40 s** (left to right). The relative humidity was 35%. The images show that the transport properties of 16-mercaptohexadecanoic acid and of ODT differ substantially. (C) Lateral force image of an array of dots generated by DPN. Each dot was generated by holding an ODT-coated tip in contact with the surface for ~**20 s**. Writing and recording conditions were the same as in (A). (D) Lateral force image of a molecule-based grid. Each line is 100 nm in width and 2 μm in length and required 1.5 min to write.

Different molecules result in different surface friction.

Science,1999,283,661-663

Some facts about DPN

- The resolution of DPN depends on several parameters:

1. the grain size of the substrate affects DPN resolution much as the texture of paper controls the resolution of conventional writing.
2. chemisorption and self assembly of the moleucles can be used to limit the diffusion of the molecules after deposition. The ODT patterns are stable whereas water forms metastable patterns.
3. the tip-substrate contact time and thus the scan speed influence DPN resolution.
4. relative humidity seems to affect the resolution of the lithographic process by controlling the rate of ODT transport from the tip to the substrate. The size of the water meniscus that bridges the tip and substrate depends on relative humidity. For example, the **30-nm**-wide line required **5 min** to generate in a **34%** relative humidity environment, whereas the **100-nm** line required **1.5 min** to generate in a **42%** relative humidity environment.

- DPN is a simple but powerful method for transporting molecules from AFM tips to substrates at resolutions comparable to those achieved with much more expensive and sophisticated competitive lithographic methods, such as **electron-beam lithography**.
- In practice, DPN experiments are generally limited by factors such as the **solubility** of the desired ink, the **transfer** and **stability** of the material within the water meniscus, and the **adsorption** of the material on the substrate surface. Thus, the **selection of stable inks** that can be transferred from the tip to the substrate is critical to a DPN experiment. Inks can be molecules, sol-gel materials, biological species like proteins.

Science,1999,283,661-663

Multiple Ink Nanolithography:

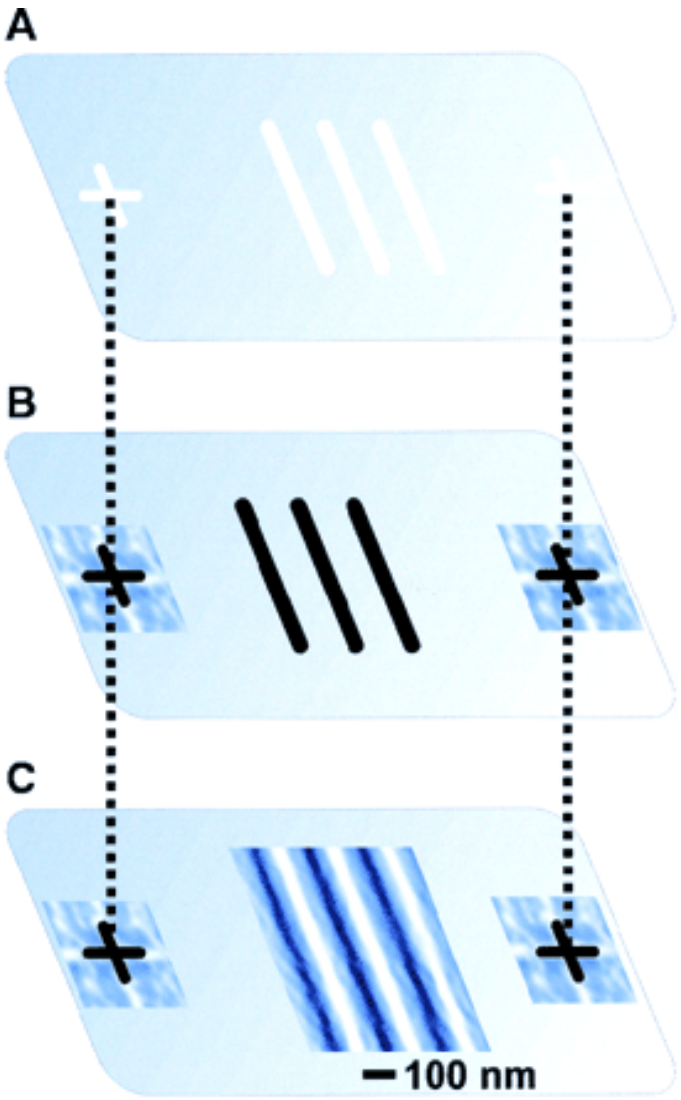


Diagram depicting the method for generating aligned soft nanostructures. (A) The first pattern is generated with **MHA** (denoted by white lines), along with microscopic alignment marks (cross-hairs), by DPN. The actual lines are not imaged to preserve the pristine nature of the nanostructure. (B) The second set of parallel lines is generated with **ODT** molecules, on the basis of coordinates calculated from the positions of the alignment marks in (A). (C) LFM image of the interdigitated 50-nm-wide lines separated by 70 nm.

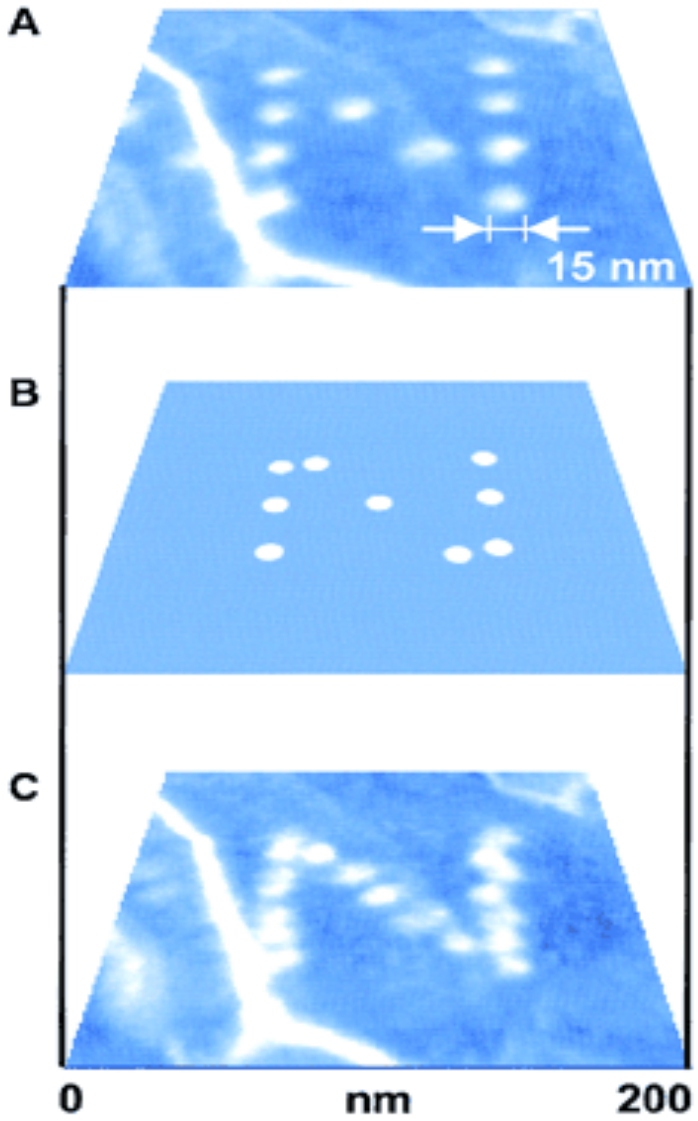
Science,1999,286,523-525

Second paper on the same topic in the same journal in the same year !

Multiple Ink Nanolithography:

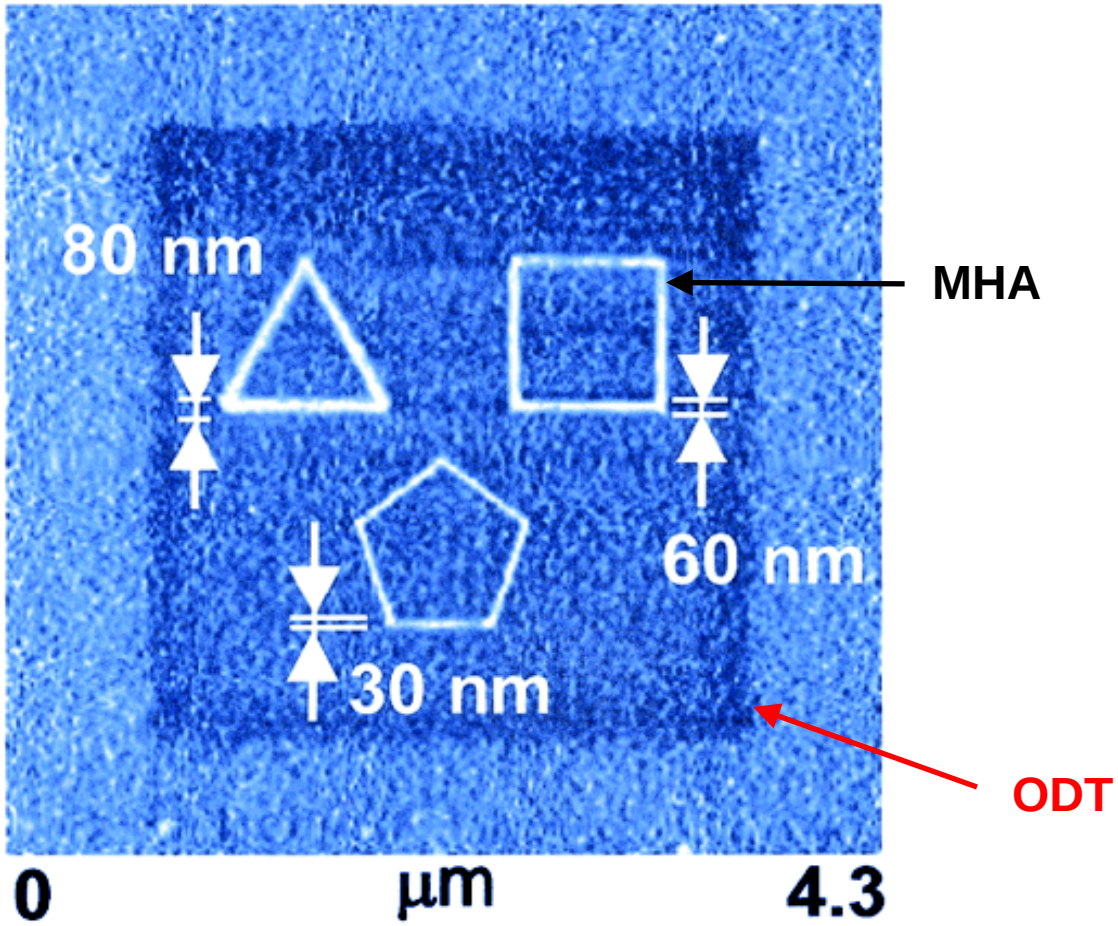
- The formation of intricate nanostructures will require the ability to maintain surface registry during several patterning steps.
- At present, stamping procedures pose significant alignment problems with respect to multiple inks.
- Traditional high-resolution techniques, such as electron and ion beam lithography, rely on resist layers and the back-filling of etched areas with component molecules. These indirect patterning approaches can compromise the chemical purity of the structures generated and pose limitations on the types of materials and number of different materials that can be patterned.
- A scanning probe method, dip-pen nanolithography (DPN), can be used to pattern monolayers of different organic molecules down to a 5-nanometer separation.
- An "overwriting" capability of DPN allows one nanostructure to be generated and the areas surrounding that nanostructure to be filled in with a second type of "ink."

Science,1999,286,523-525



Schematic diagram with lateral force microscopy (LFM) images of nanoscale molecular dots showing the essential requirements for patterning and aligning multiple nanostructures by DPN. (A) A pattern of 15-nm-diameter **MHA** dots on Au(111) imaged by LFM with an MHA-coated tip. (B) Anticipated placement of the second set of **MHA** dots as determined by calculated coordinates based on the positions of the first set of dots. (C) Image after a second pattern of MHA nanodots has been placed within the first set of MHA dots. The white jagged line is an Au(111) grain boundary.

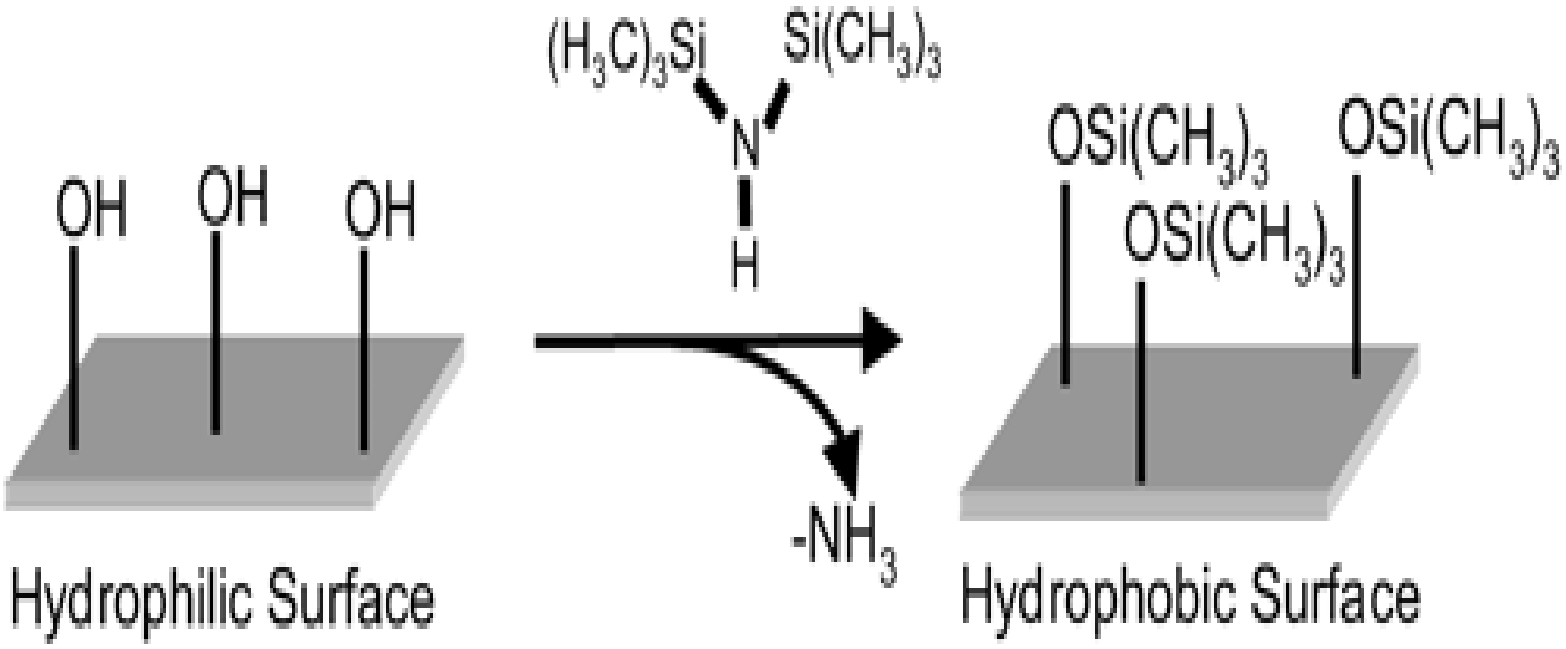
Science,1999,286,523-525



SAMs in the shapes of polygons drawn by DPN with **MHA** on an amorphous Au surface. An **ODT** SAM has been overwritten around the polygons.

Science,1999,286,523-525

"Dip-Pen" Nanolithography on Semiconductor Surfaces :



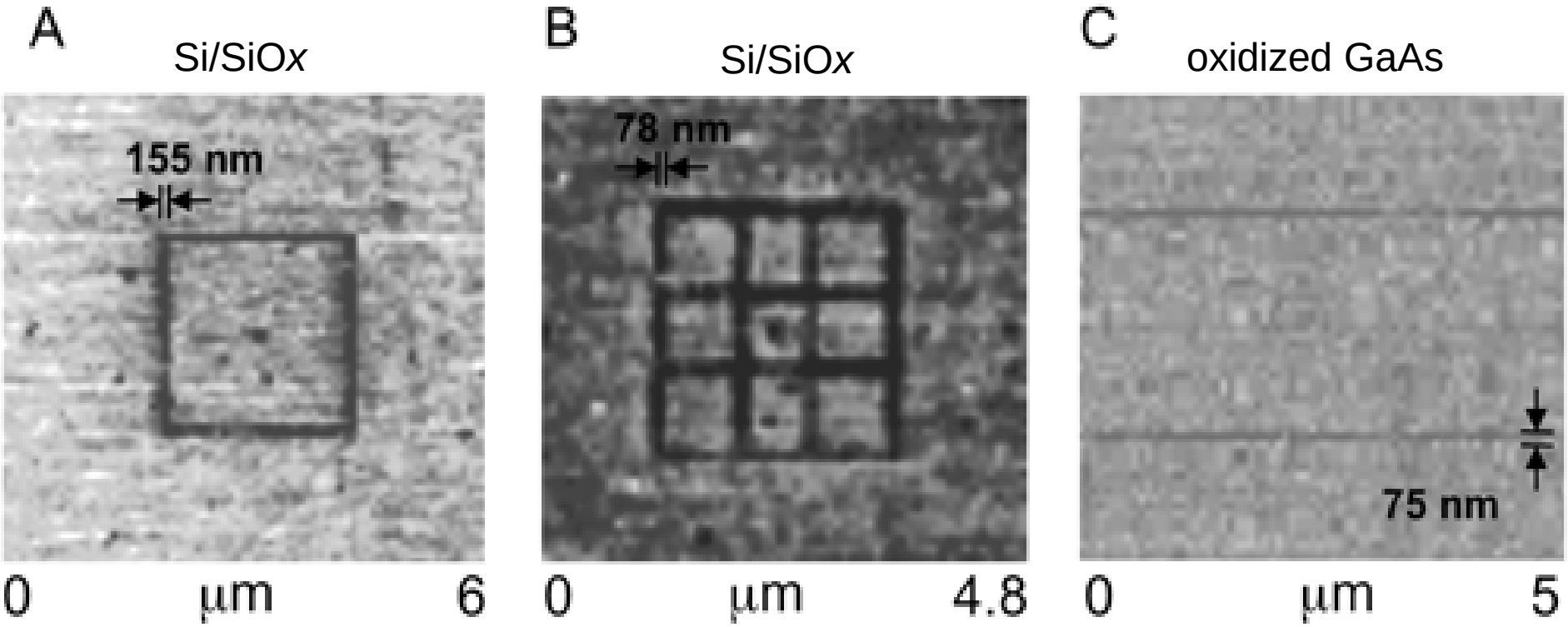
Surface: hydrophilic → hydrophobic

JACS,2001,123- 7887-7889

"Dip-Pen" Nanolithography on Semiconductor Surfaces :

- Dip-Pen Nanolithography (DPN) can not only apply to gold surface using alkyl or aryl thiols as inks, but also to semiconductor surfaces, such as silicon and gallium arsenide.
- Hexamethyldisilazane (HMDS) is used as the ink to pattern and modify (polarity) the surface of semiconductors.
- Lateral force microscopy (LFM) can be used to differentiate between oxidized semiconductor surfaces and patterned areas with the deposited monolayers of HMDS.
- The choice of the silazane ink is a critical component of the process since the traditional adsorbates such as trichlorosilanes are incompatible with the water meniscus and polymerize during ink deposition.
- This work provides insight into additional factors, such as temperature and adsorbate reactivity, that control the rate of the DPN process and paves the way for researchers to interface **organic and biological structures** generated via DPN with electronically important **semiconductor** substrates.

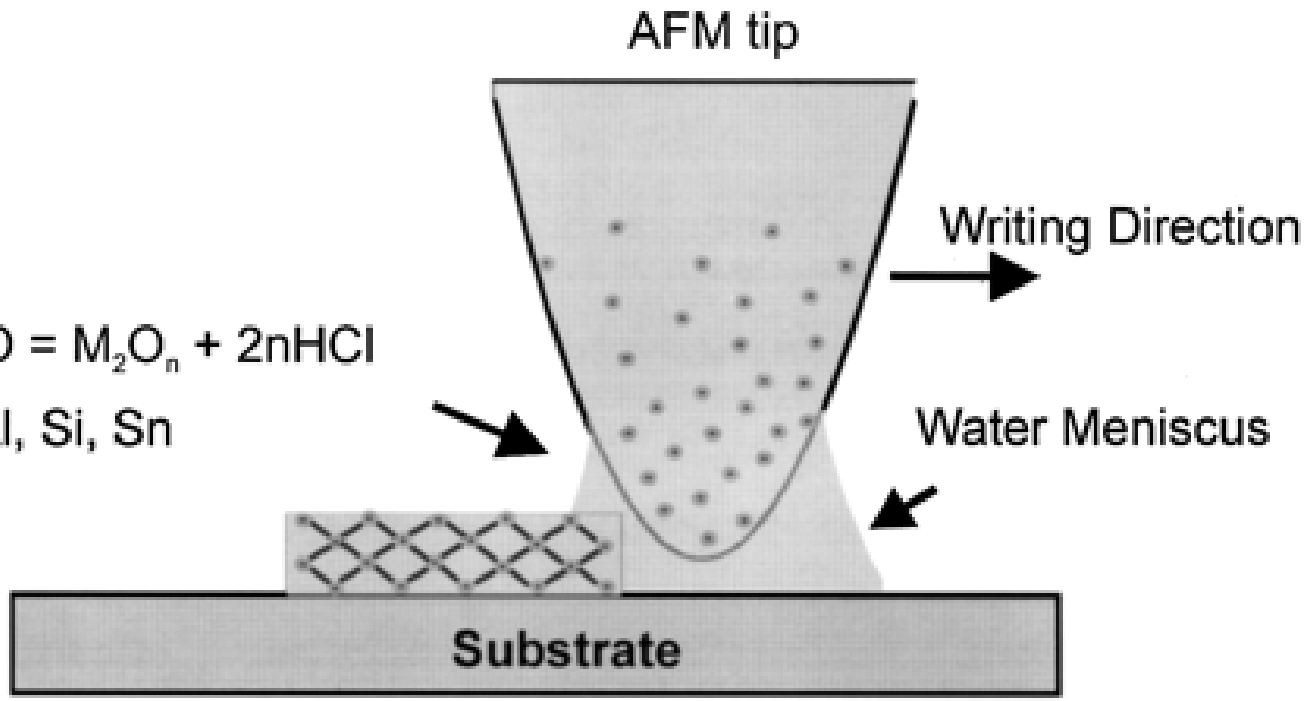
JACS,2001,123- 7887-7889



Lateral force microscopy (LFM) images of DPN-generated TMS monolayer patterns on semiconductor surfaces. All LFM images were recorded at a scan rate of 4 Hz. In all cases lighter contrast areas (higher friction) correspond to the hydrophilic (-OH group rich) semiconductor surface and darker areas (lower friction) are due to the deposited silazane via DPN: (a) square TMS pattern (2.4 m edge width) on Si/SiO*x* with a writing speed of 0.08 m/s; (b) a TMS grid on Si/SiO*x* substrate (2.4 m edge width) with a writing speed of 0.04 m/s; and (c) a parallel line pattern on oxidized GaAs with a writing speed of 0.02 m/s.

JACS,2001,123- 7887-7889

Patterning of Solid-State Features

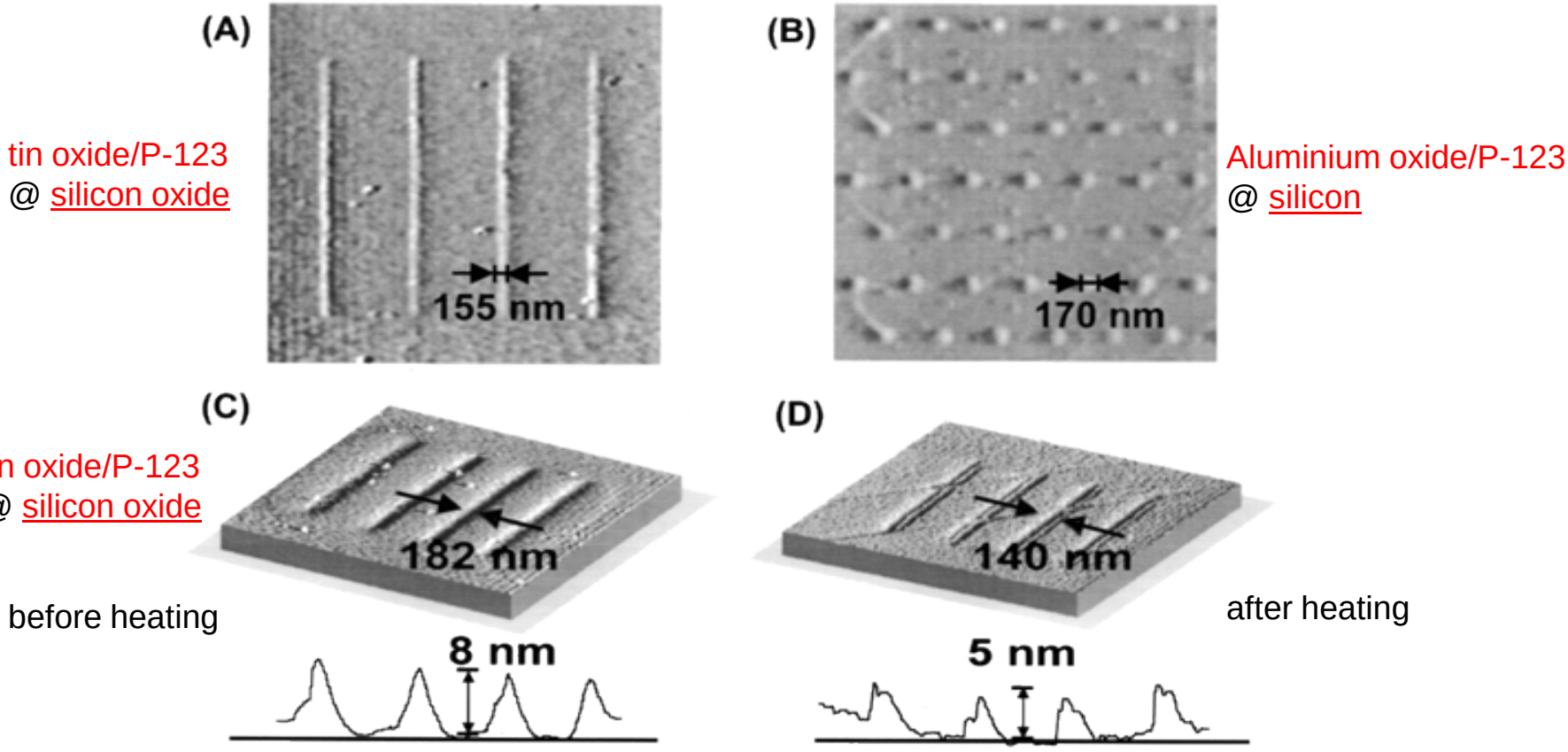


JACS,2002,124,1560-1561

"Dip-Pen" Patterning of Solid-State Features :

- A DPN based method for the direct patterning of organic/inorganic composite nanostructures on silicon and oxidized silicon substrates.
- It works by the hydrolysis of metal precursors in the meniscus between an AFM tip and a surface according to the reaction $2MCl_n + nH_2O \rightarrow M_2O_n + 2nHCl$; M = Al, Si, and Sn.
- The inks are hybrid composites of inorganic salts with amphiphilic block copolymer surfactants.
- Three proof-of-concept systems involving Al_2O_3, SiO_2, and SnO_2 nanostructures on silicon and silicon oxide surfaces have been studied.
- Arrays of dots and lines can be written easily with control over feature size and shape on the sub-200 nm level.
- This work is important because it opens up the opportunity for using DPN to deposit solid-state materials rather than simple organic molecules onto surfaces.

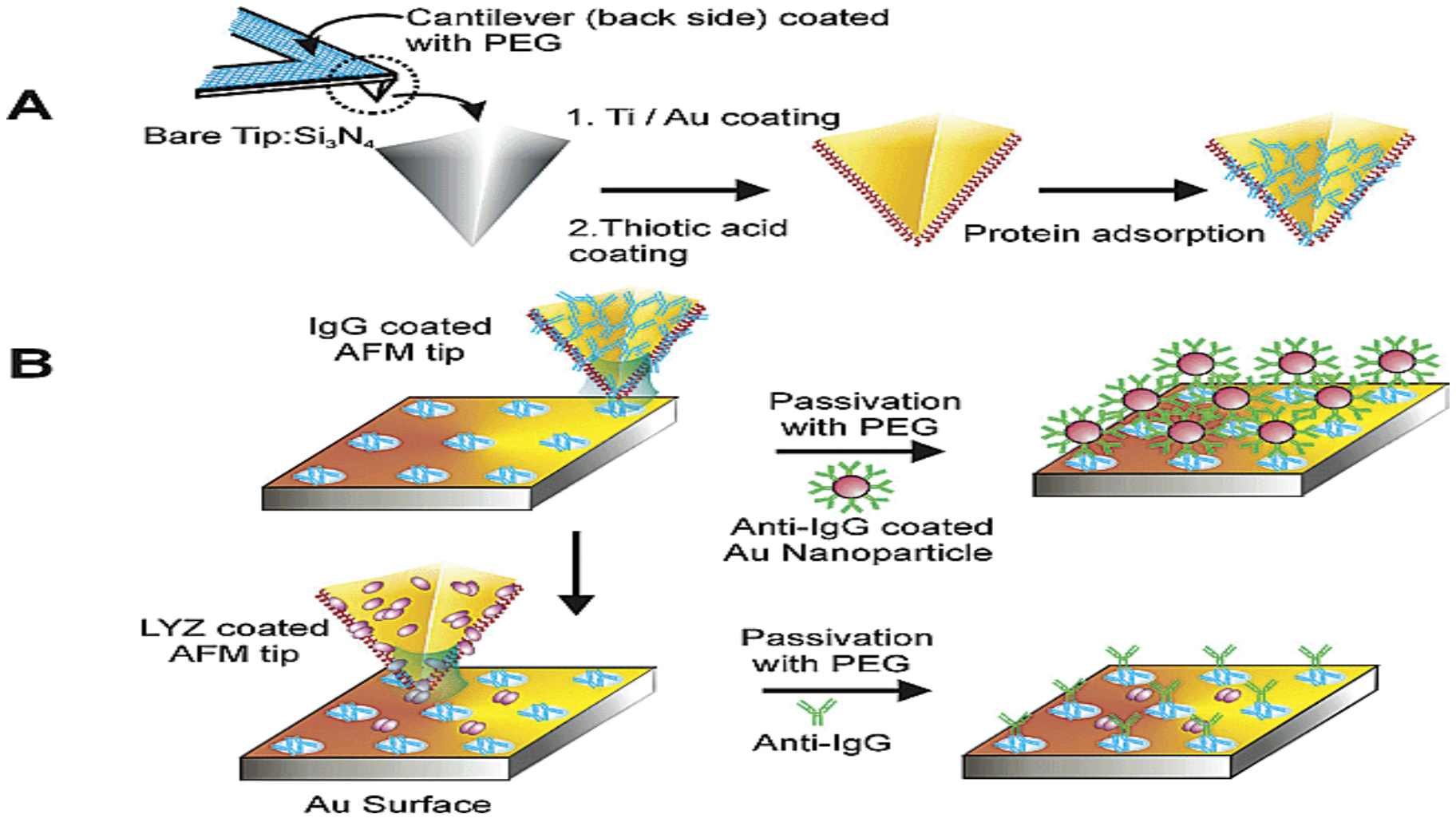
JACS,2002,124,1560-1561



(a) Topographic AFM image of composite tin oxide/P-123 nanostructures on silicon oxide; the writing speed for each line is 0.2 m/s. (b) Lateral force microscope (LFM) image of a dot array of aluminum oxide/P-123 composite nanostructures formed on silicon; the holding time for each dot is 1 s. AFM images collected before (c) and after (d) heating silicon oxide/P-123 composite nanostructures in air at 400 C for 2 h; the writing speed is 0.1 m/s. Note the lateral dimensions are enlarged due to tip convolution.

JACS,2002,124,1560-1561

"Dip-Pen" Patterning of Proteins



(A) Tip Modification Scheme; (B) Protein Patterning Schemes. lysozyme (LYZ), immunoglobulin-gamma (IgG)

JACS,2003,125,5588-5589

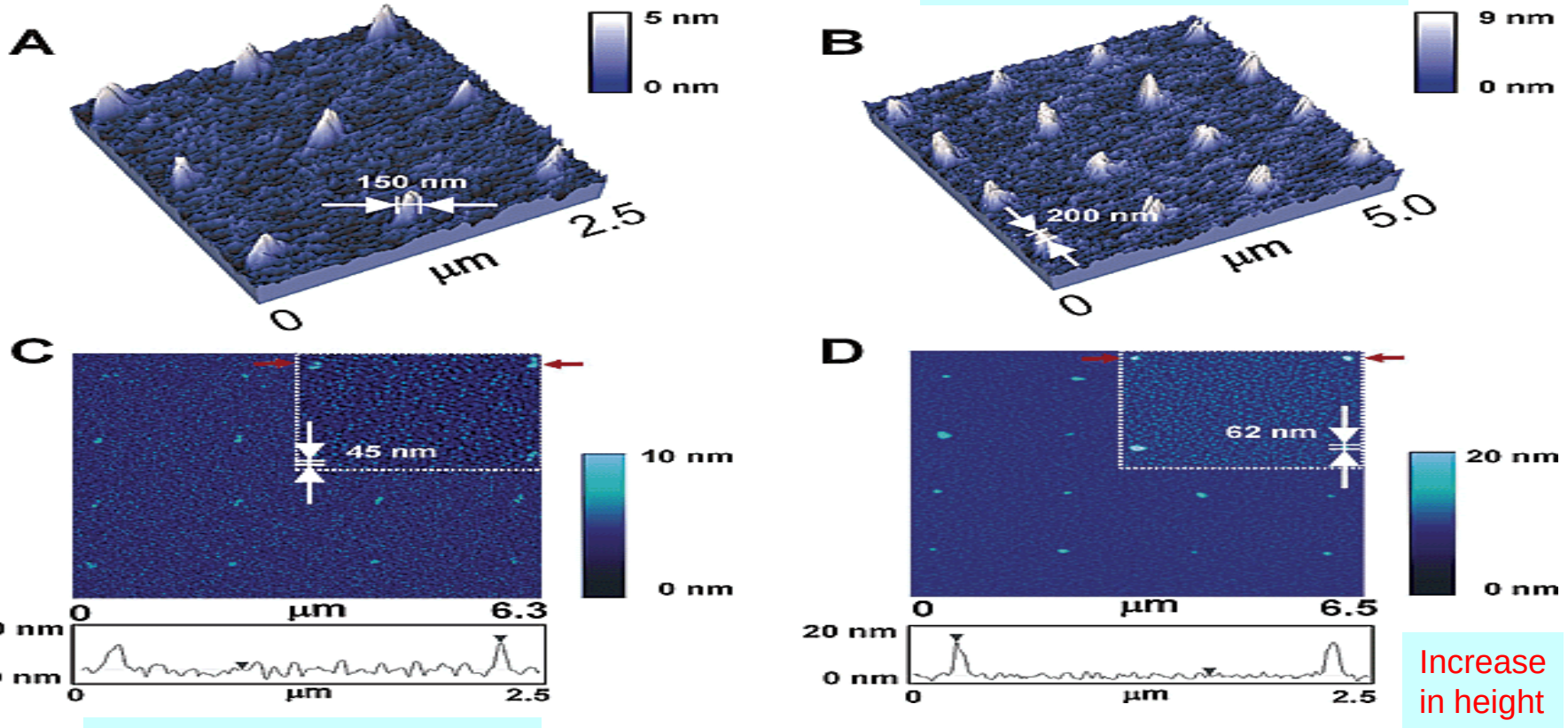
"Dip-Pen" Patterning of Proteins :

- Microarrays of biomolecules such as DNA and proteins have proven useful as high-throughput screening tools in proteomics, genomics, and the identification of new pharmaceutical compounds.
- Biorecognition between proteins is inherently a *nano-* rather than a *micro*scopic phenomenon, and thus requires nanoscale arrays.
- As the complexity of these arrays and corresponding number of features increase, the ability to reduce feature size becomes more important, especially since the area occupied by an array will affect the amount and volume of a sample that can be used with a particular chip.
- To be able to generate nanoarrays of *multicomponent* systems, it is imperative that new surface analytical tools as well as the complementary chemistry be developed for directly placing a set of different protein structures on a surface of interest with nanoscale resolution, high-registration alignment capabilities, and control over the biological activity of the resulting structures.
- Chemically modified AFM tips and dip-pen nanolithography (DPN) can be used to generate two-component nanoarrays of native proteins that are biologically active and capable of recognizing a biological complement in solution.

JACS,2003,125,5588-5589

lysozyme

IgG *(immunoglobulin-gamma)*



Increase in height

Before Treated with anti-IgG coated Au nanoparticles

After treated with anti-IgG coated Au nanoparticles

Protein nanoarrays prepared via direct-write DPN. (A) Contact mode image (contact force 0.1 nN) of lysozyme nanodot arrays. Each dot took 20 s to form. (B) Contact mode image (contact force 0.1 nN) of IgG nanodot arrays. Each dot took 30 s to form. An IgG nanodot array before (C) and after (D) treatment with a solution anti-IgG coated Au nanoparticles: Images were taken at 0.5-Hz scan rate in tapping mode. Each dot took 5 s to form.

JACS,2003,125,5588-5589

Mixed array of IgG and Lysozyme
After treated with anti-IgG

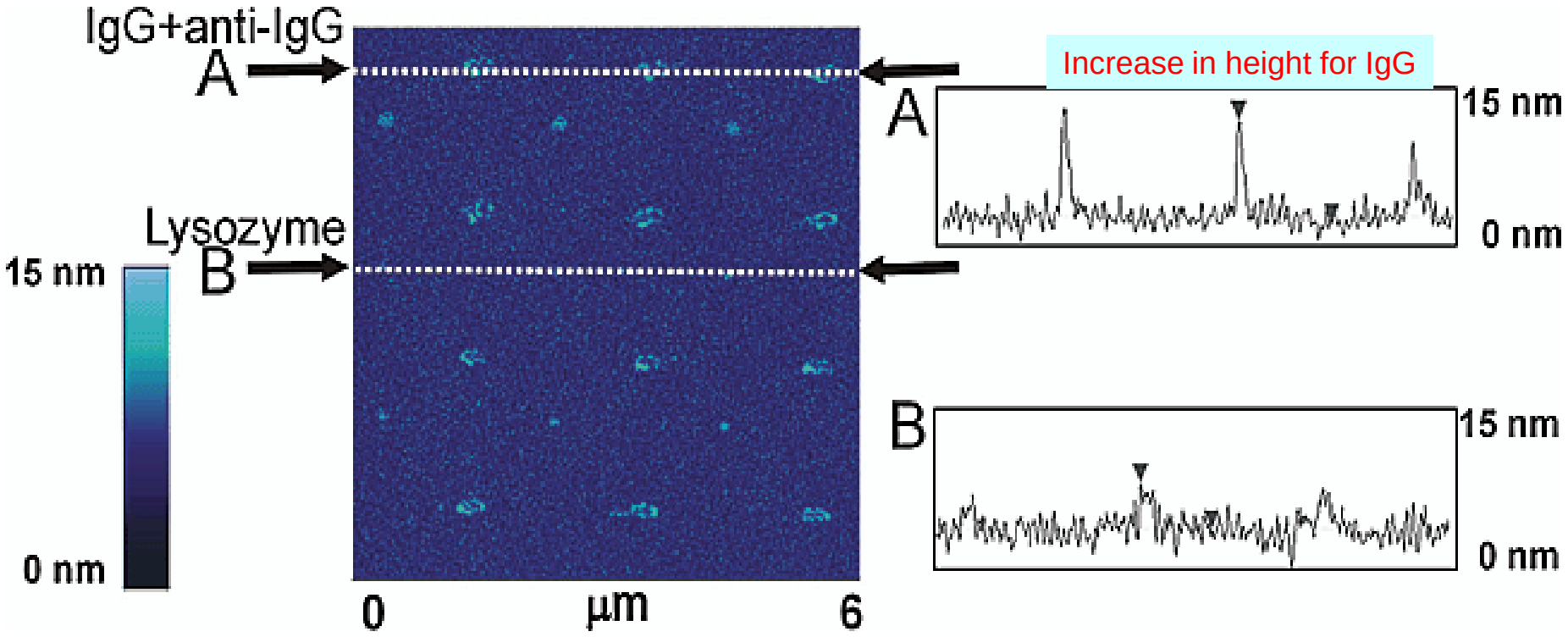
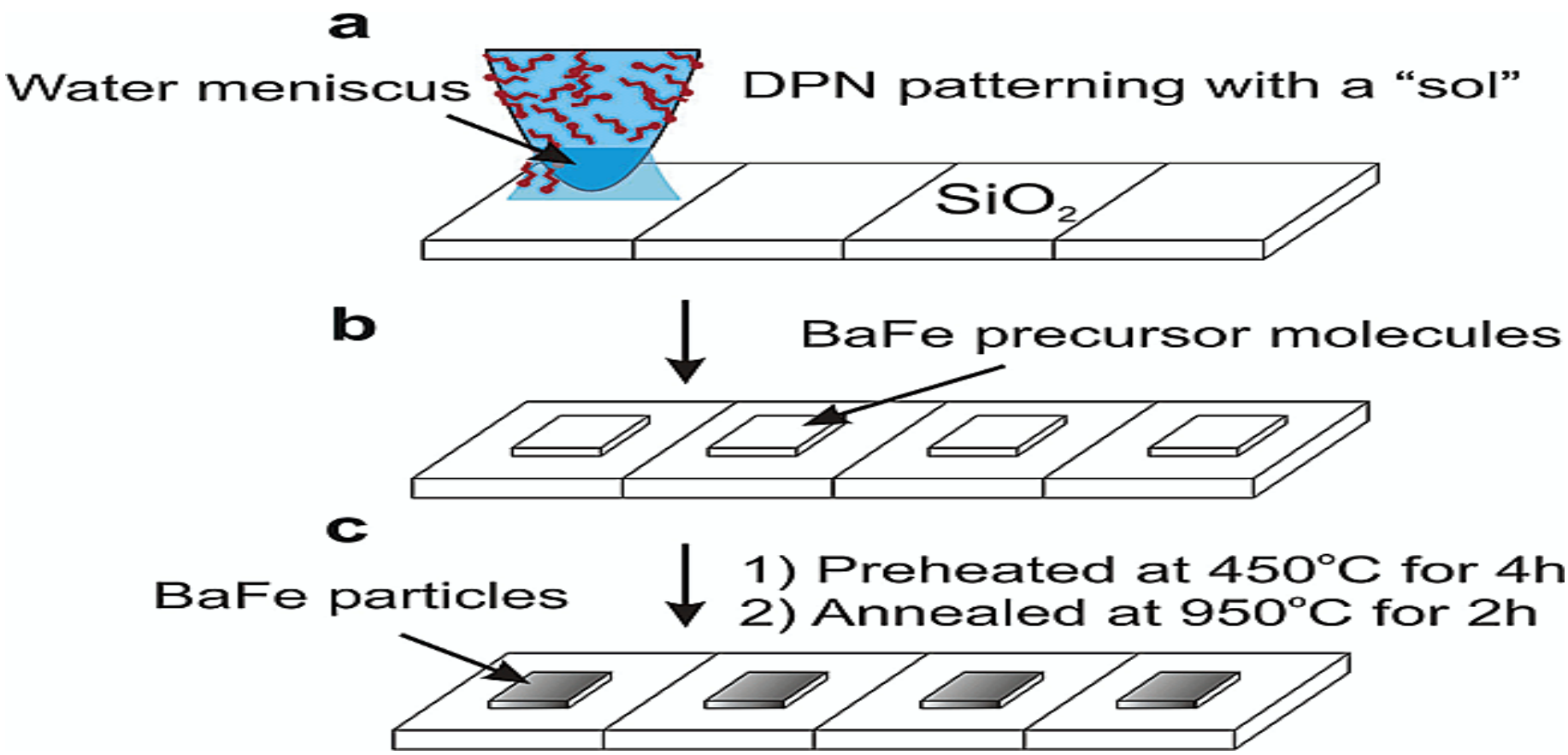


Figure 2 Two-component protein pattern after reaction with anti-IgG. (A) A height increase of 5.5 ± 0.9 nm (*n* =10) in the IgG features is observed by AFM. (B) No height increase is observed. The image was taken under the same conditions in Figure 1 (C) and (D).

JACS,2003,125,5588-5589

"Dip-Pen" Patterning of magnetic materials: *approach to high density recording and storage*



Schematic diagram depicting the patterning of magnetic BaFe nanostructures on silicon oxide. (a) An atomic force microscope (AFM) tip coated with a precursor solution of barium ferrite is brought into contact with the silicon oxide substrate. (b) The solution is transferred to the substrate as the tip is traversed across it. (c) Post-annealing yields the desired BaFe nanostructures.

NANO LETTERS,2003,3,757-760

"Dip-Pen" Patterning of magnetic materials: *approach to high density recording and storage*

- Over the past decade, there has been considerable interest in methods for synthesizing and patterning nanoscale magnetic materials.
- These nanomaterials show novel size-dependent properties, are potentially useful for high-density recording.
- Two of the main challenges in this field are:
  (a) site- and shape-specific patterning of hard magnetic nanostructure on the sub-100 nm scale;
  (b) ability to reliably and reproducibly read/write such minute features.
- The conventional top-down approach in recording media is plagued by the difficulties of etching and patterning novel hard magnetic systems, especially as the individual recording elements approach the superparamagnetic limit at room temperature operations.
- DPN can be used as a direct-write method for fabricating "hard" magnetic barium hexaferrite, $BaFe_{12}O_{19}$ (BaFe), nanostructures.
- This method utilizes a conventional atomic force microscope tip, coated with the BaFe precursor solution, to generate patterns that can be post-treated at elevated temperature to generate magnetic features consisting of barium ferrite in its hexagonal magnetoplumbite (M-type) structure.
- Features ranging from several hundred nm down to below 100 nm were generated.

NANO LETTERS,2003,3,757-760

Features down to below 100 nm were generated

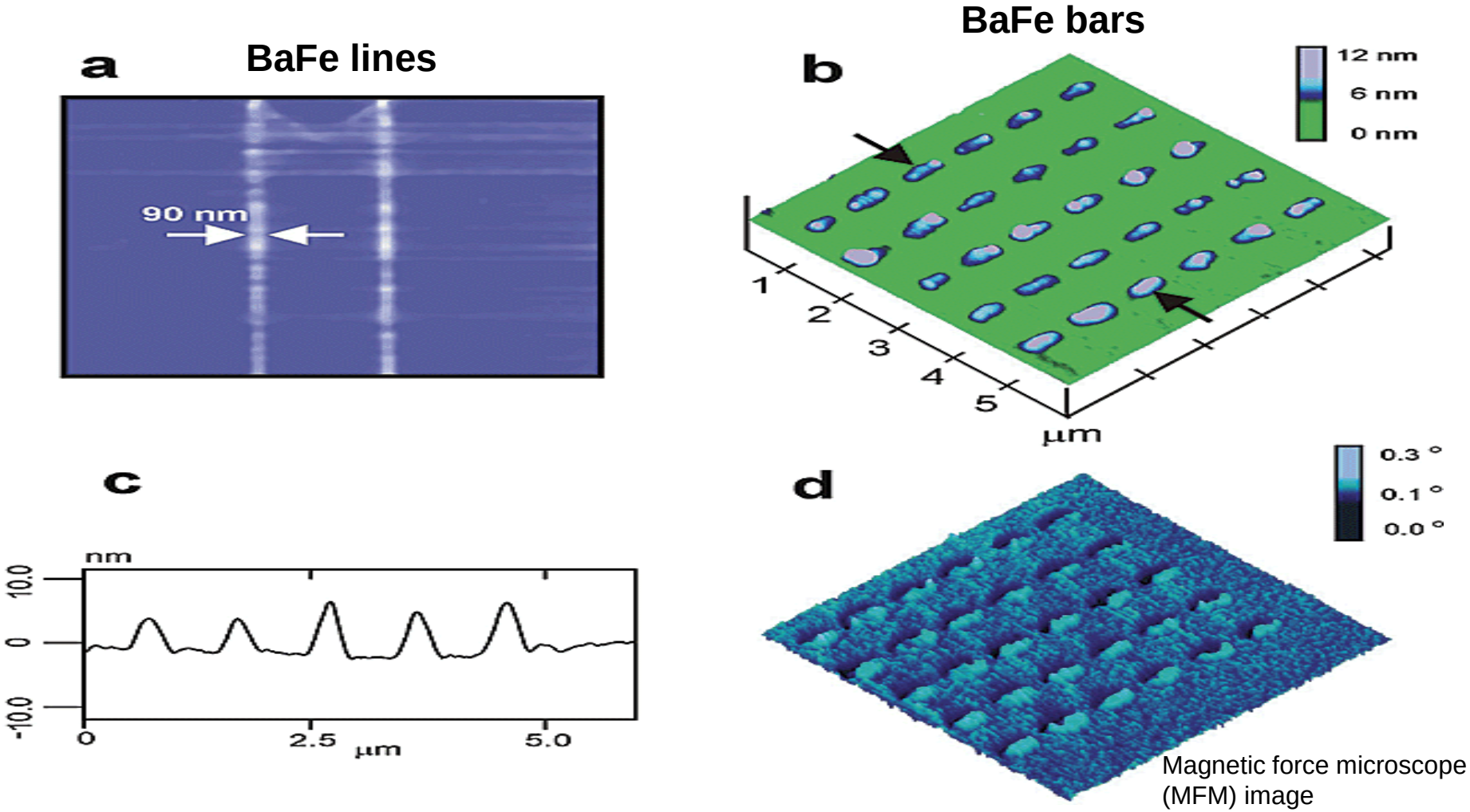
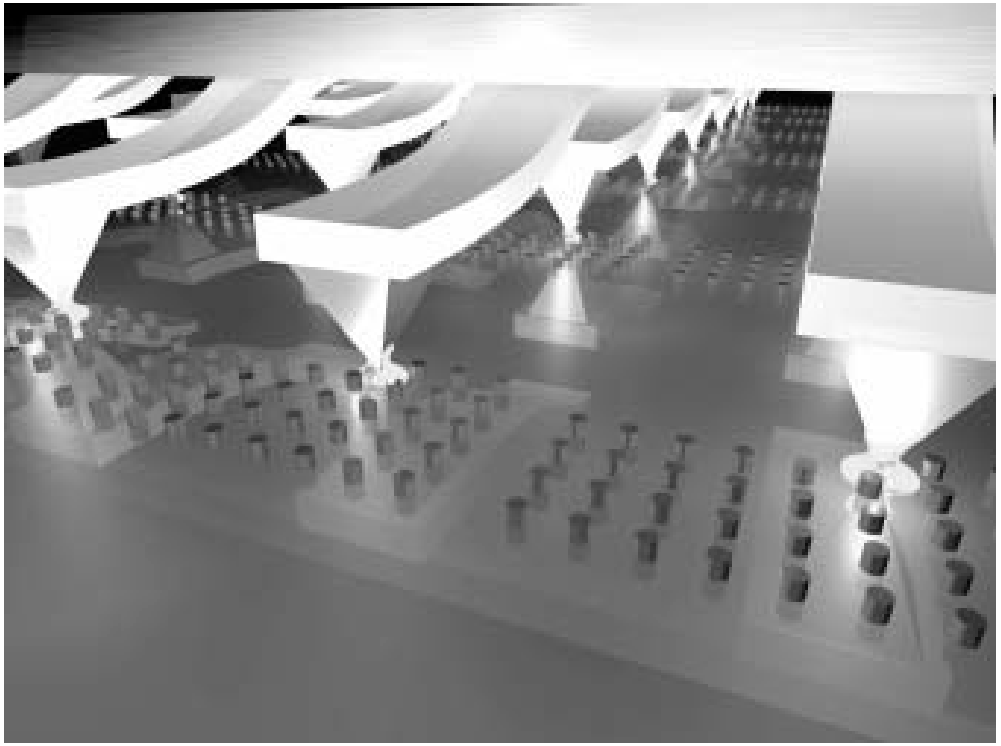


Figure 3 Scanning probe microscope (SPM) studies of the BaFe patterns. (a) Topographic AFM image of magnetic BaFe lines on the silicon oxide substrate. The speed for the BaFe precursor deposition is 0.2 m/s. (b) Topographic AFM image of an array of magnetic bars. The deposition speed is 0.1 m/s. (c) Cross-sectional topography trace of a line (marked by the arrows in b). (d) Magnetic force microscope (MFM) image obtained from these magnetic bars.

NANO LETTERS,2003,3,757-760

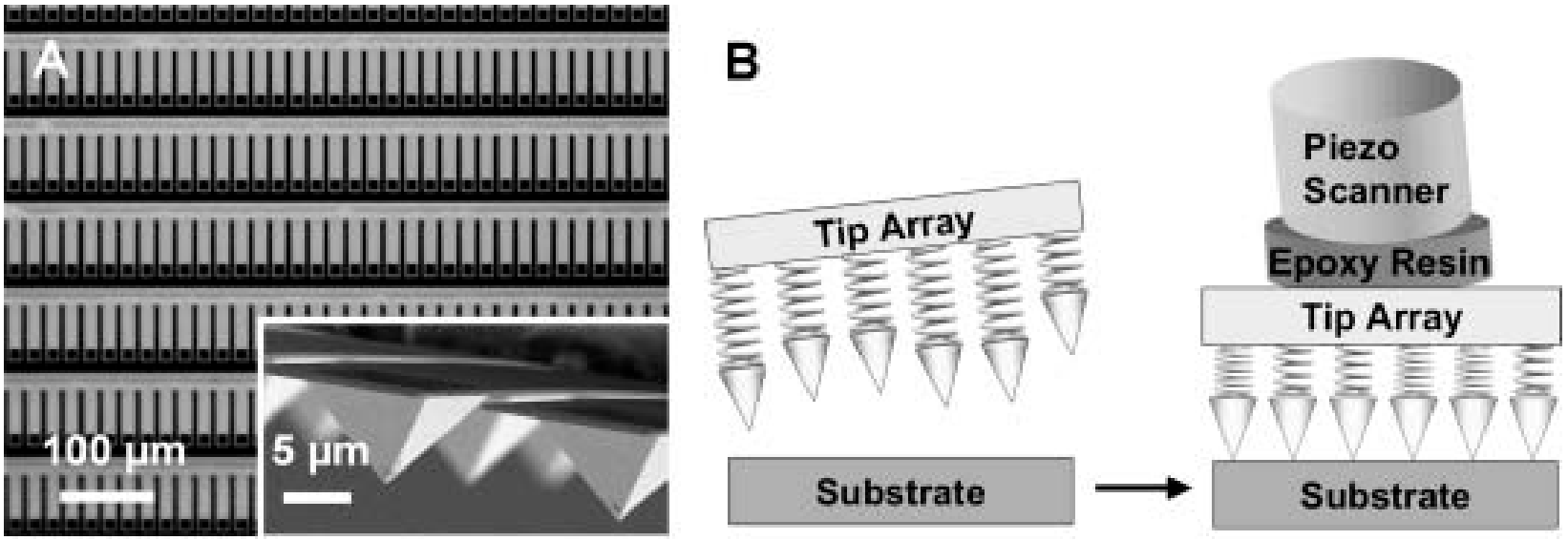
Massively Parallel Dip-Pen Nanolithography with 55 000-Pen Two-Dimensional Arrays



Scheme 1. Massively parallel DPN with a passive, wire-free, 2D cantilever array

Mirkin, C. A. et al. *Angew. Chem., Int. Ed.* **2006**, *45*, 7220–7223.

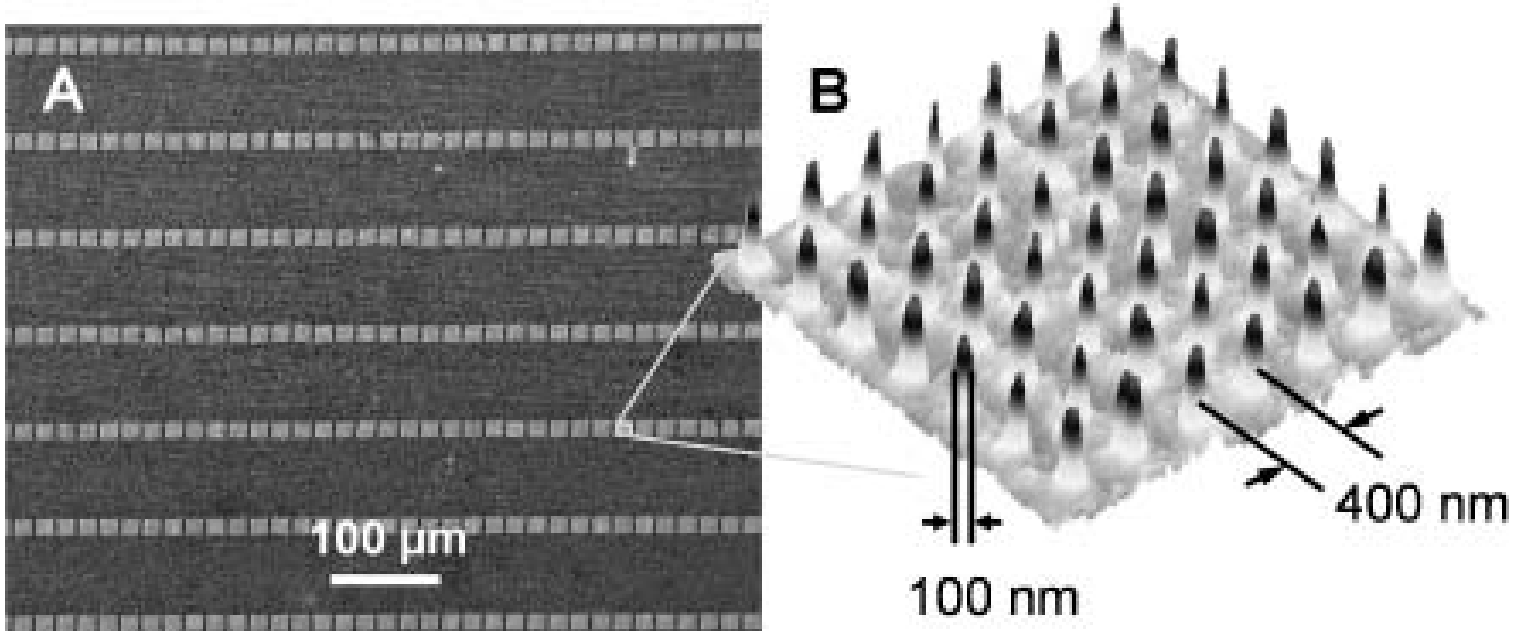
Massively Parallel Dip-Pen Nanolithography with 55 000-Pen Two-Dimensional Arrays



A) Optical micrograph of part of the 2D array of cantilevers used for patterning. Inset: SEM image of the cantilever arrays at a different viewing angle. B) Schematic of the gravity-driven alignment method used for massively parallel DPN with a 2D cantilever array. Each pen was brought into contact with the substrate under the weight of the whole pen array. Subsequently, the exact position of the pen array was locked to the AFM scanner head by an epoxy resin.

Mirkin, C. A. et al. *Angew. Chem., Int. Ed.* **2006**, *45*, 7220–7223.

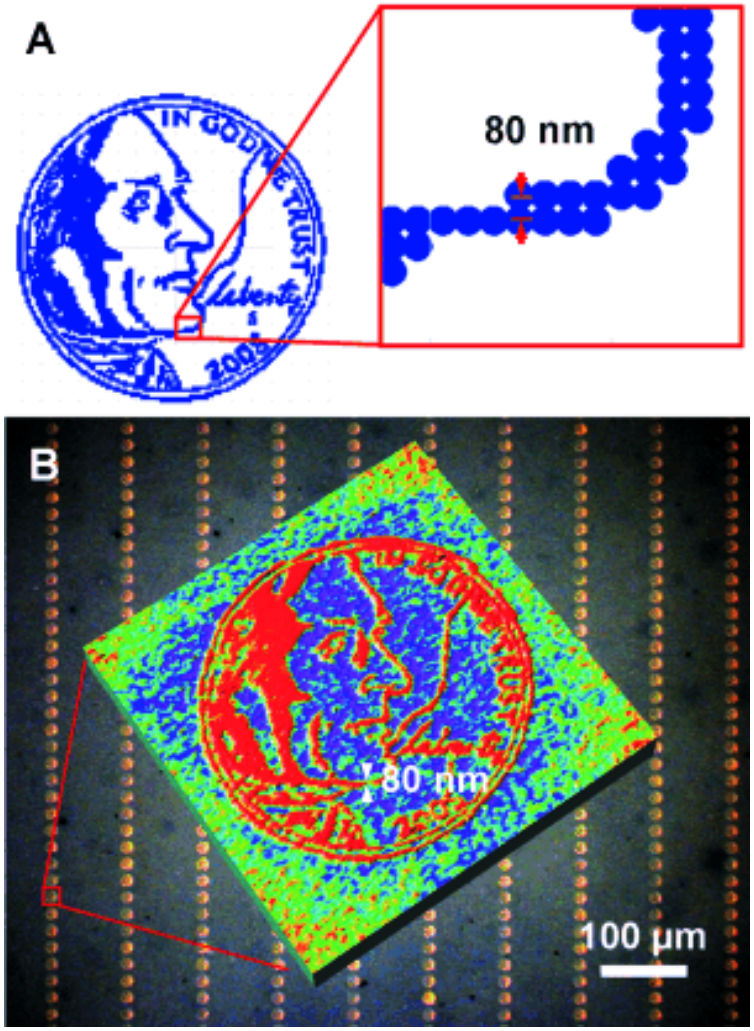
Massively Parallel Dip-Pen Nanolithography with 55 000-Pen Two-Dimensional Arrays



A) Large-area SEM image of part of an 88 000 000-gold-dot array (40×40 within each block) on an oxidized silicon substrate. B) Representative AFM topographical image of part of one of the blocks, where the dot-to-dot distance is 400 nm, and the dot diameter is (100±20) nm.

Mirkin, C. A. et al. *Angew. Chem., Int. Ed.* **2006**, *45*, 7220–7223.

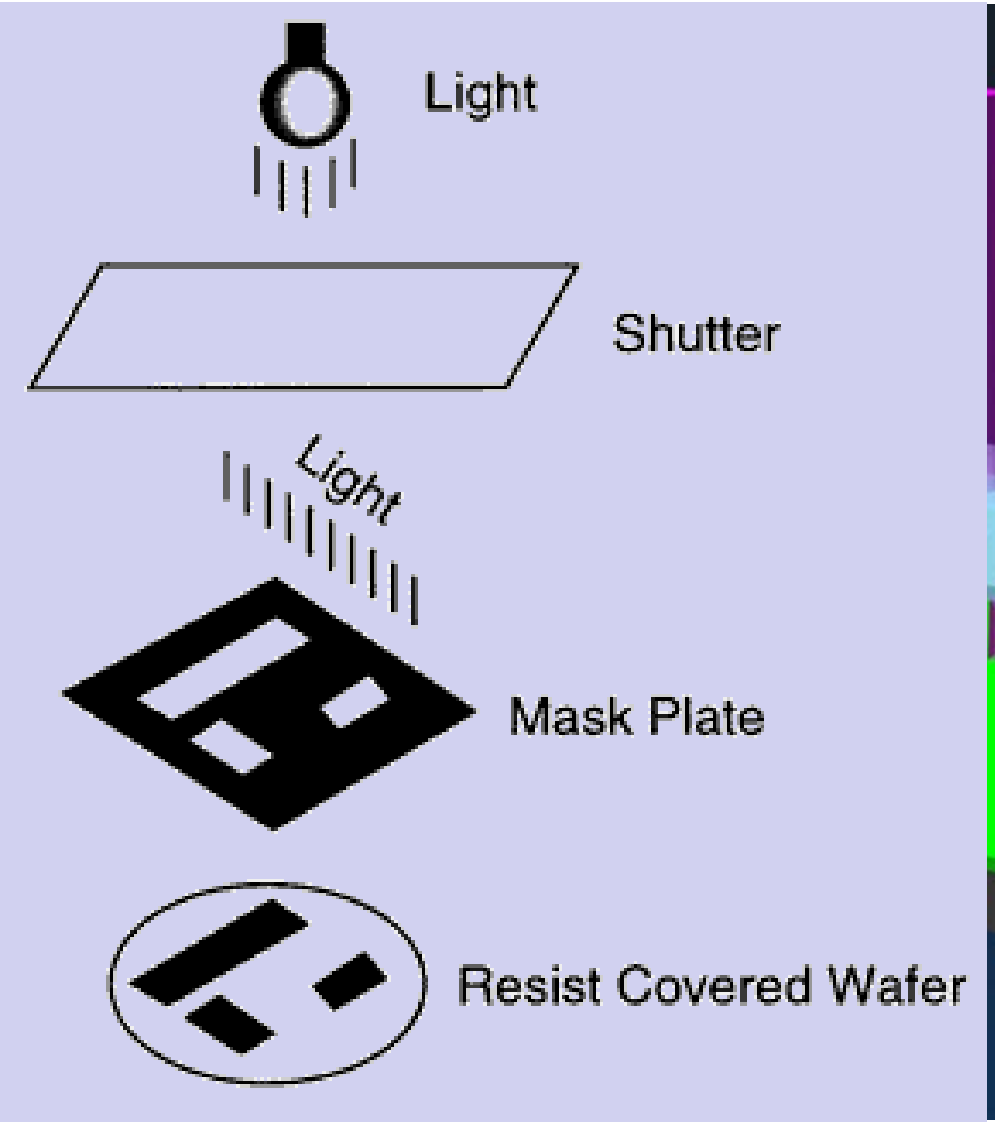
Massively Parallel Dip-Pen Nanolithography with 55 000-Pen Two-Dimensional Arrays

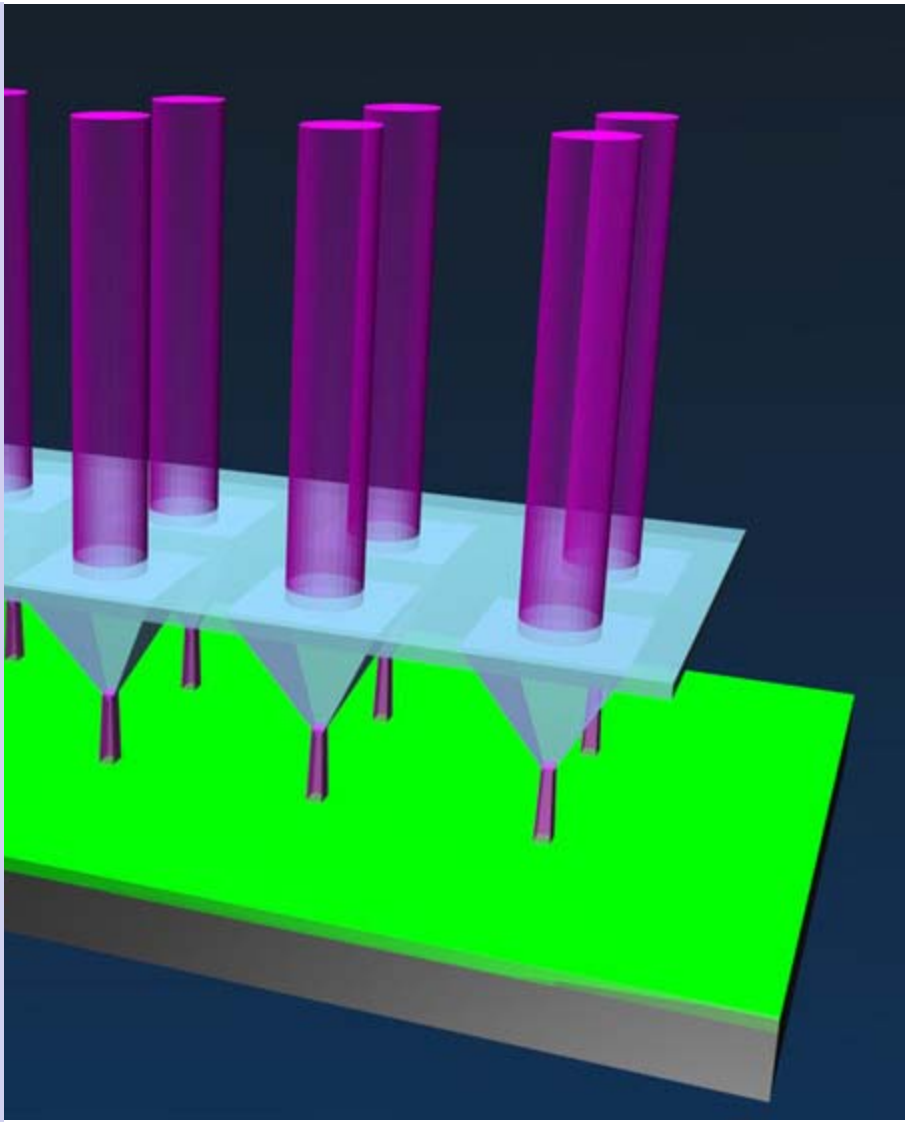


A) Dot matrix map representing the front face of the 2005 US five-cent coin. The coin bears a picture of Thomas Jefferson, who helped develop the polygraph, a letter duplicator that relies on an array of macroscopic pens. The lines of the chin are composed of dots of 80-nm diameter . B) Optical micrograph of a representative region of the substrate on which the approximately 55 000 duplicates were generated. Each of the circular features is a miniaturized replica of the face of the five-cent coin. Inset: High-resolution topographical AFM image of a representative replica.

Mirkin, C. A. et al. *Angew. Chem., Int. Ed.* **2006**, *45*, 7220–7223.

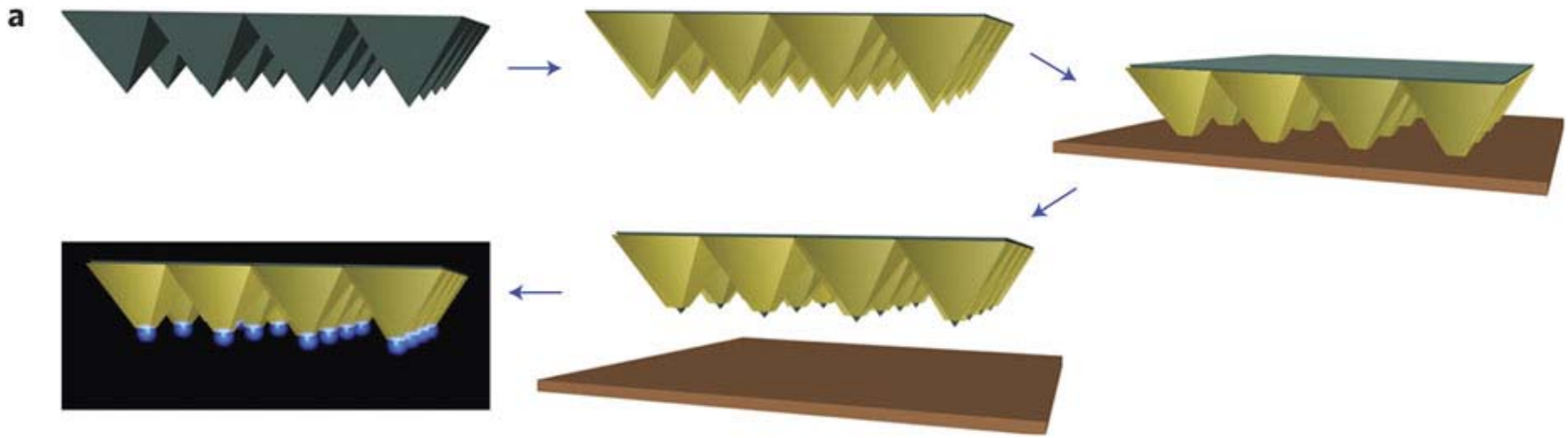
A Cheap, Fast Way to Write Nanoscale Patterns

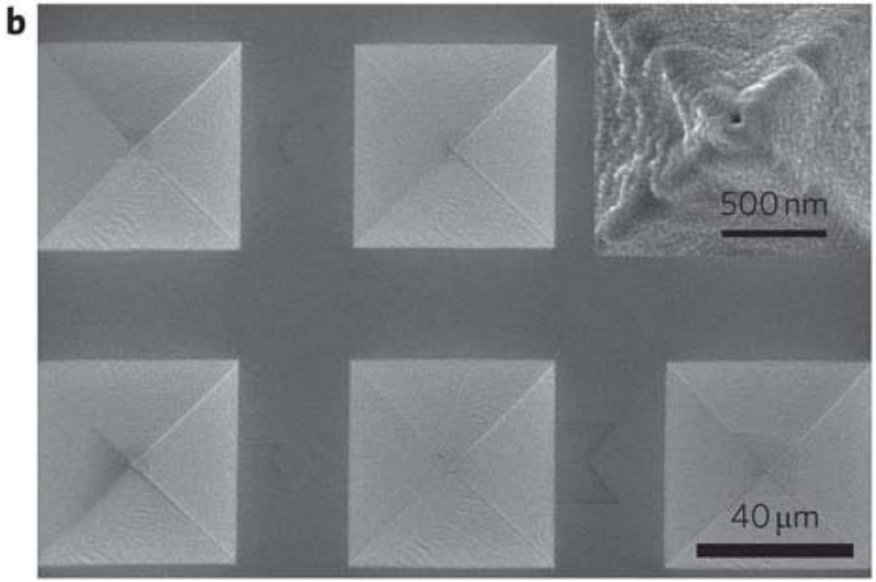


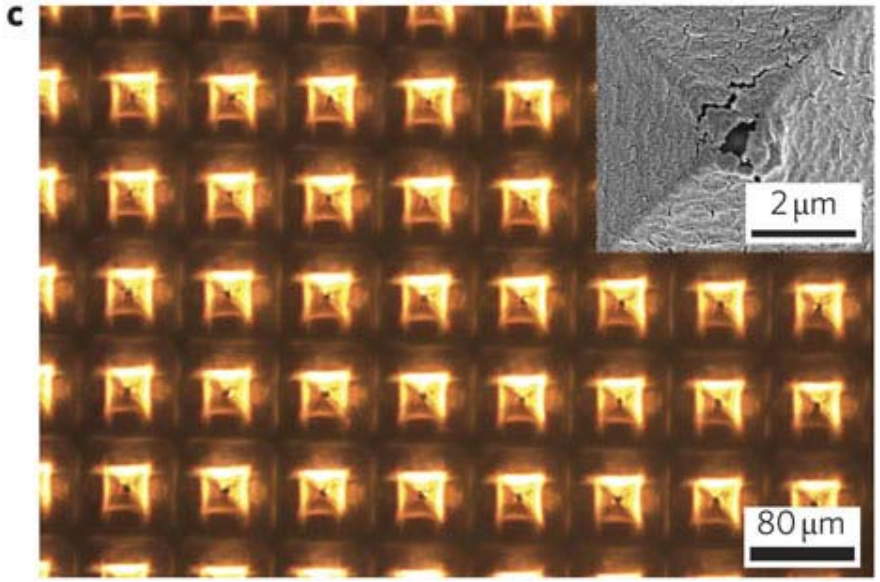


Mirkin, C. A. et al. ***Nature Nanotechnology*** Volume: 5 , Pages: 637–640 (2010).

Fabrication of a beam pen array



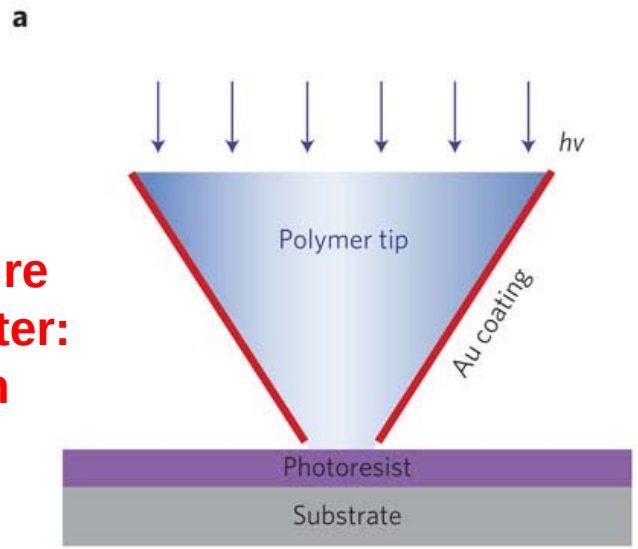


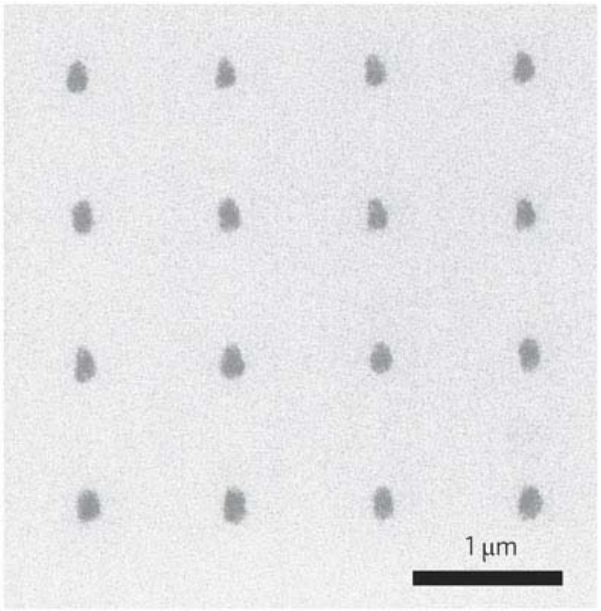


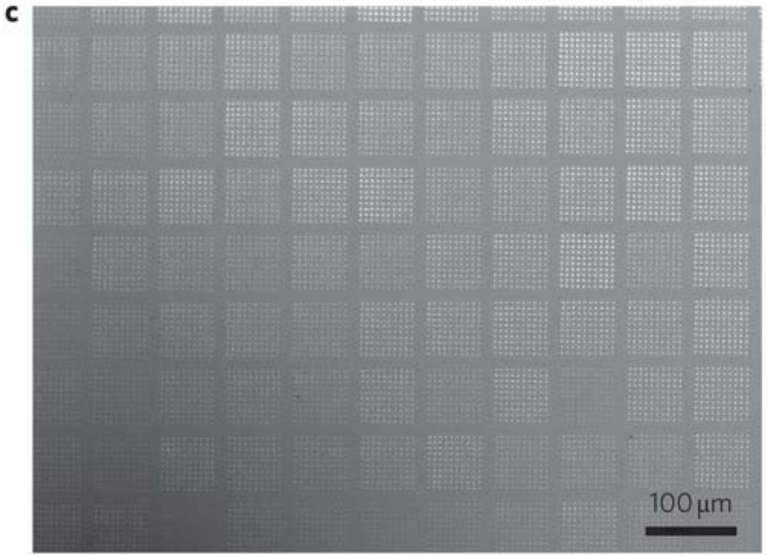
Mirkin, C. A. et al. ***Nature Nanotechnology*** Volume: 5 , Pages: 637–640 (2010).

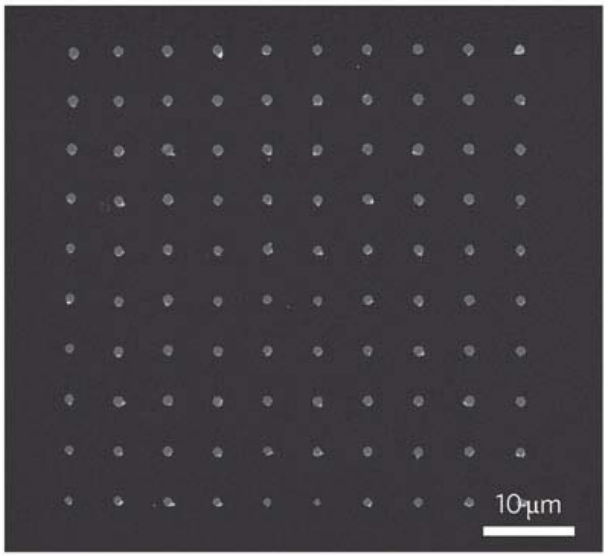
Large-area patterning and sub-diffraction limit features.

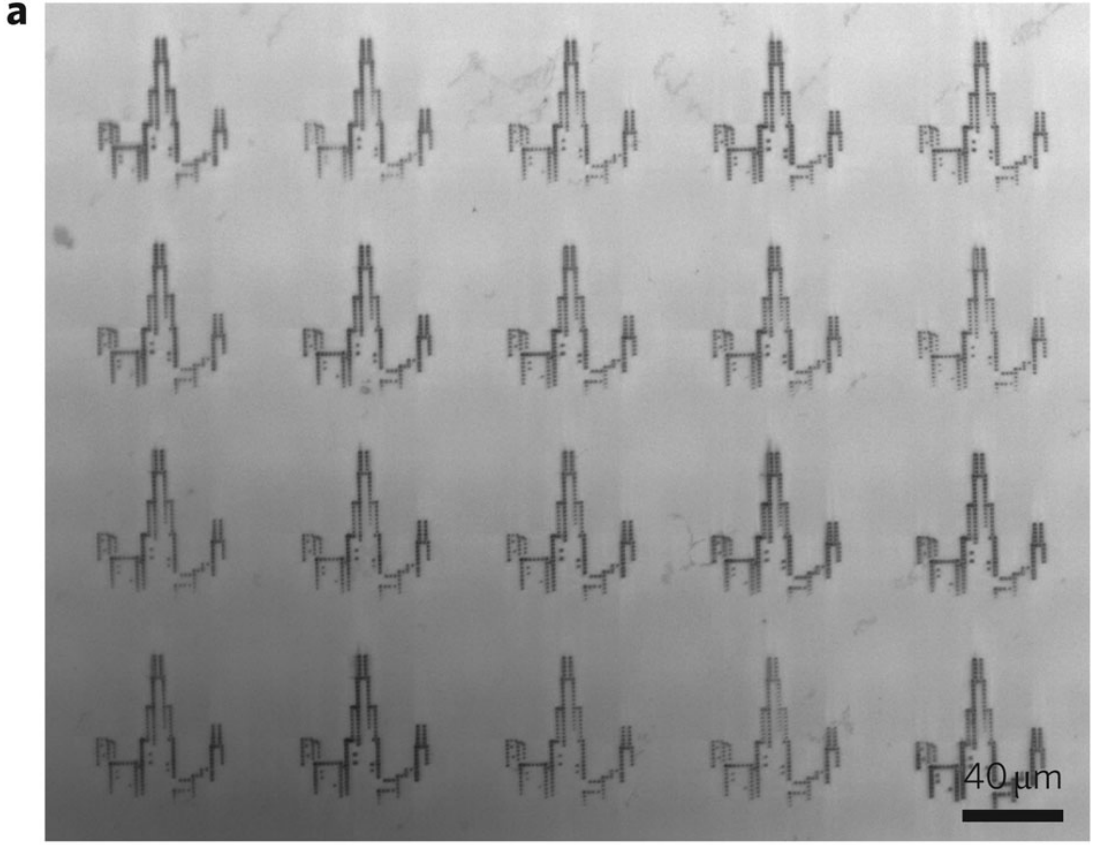
Aperture Diameter: 111 nm





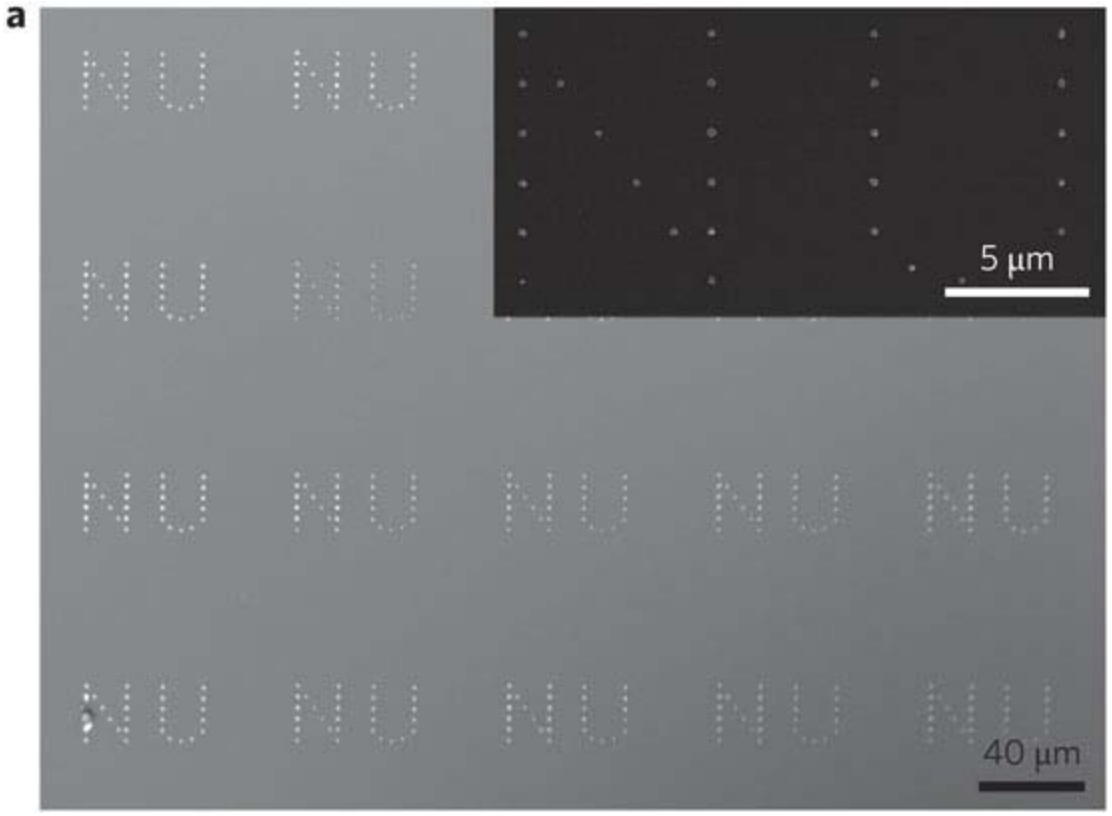


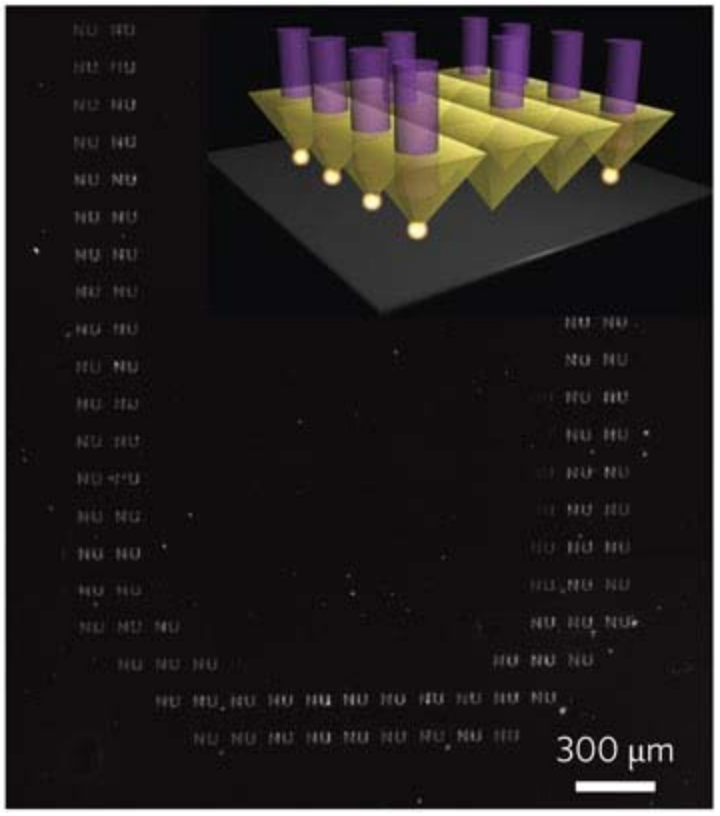


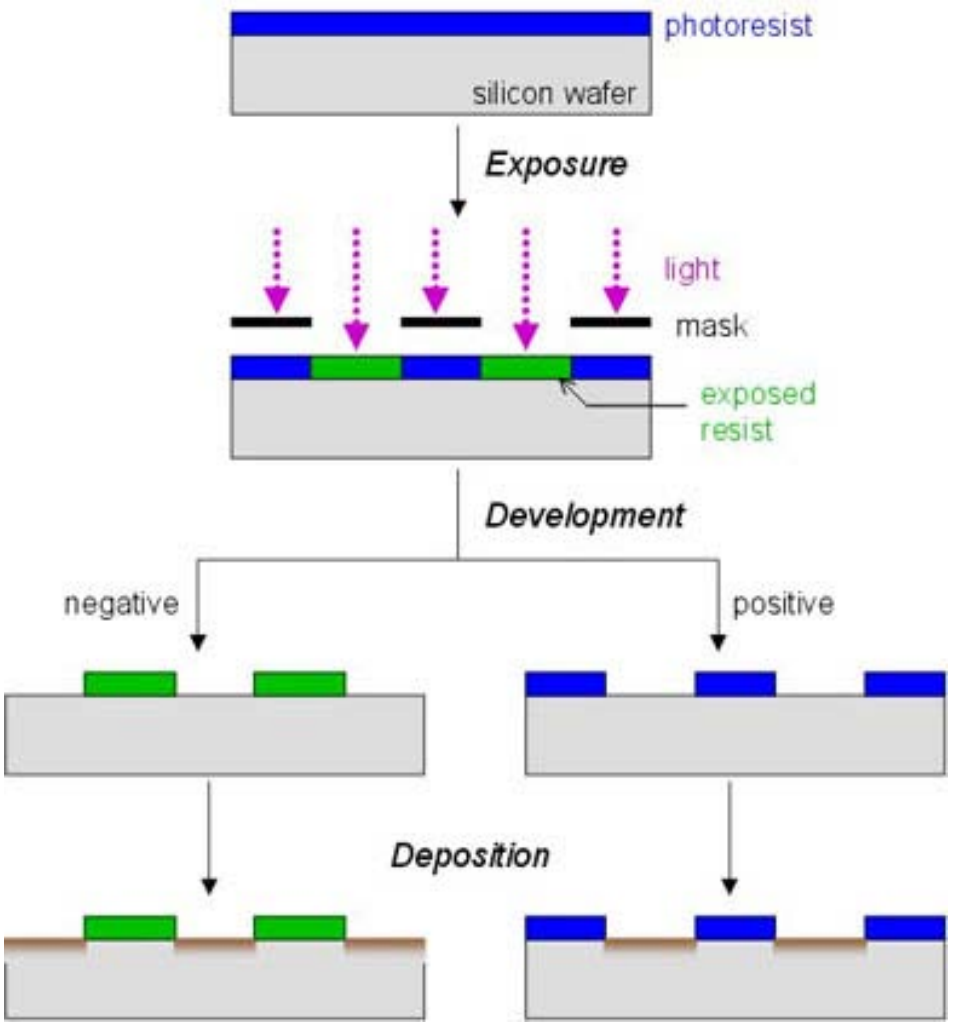


Arbitrary pattern fabrication capability: Chicago Skyline

Orthogonal levels of patterning control provided by macroscale addressability of pens







Photolithography method

- A photoresist is a light-sensitive material used in several industrial processes, such as photolithography and photoengraving to form a patterned coating on a surface.
- A **positive resist** is a type of photoresist in which the portion of the photoresist that is exposed to light becomes soluble to the photoresist developer. The portion of the photoresist that is unexposed remains insoluble to the photoresist developer.
- A **negative resist** is a type of photoresist in which the portion of the photoresist that is exposed to light becomes insoluble to the photoresist developer. The unexposed portion of the photoresist is dissolved by the photoresist developer.