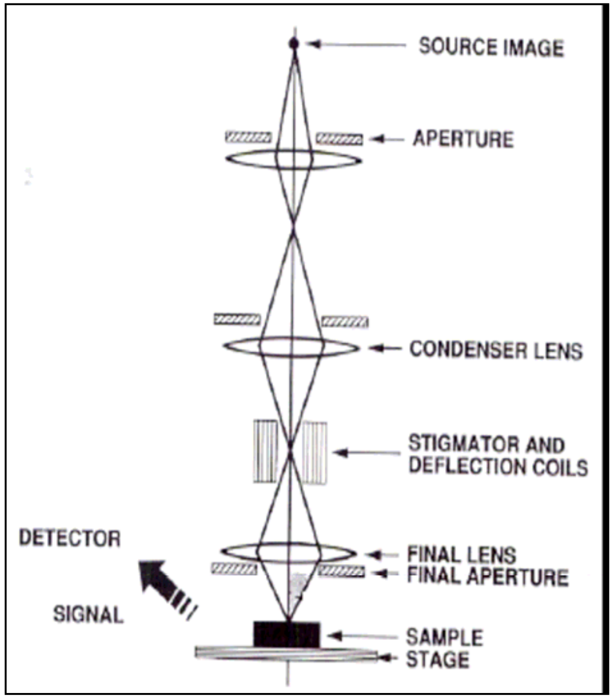
1. Nanolithography

ELECTRON BEAM LITHOGRAPHY (EBL)

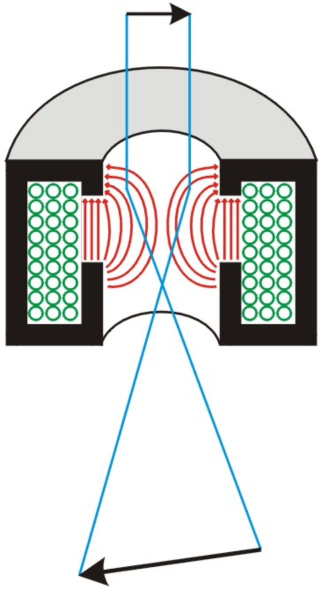
<u>Direct write e-beam lithography:</u>

- based on scanning electron microscope (SEM)
- small scanning Gaussian electron spot (diameter 1-5 nm) exposes resist
- maximum scanning range 100 - 1000 μm due to aberrations and distortions
- mechanical movement of sample (interferometric position measurement) in combination with e-beam scanning to cover large sample size (stitching)



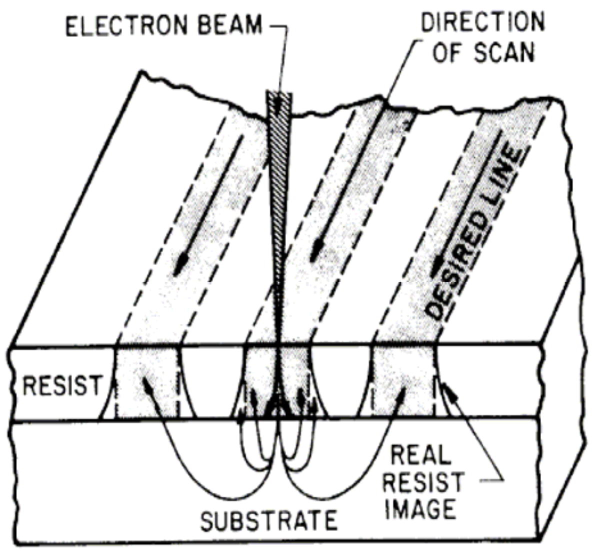
- magnetic lenses for electron optics:

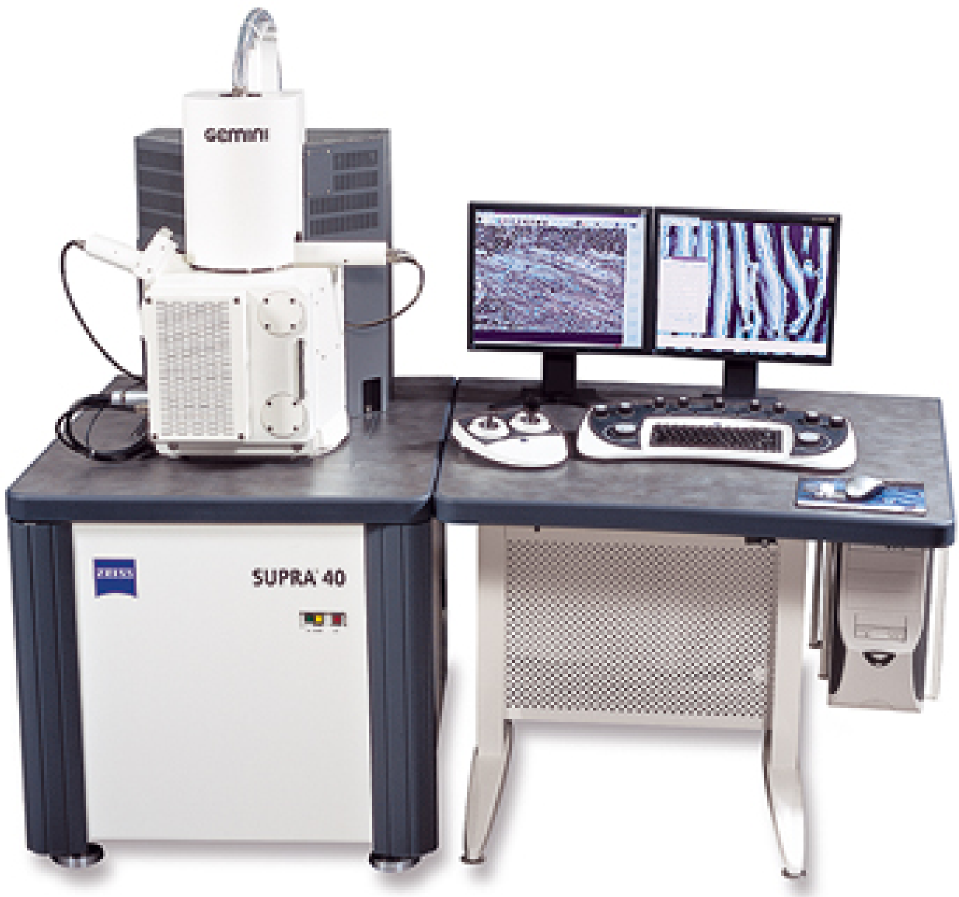
- e-beam is scanned by deflectors (either electrostatic or magnetic)
- one deflector is used to blank the beam on/off



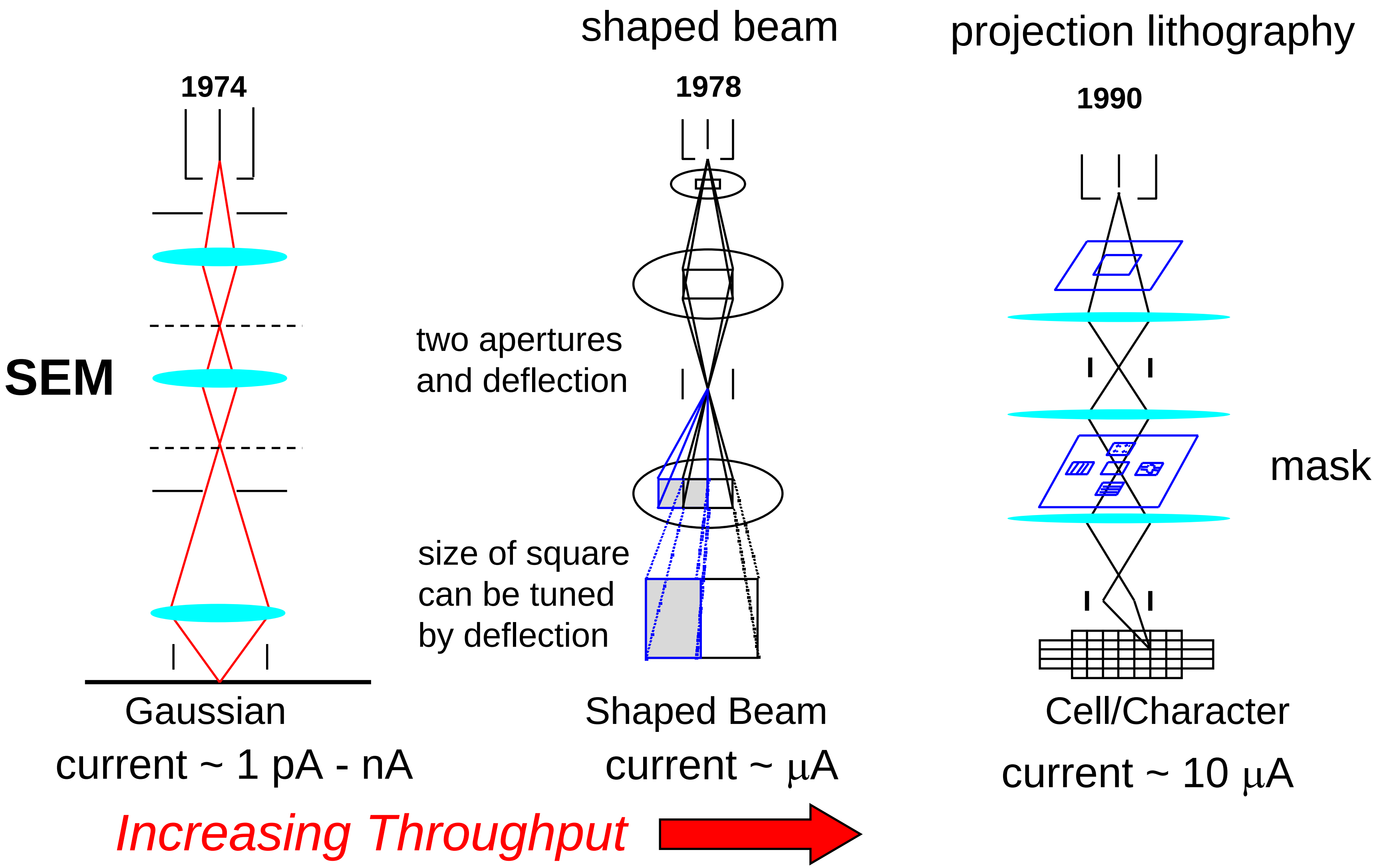
1. Nanolithography

- resolution about 20 nm due to electron scattering in resist
- two EBL-systems in Otaniemi, third one will installed in December 2005





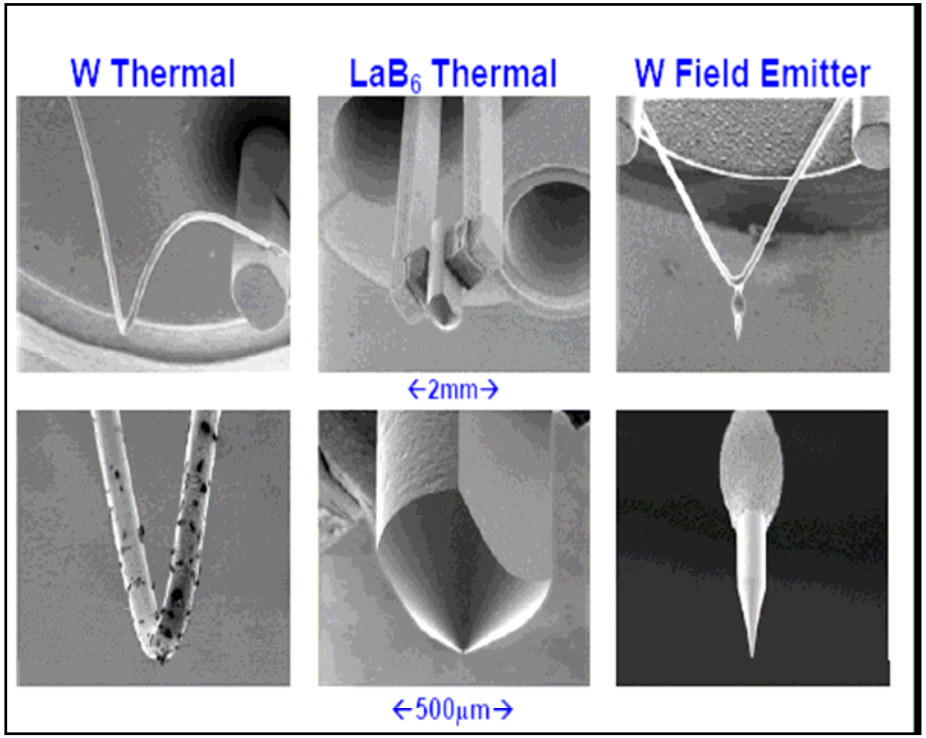
1. Nanolithography



1. Nanolithography

- electron source thermal or field emitter, better resolution with field emitter
- typical current ~ nA, resist requires ~ $\mu C/cm^2$, thus exposure takes hours

electron sources:

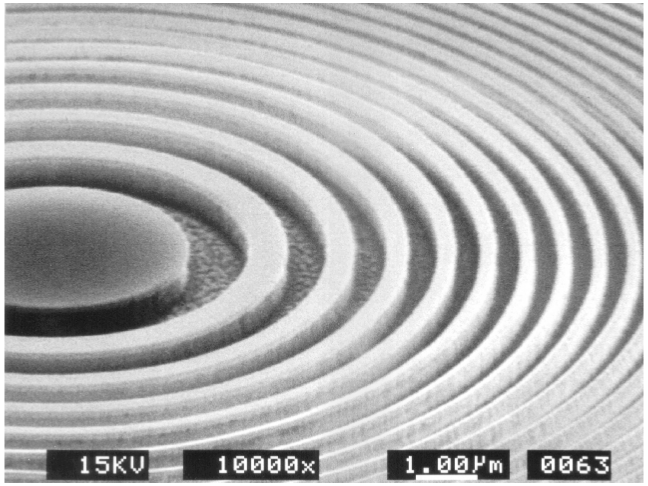


- better resolution
- long lifetime

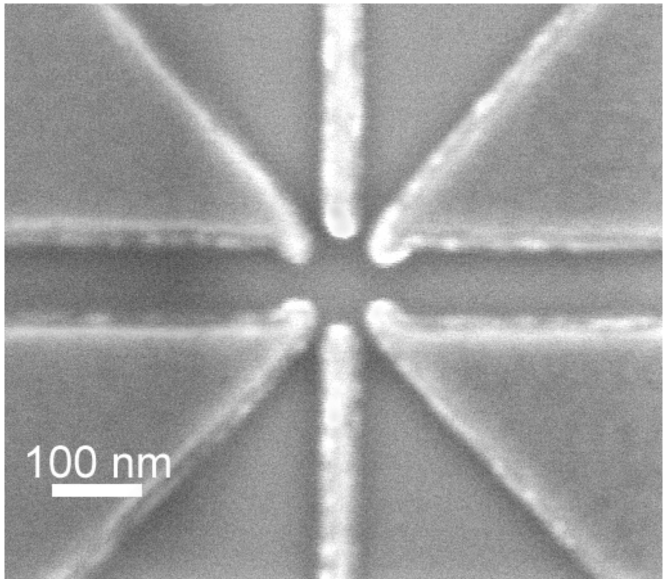
1. Nanolithography

Examples of EBL structures:

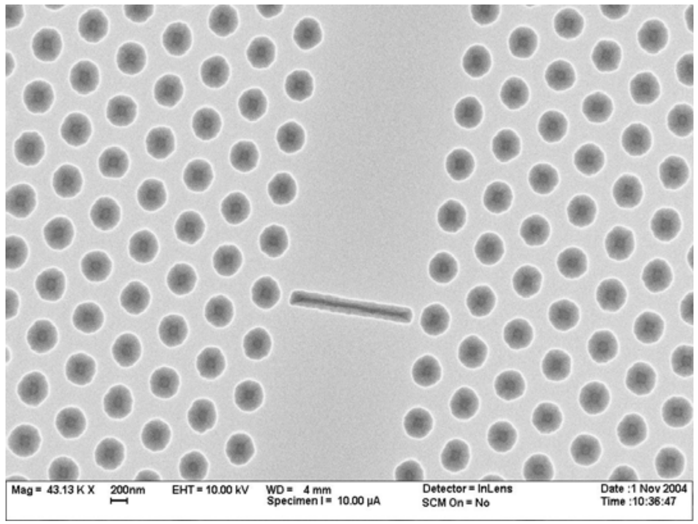
Bragg-Fresnel lens for x-rays:



Single electron transistor:



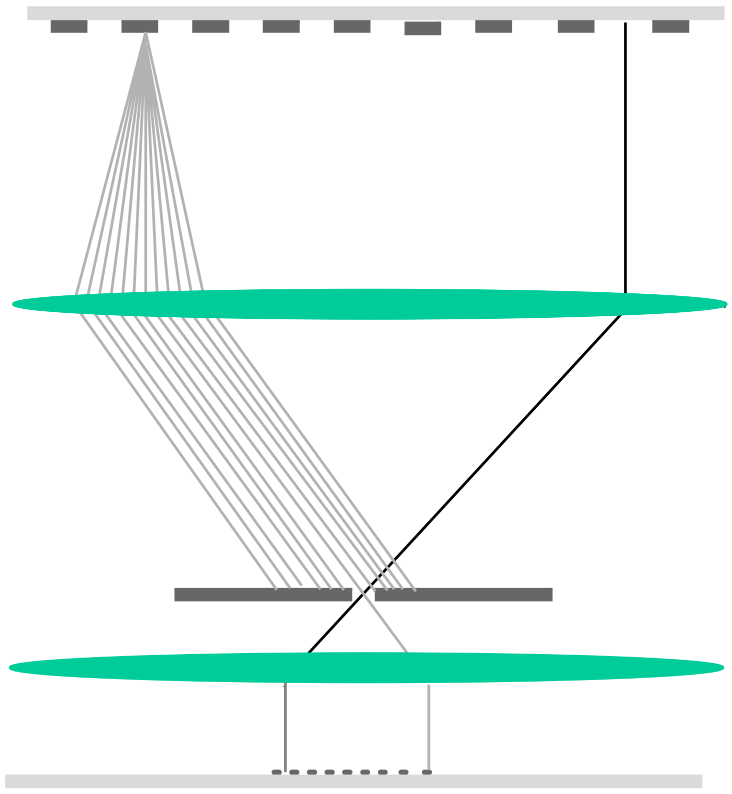
Photonic crystal:



1. Nanolithography

<u>Electron beam projection lithography:</u>

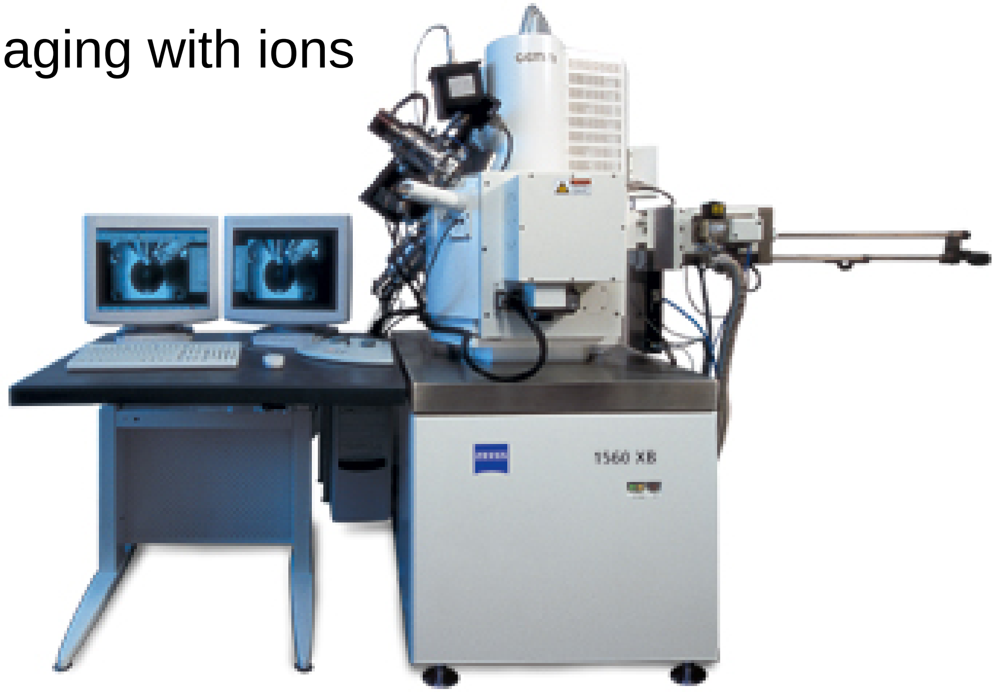
- current tens of μA, voltage 100 kV, resolution about 100 nm
- mask either scattering stencil or continuous membrane
- scattering stencil: membrane (2 μm Si)
  scatters electrons, holes in membrane
  let electrons pass without scattering
- continuous membrane: thin membrane
  (100 nm SiN) transparent to electrons, pattern
  is e.g. 25 nm W layer which scatters electrons
- projection 4x demagnified
- resists like in DUV lithography

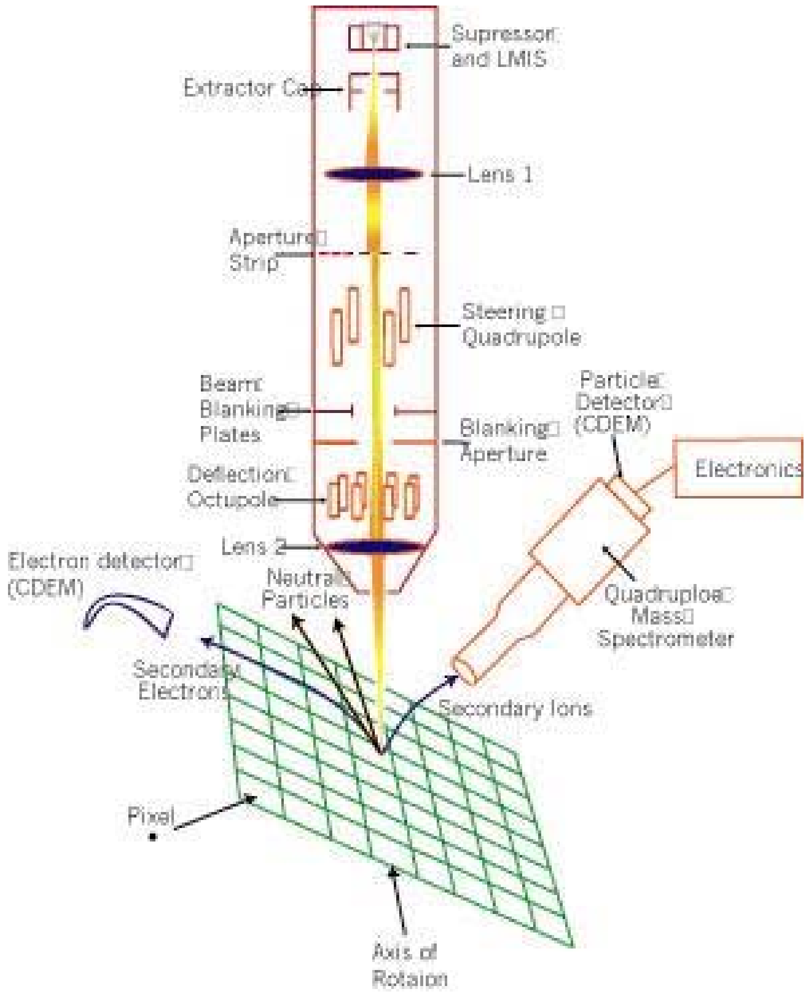


1. Nanolithography

<u>Focused ion beam (FIB) lithography:</u>

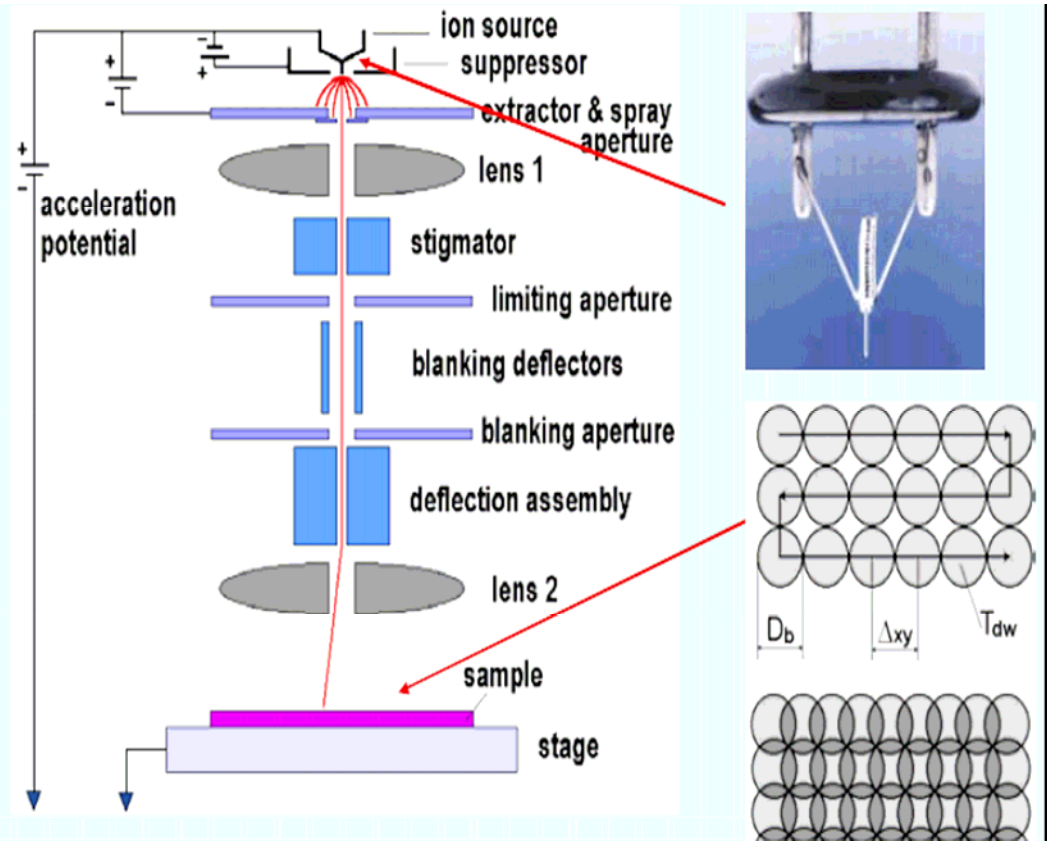
- like SEM but Ga^+ ions are used instead of electrons
- beam diameter 5 - 10 nm
- current 1 pA - 10 nA, ~10 A/cm^2
- imaging with ions





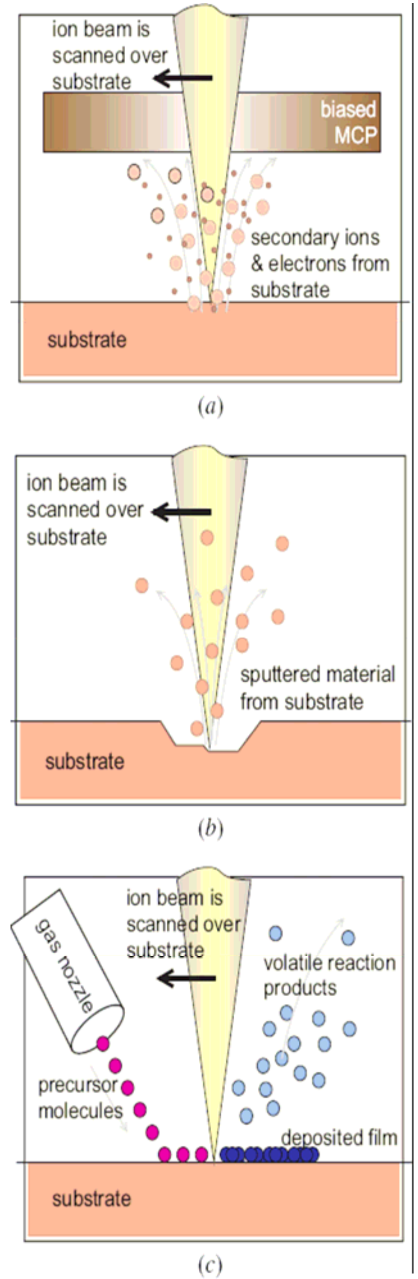
1. Nanolithography

FIB principle:



FIB modes:

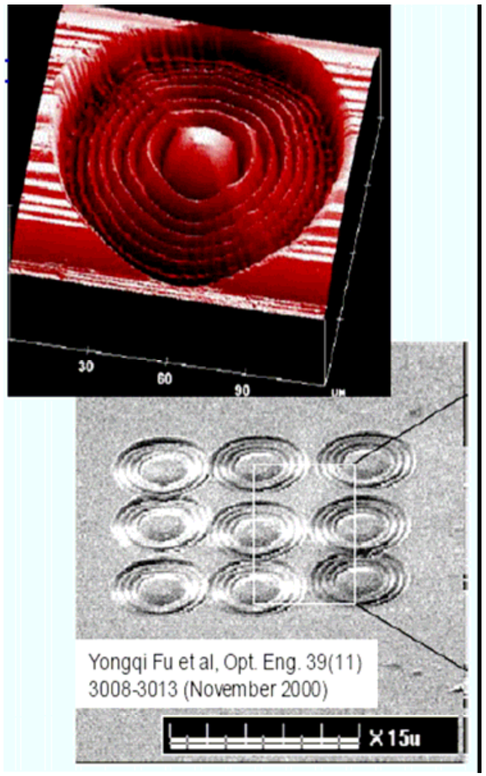
- imaging
- milling
- deposition



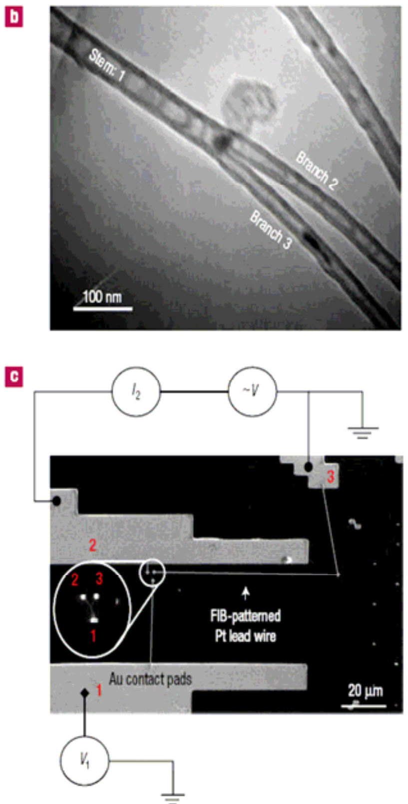
1. Nanolithography

- conventional FIB lithography is a serial technique (point-by-point) through resist exposure, sputtering (material removal) or deposition => very slow
- excellent for rapid prototyping of nanostructures (no mask or resist needed)

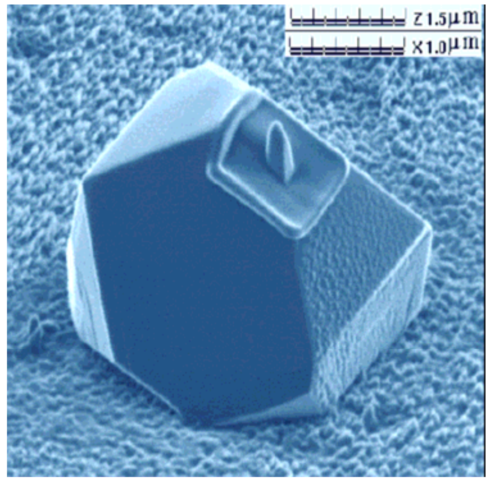
nano-optics:

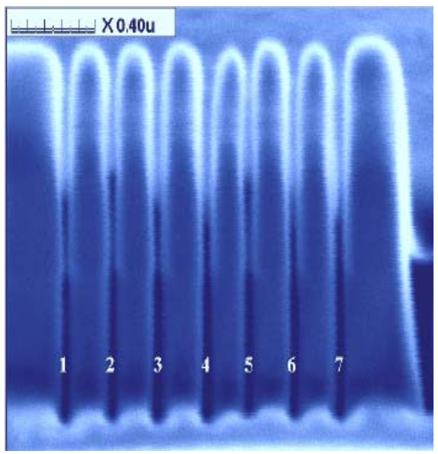


contacts for CNT's:



FIB-milled diamond:





30 nm wide, 600 nm deep trenches in diamond film

1. Nanolithography

FIB nanomachining:

TEM sample milling (50-100 nm thick)   deposition & sputtering

TEM = transmission electron microscope

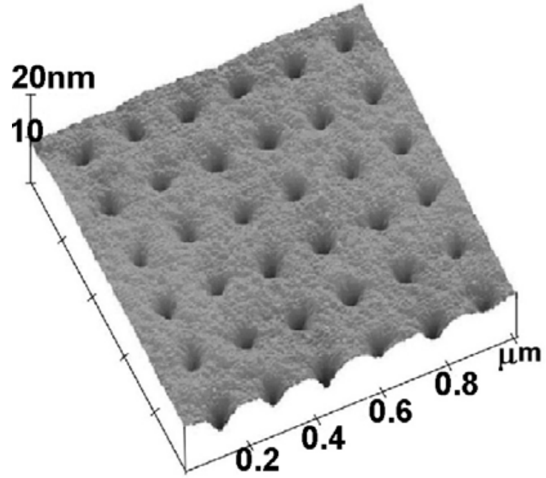
1. Nanolithography

The mechanisms in FIB lithography:

1) Physical sputtering
 - Ga+ atoms (energy 25 - 50 keV): min feature size 30 nm with 10 nm beam
2) FIB-induced deposition
 - organic vapor (1 - 10 mtorr) introduced in the chamber using thin tube
 - local deposition of metallic species (Pt, W, Au) and insulators: min feature size 50 - 70 nm for 10 nm beam
3) FIB modification of molecular structure of resist material, line widths <10 nm with PMMA resist reported

With current of tens nA, the etching/deposition rate is ~10 $\mu m^3/s$

Example of a fast FIB process of PMMA resist:

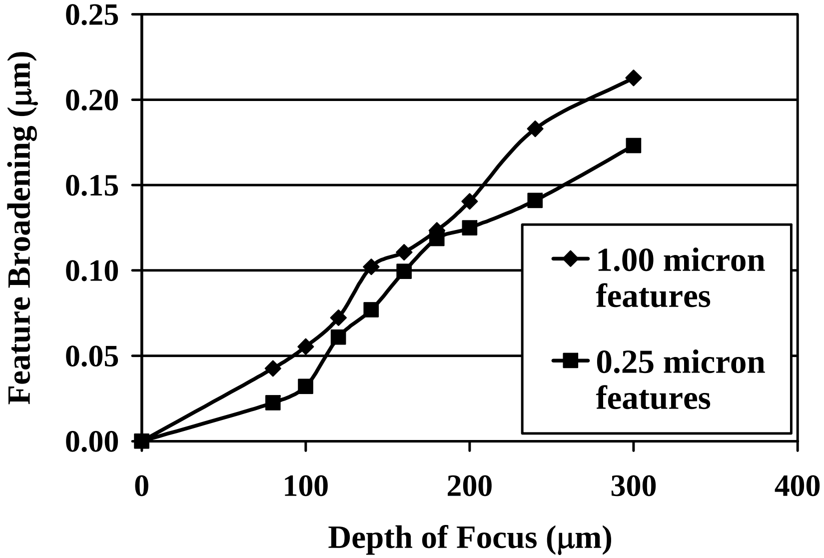


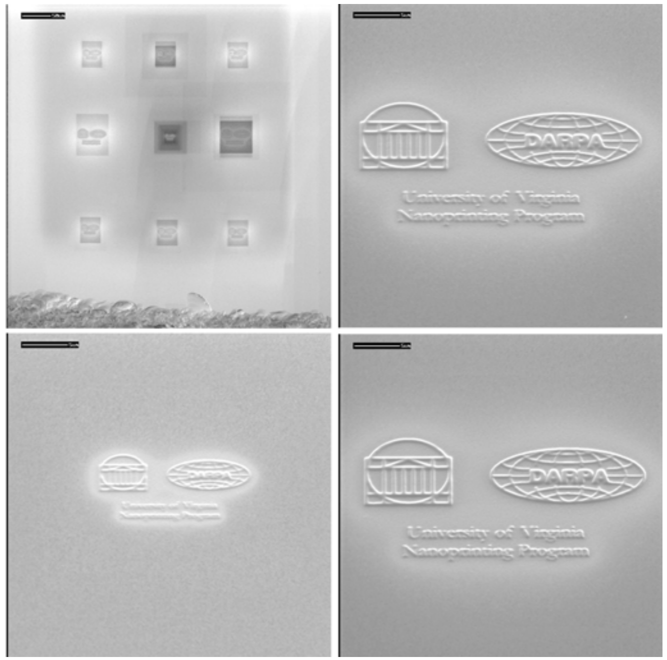
Atomic force microscope image of topography in PMMA following FIB exposure at 1pA beam current and a total irradiation time of 20 µs per feature.

1. Nanolithography

Damage and other mechanisms in FIB lithography:

- 30 keV Ga^+ ions create defects in the structure
- in Si, amorphous Ga-rich zone (~30 nm thick) is produced
- field of view is high (see fig.), samples with high curvature can be fabricated at high resolution
- FIB useful in error correction of IC's and masks





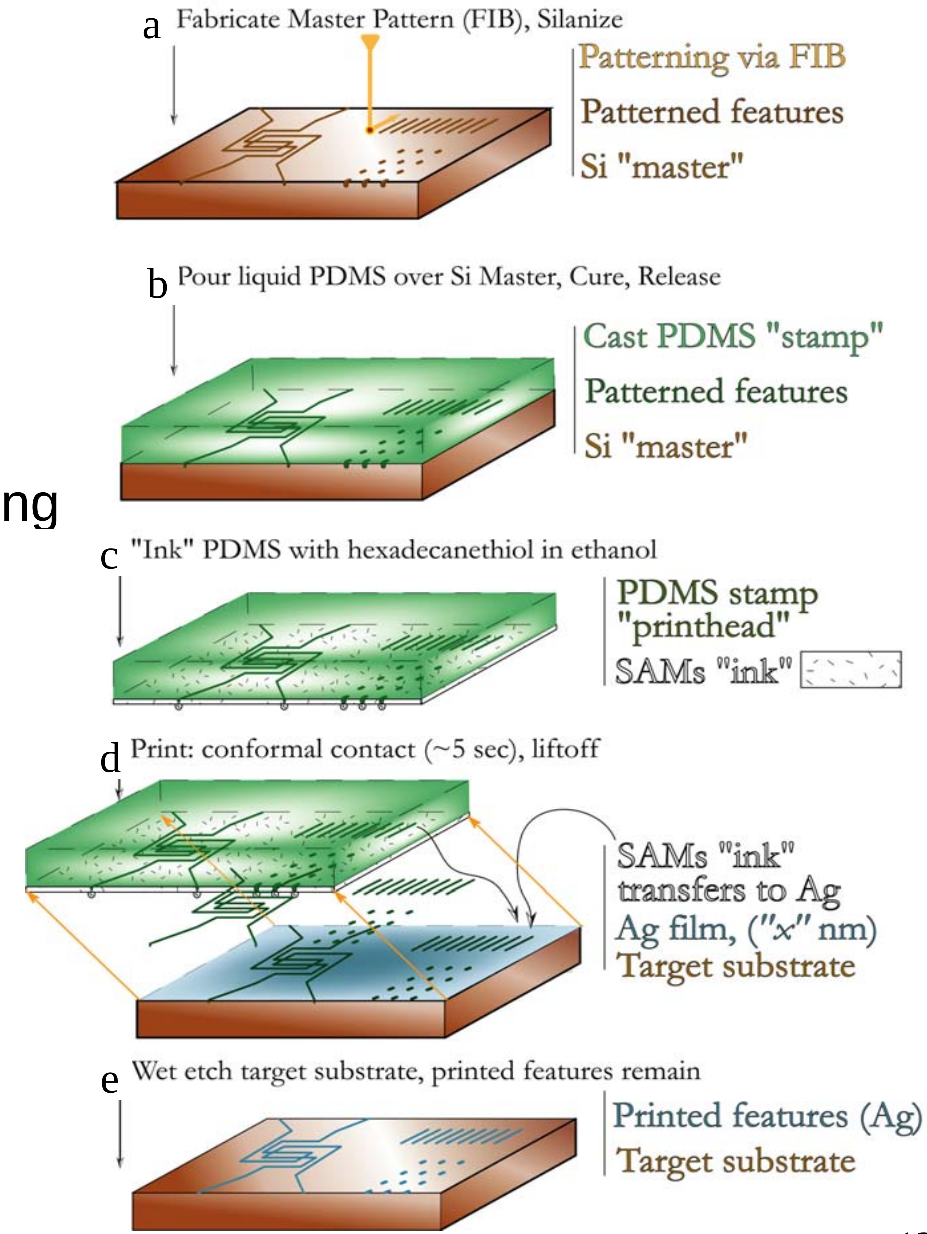
FIB-induced Pt deposition onto the periphery of a 5 cm radius of curvature gold-coated glass lens, corresponding to height differences of order 30 μm recorded without refocusing of the ion beam.

Sub 100 nm resolution is maintained over the entire field.

1. Nanolithography

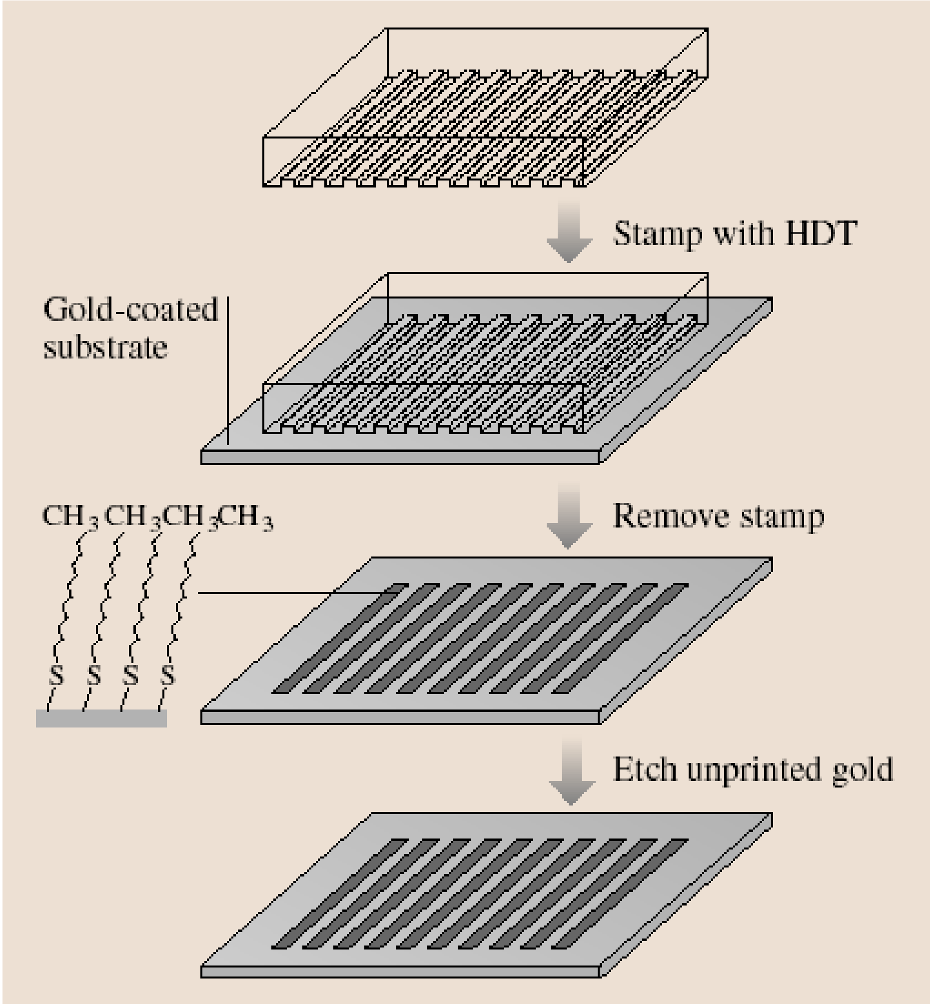
EMERGING NANOLITHOGRAPHIES:

Microcontact printing (μCP) techniques:
- Si “master” is formed using lithography
- elastomer (PDMS) is poured over the master and cured
- release of the mold from the master
- coating PDMS with organic self assembling monolayer (SAM), such as HDT (thiol)
- thiol coated PDMS is put into contact with a noble metal (Au, Ag) surface, thiol has high affinity to metal surface
- after lift-off features of master are copied to the surface by thiols that can be used as a mask in wet etching

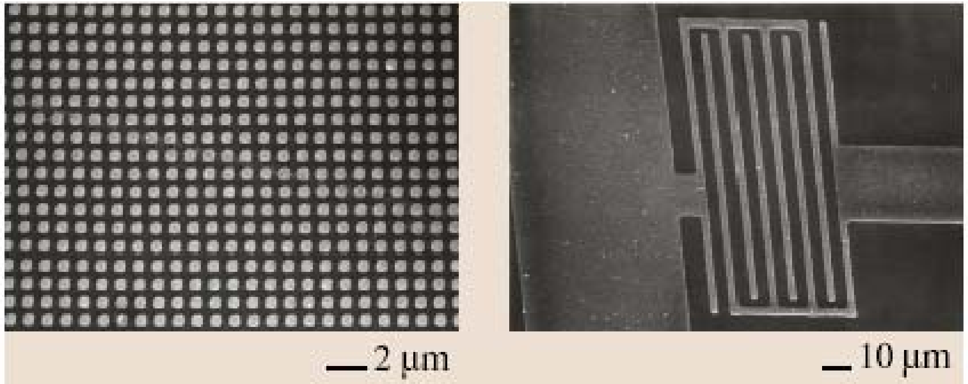


1. Nanolithography

- features from sub 100 nm to tens of μm can be printed quickly
- 3-d structures can be fabricated
- relatively low cost, master can be used several times



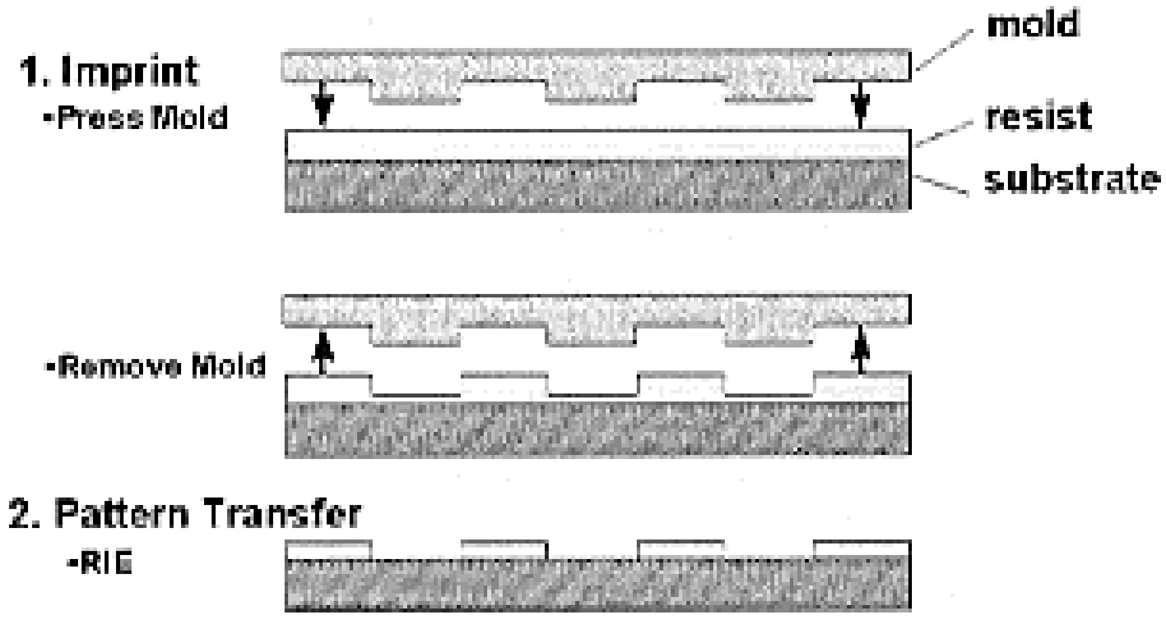
structures made by microcontact printing



1. Nanolithography

Nanoimprinting techniques:

- topographic master is fabricated e.g. by e-beam lithography
- softened polymer resist film is used for imprinting (see fig.)
- polymer is cured by cooling below glass transition temperature, or by UV light
- anisotropic etching, typically RIE is used to remove compressed resist
- resolution is very good, sub-10 nm structures have been made
- full wafer scale fabrication at low cost

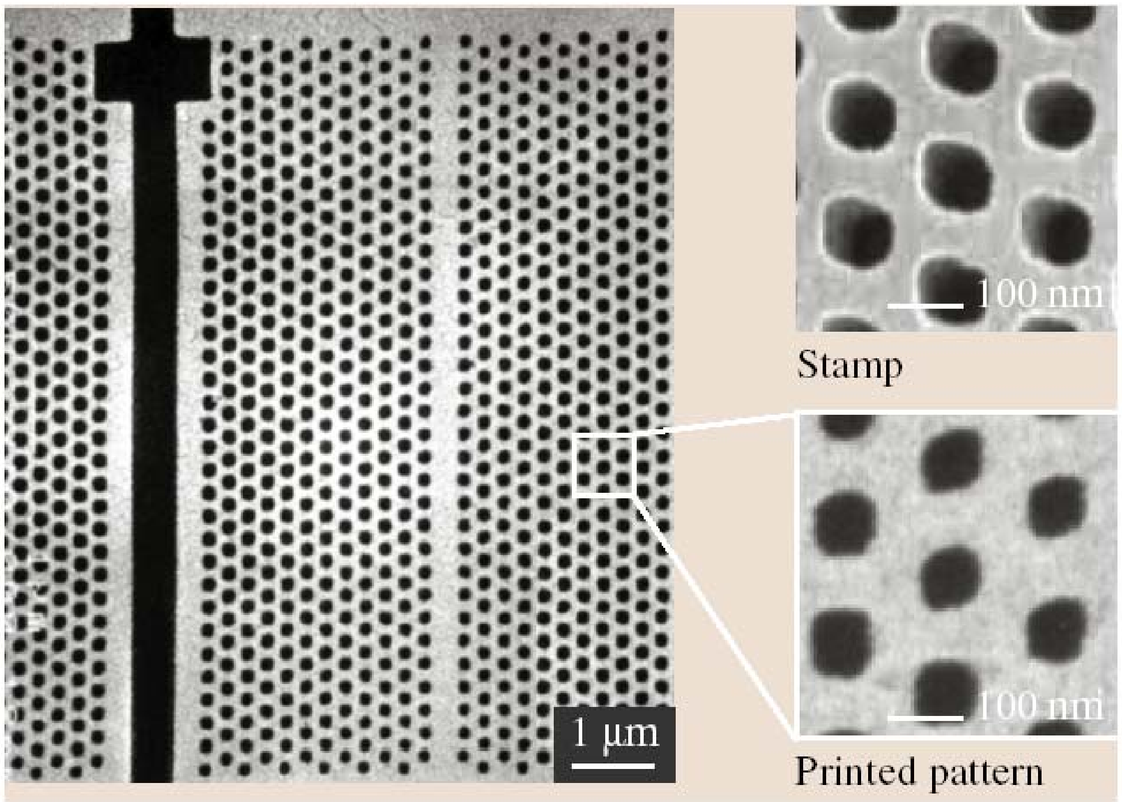


1. Nanolithography

Example of nanoimprinting: photonic crystal waveguide
- stamp is Au/Ti coated GaAs wafer patterned by e-beam lithography
- resolution is 5 - 10 nm

First work:

Chou et al. Science 1996



1. Nanolithography

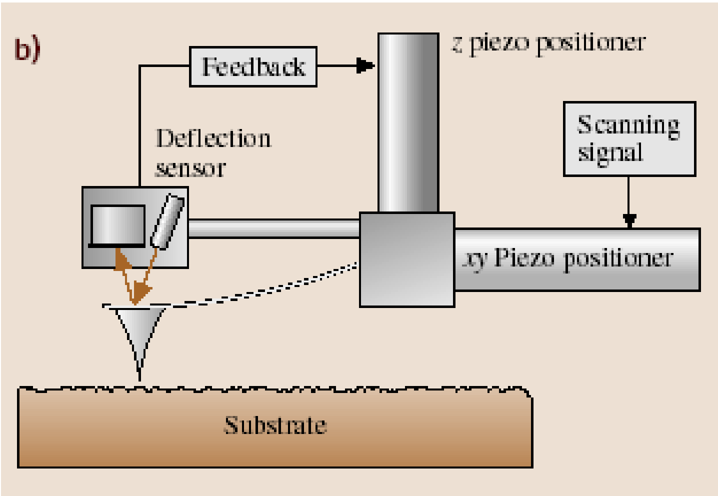
Scanning probe based techniques (more in chapter 3):

- ultimately scanning probe microscopes (SPM) can manipulate structures atom-by-atom, generally resolution is < 1 nm
- writing process is very slow, 1 - 100 μm/s for a single ultranarrow line
- SPM lithography useful in research labs

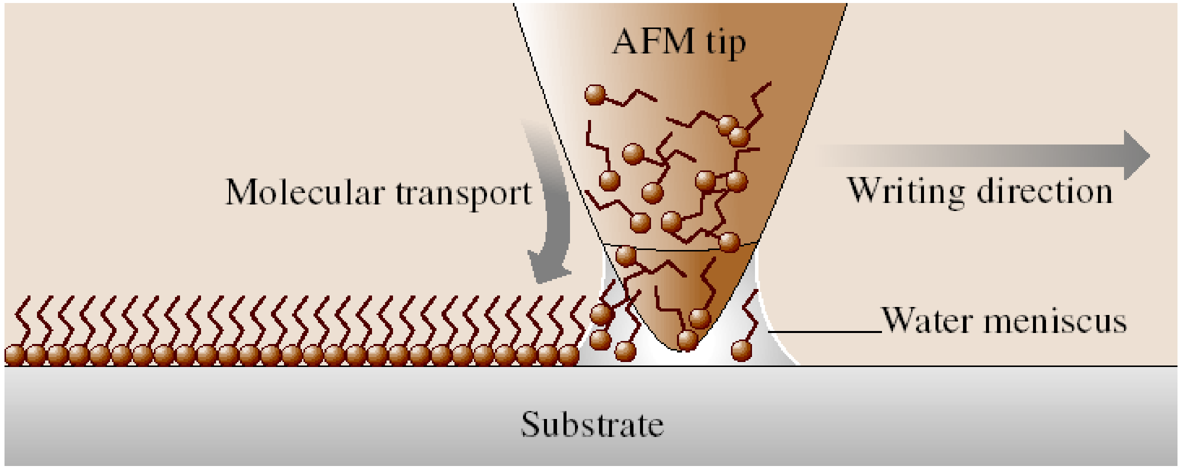
SPM techniques:
STM scanning tunneling microscopy
AFM atomic force microscopy
LFM lateral force microscopy
etc.

Dip-pen nanolithography (see fig.)

- molecules are written to the substrate using AFM tip
- high resolution, but very slow



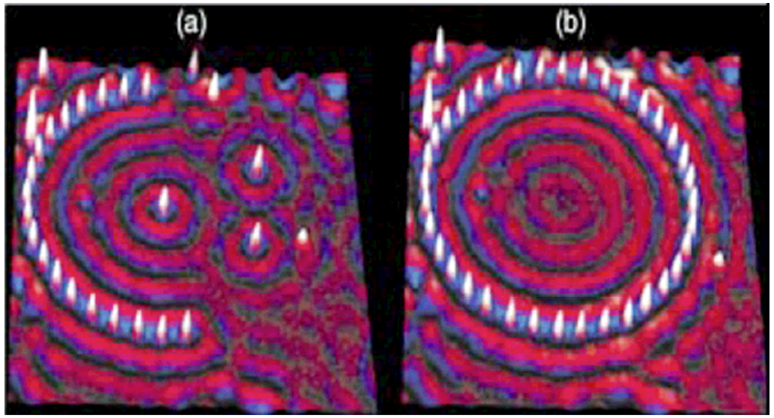
atomic force microscope (AFM)



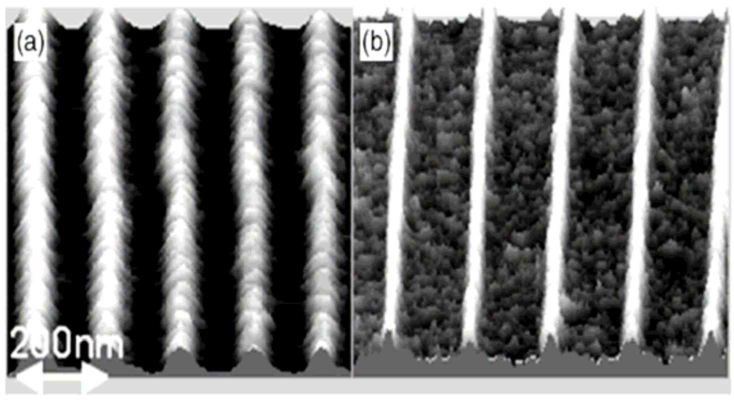
dip-pen nanolithography

1. Nanolithography

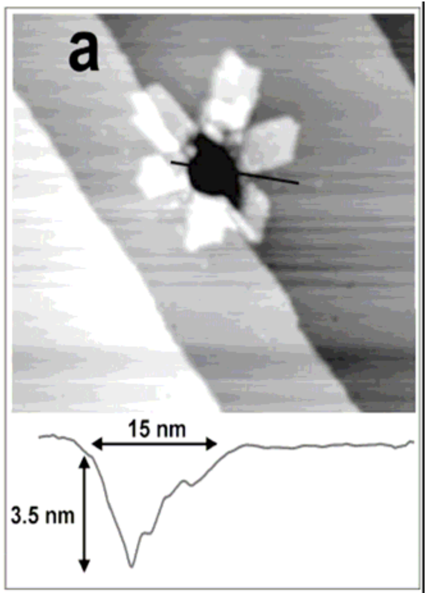
Manipulation of 36 Ag atoms on Ag surface by low temperature STM:



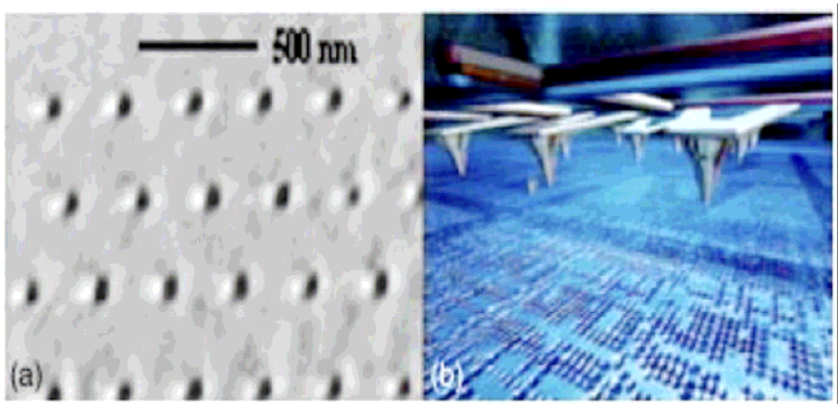
AFM-induced oxidation of Si surface a) 90 nm linewidth at 61% ambient humidity and b) 23 nm linewidth at 14% humidity:



Nanoindentation by STM tip:



a) Thermomechanical writing of polycarbonate by AFM b) parallel-AFM for storage (IBM Millipede):



2. Self-assembly and self-organization

BOTTOM-UP TECHNIQUES - chemical approaches-

The advantages of molecular self-assembly:

- directly nm-sized technique by assembly of molecules to defined structures
- potential for better versatility
- 3-dimensional structures possible
- imitation of structures of nature

Present status of molecular self-assembly:

- in very early stage, more science than technology
- assembly process difficult to control
- can be used in some parts of top-down techniques

2. Self-assembly and self-organization

Intermolecular interactions and molecular recognition:

- self-assembly is based on non-covalent interactions between molecules:

- molecular recognition: ”glue” interactions by ionic interactions, hydrogen bonds, $\pi-\pi$ stacking, dispersion forces, hydrophobic effects and dative bonding

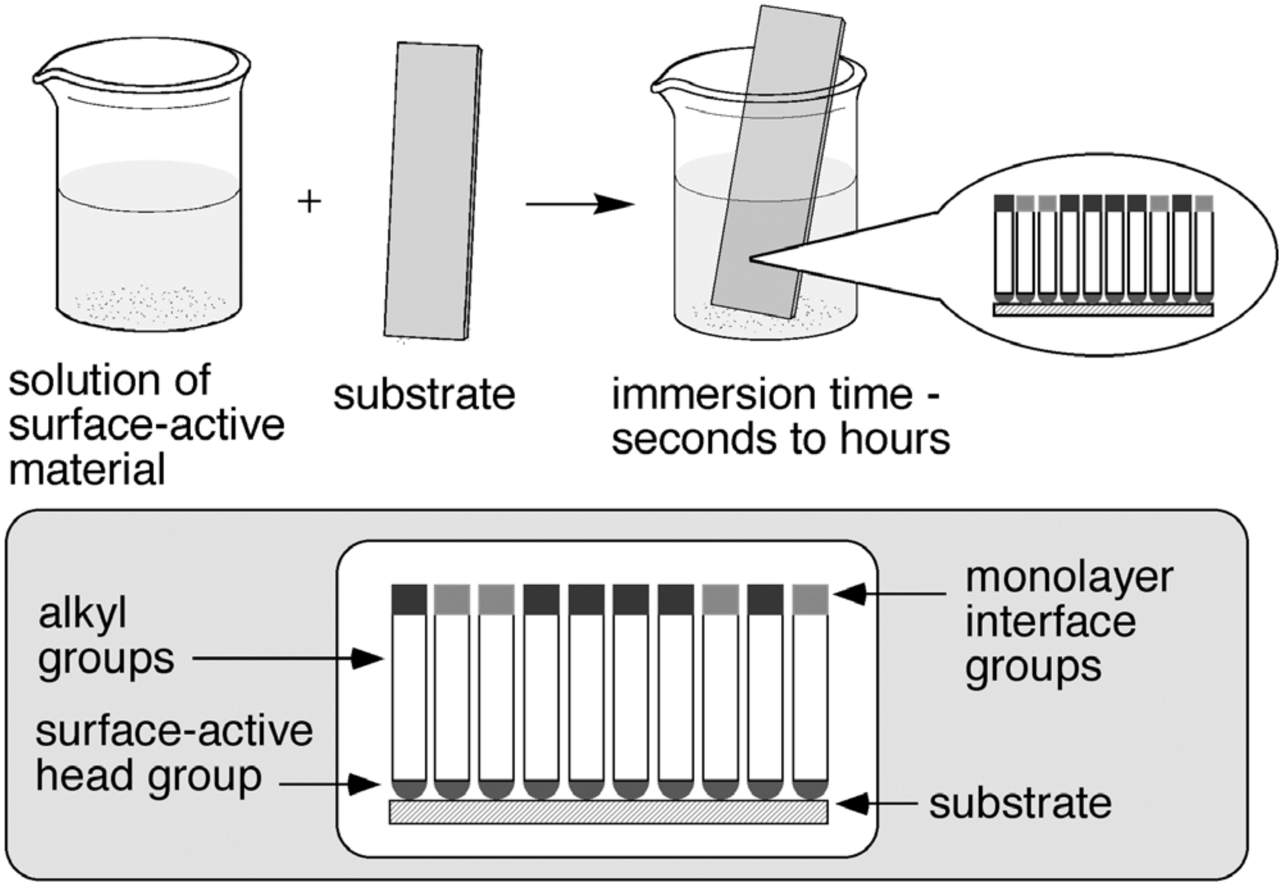
- molecular programming: placement of recognition elements to facilitate a discriminating self-assembly process

Next few selected examples of self-assembly are presented.

2. Self-assembly and self-organization

Self-assembled monolayers (SAMs):

- self-assembled monolayers of long-chain amphifilic molecules (both hydrophilic and hydrophobic functionalities)
- can be fabricated easily (see fig.)

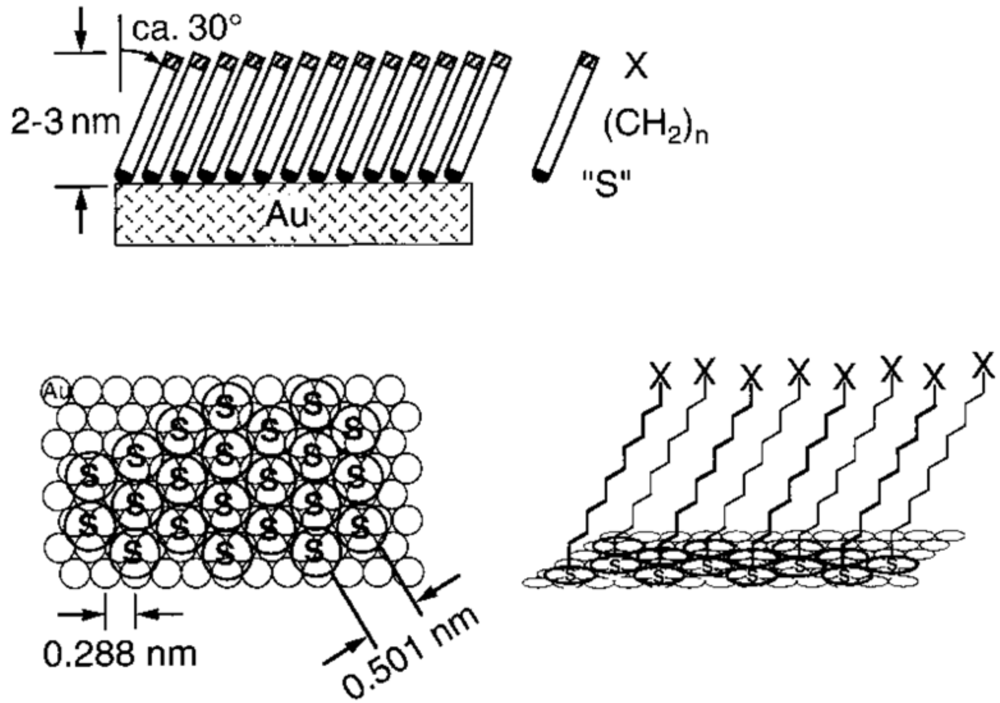


2. Self-assembly and self-organization

Alkanethiolate monolayer on gold is a widely studied SAM system:

- long-chain alkanethiolate consists of ”S”, methyl groups $(CH_2)_n$ and X parts
- sulphur atoms attach in hexagonal close packed form on the Au surface
- methyl groups tilt at an angle 30° due to van der Waals interactions
- for long chains (n > 11) densely packed highly-ordered monolayers are achieved
- X can be changed to other than methyl groups (functionalization)

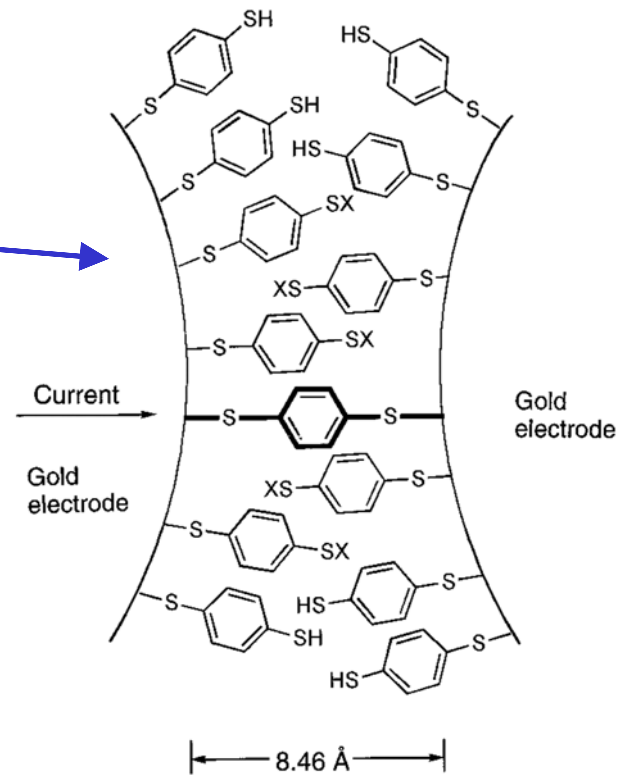
$$X(CH_2)_nSH + Au^0 \longrightarrow X(CH_2)_nS^- + Au^I + 1/2\ H_2$$

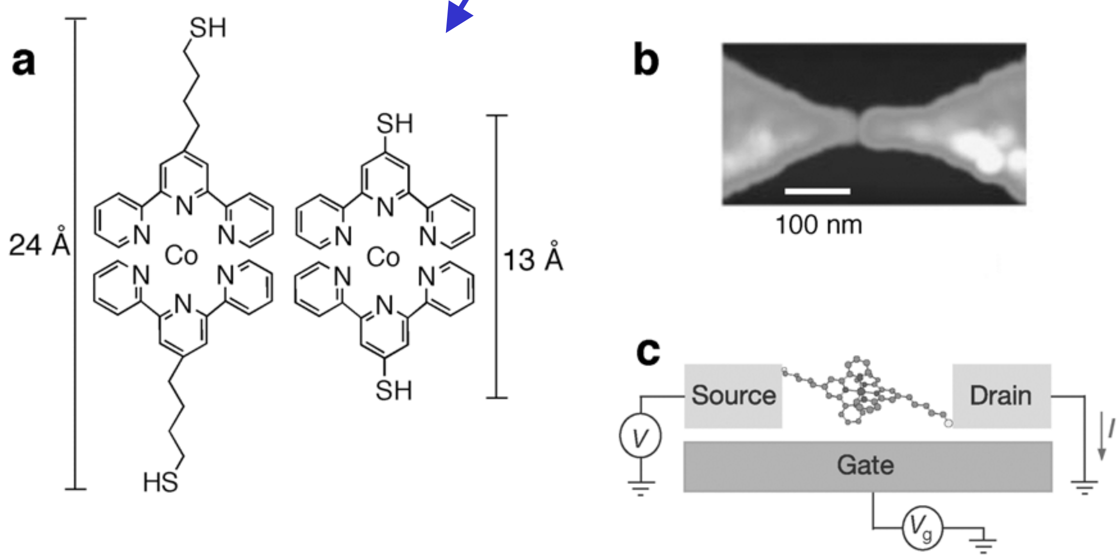


2. Self-assembly and self-organization

Gold SAMs for molecular-based electronics:

- thiol/gold platform good for fundamental studies
- proof-of-principle, conductance of single benzene-1,4-dithiol molecule between Au electrodes:
- single atom transistor, two terpyridine ligands coordinate single cobalt atoms and cause electric coupling between cobalt and electrodes:



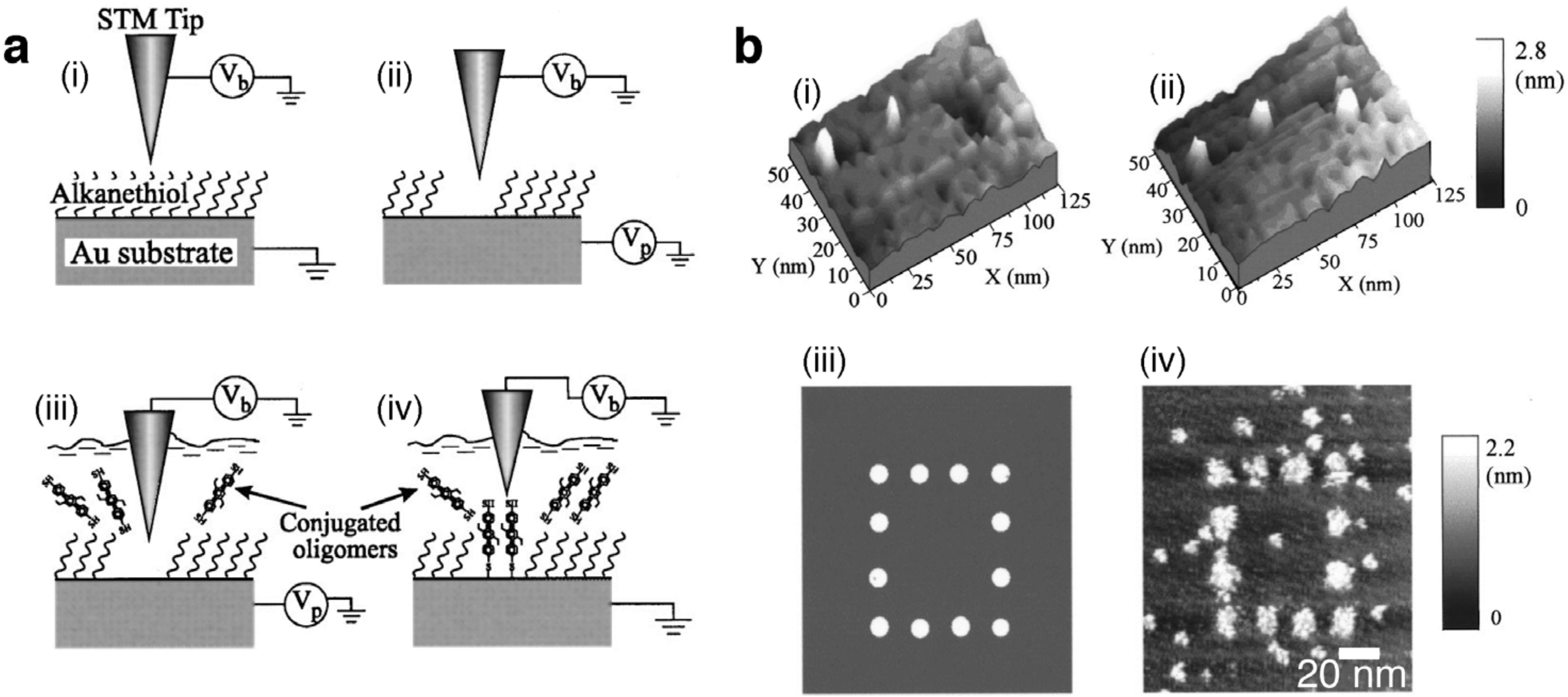


2. Self-assembly and self-organization

Nanopatterning of gold SAMs by STM:

a) STM tip is used to remove locally SAM and inserting conjugated oligomers

b) STM images of the process, (iv) shows final rectangular frame



2. Self-assembly and self-organization

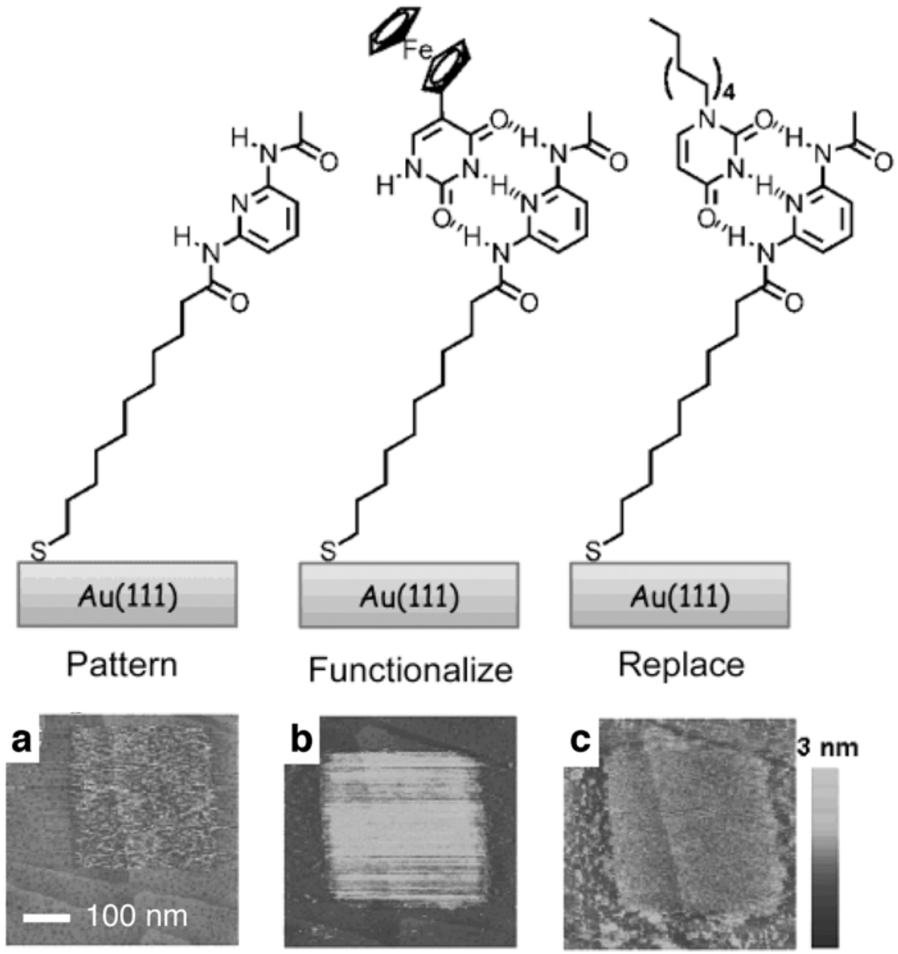
<u>Formation of molecular assemblies by STM</u>:

(a) STM image of diacyl 2,6-diaminopyridine (DAP) decanethiol binder inserted into a surrounding decanthiol monolayer.

(b) Image after binding the complementary electroactive Fc-uracil showing an increase in the current-dependent apparent height contrast.

(c) “Erased” pattern after replacing the electroactive guest with a more insulating dodecyl functionalized uracil.

NOTE: These examples show how far self-assemby is from real integrated devices!

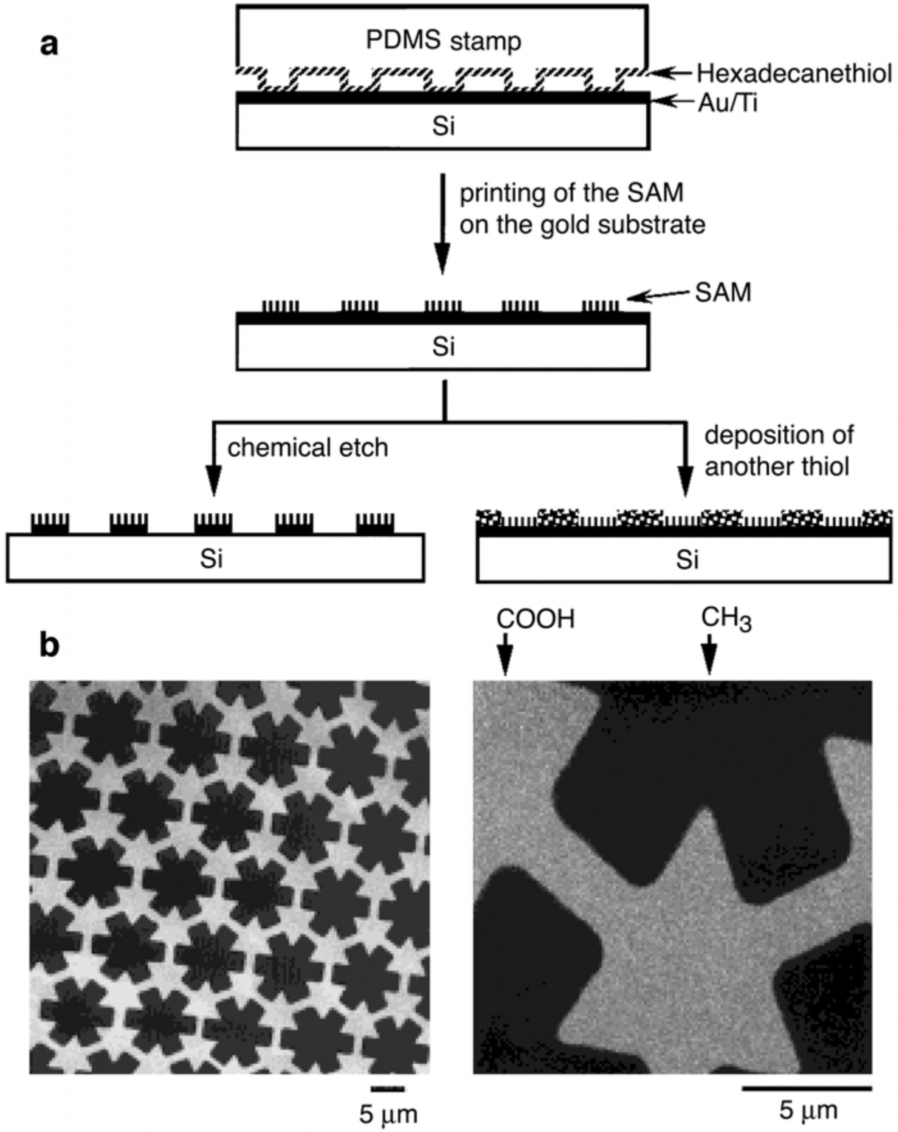


2. Self-assembly and self-organization

<u>Microcontact printing (μCP)is powerful for patterning gold/thiols</u>:

(a) Schematic illustration of the μCP procedure for patterning an alkanethiol (hexadecanethiol-HDT) on a flat gold substrate.

(b) Lateral force microscope (LFM) images of a patterned gold substrate with SAMs terminated in chemically different head groups (HDT-CH_3 and 16-mercaptohexadecanoic acid-COOH). The image contrast results from differences in frictional forces between the surface and the probe tip. Carboxylic acid terminated SAM show high measured frictional forces (light regions) and methyl terminated SAM show low measured frictional forces (dark regions).

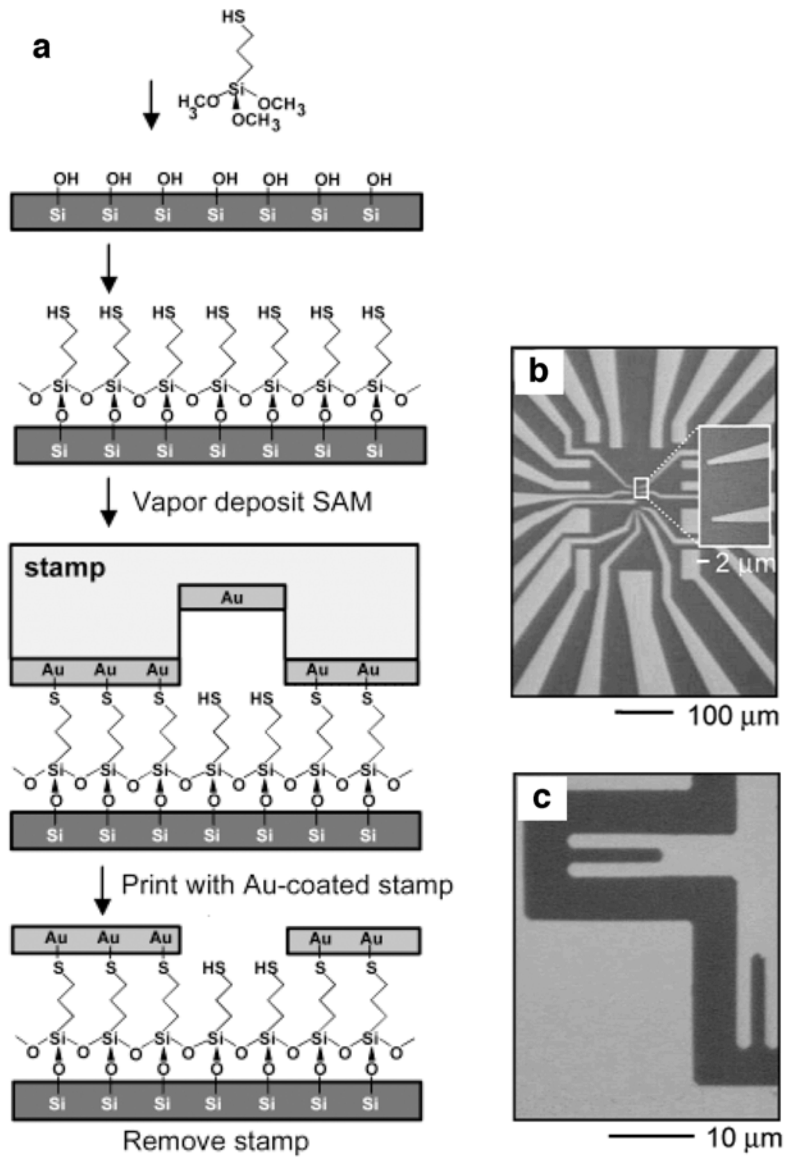


2. Self-assembly and self-organization

<u>Nanotransfer printing (nTP)</u>:

(a) Schematic representation of the nanotransfer printing (nTP) procedure to create gold patterns on Si substrates. Optical micrographs of a gold pattern formed by nTP on (b) a silica wafer, and (c) a plastic sheet [organosilsesquioxane modified poly(ethylene terephthalate)], demonstrating the wide applicability of the technique.

NOTE: stamp is fabricated by top-down lithography.



2. Self-assembly and self-organization

Organothiol monolayers on faceted metal clusters:

(a) The solution-based procedure for synthesizing alkanethiolate stabilized gold nanoparticles.

(b) Schematic illustration showing the curved surface and different regions of a nanopartice SAM.

The SAM shields gold core from agglomeration during nanoparticle formation.