SMR 1564 - 13

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

Biological Applications of Scanning Probe Microscopy (SPM)

Introduction to Atomic Force Microscopy

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These are preliminary lecture notes, intended only for distribution to participants.

Introduction to Atomic Force Microscopy

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and

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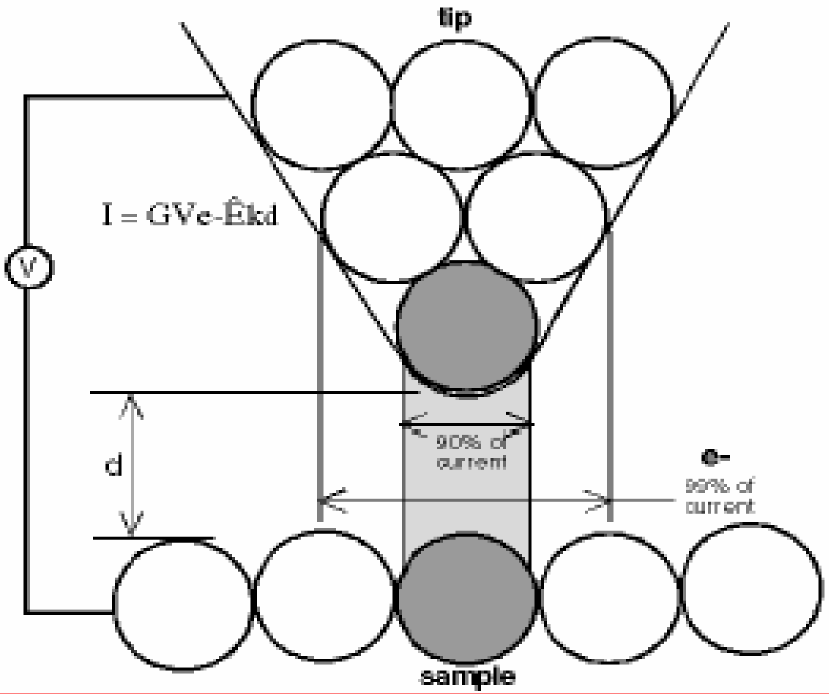
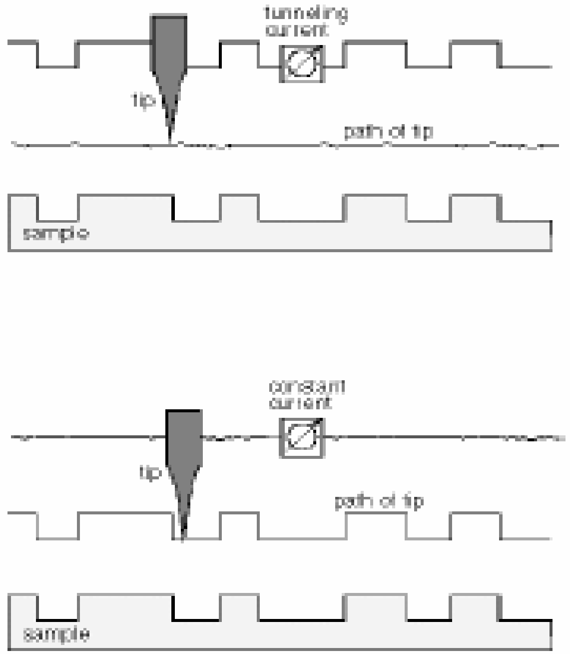
ACKNOWLEDEGEMENTS:

YING HU
and
GANG YU LIU (U.of C. Davis)
who kindly provided several images
for this lecture

Scanning Tunneling Microscope

- The scanning tunneling microscope (STM) is the ancestor of all scanning probe microscopes. It was invented in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich. Five years later they were awarded the Nobel prize in physics for its invention. The STM was the first instrument to generate real-space images of surfaces with atomic resolution.



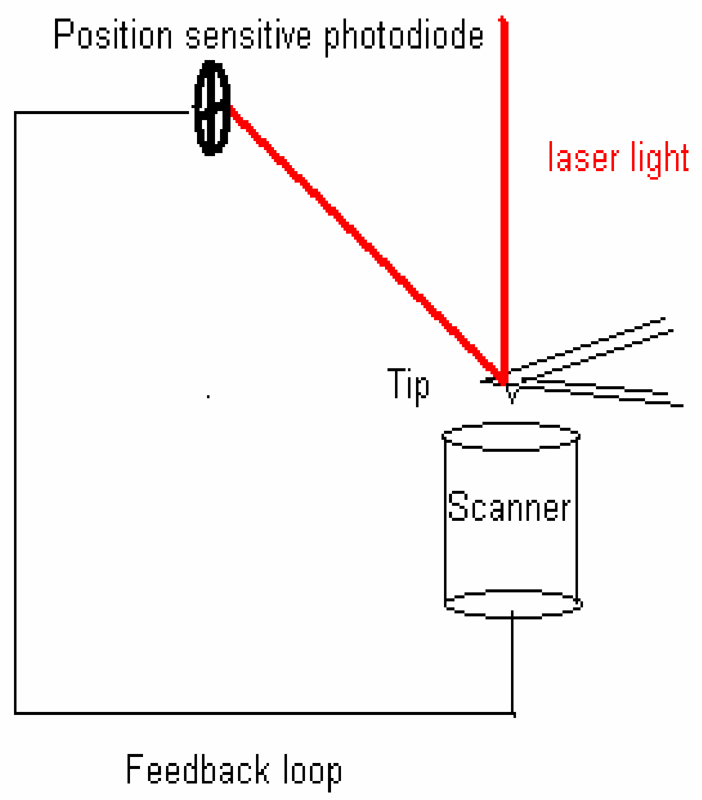


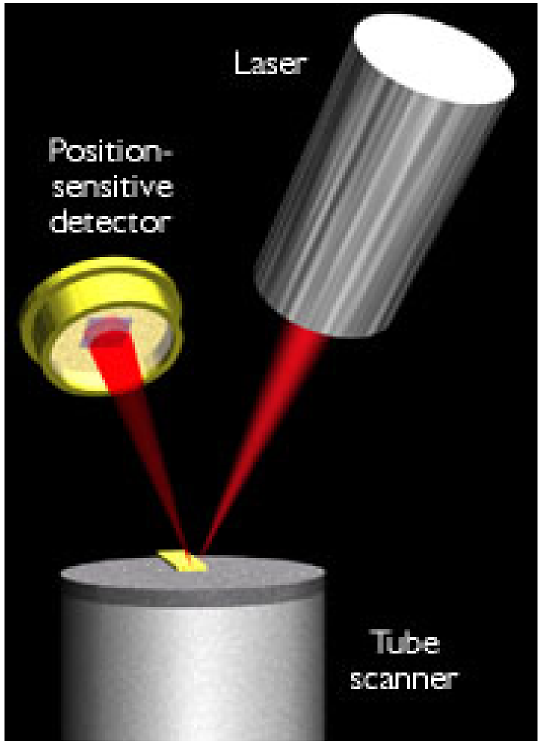
**The tip-surface interaction is highly local ---
at atomic/molecular level or better.**

→ **How to control such local interaction to do high resolution imaging?**

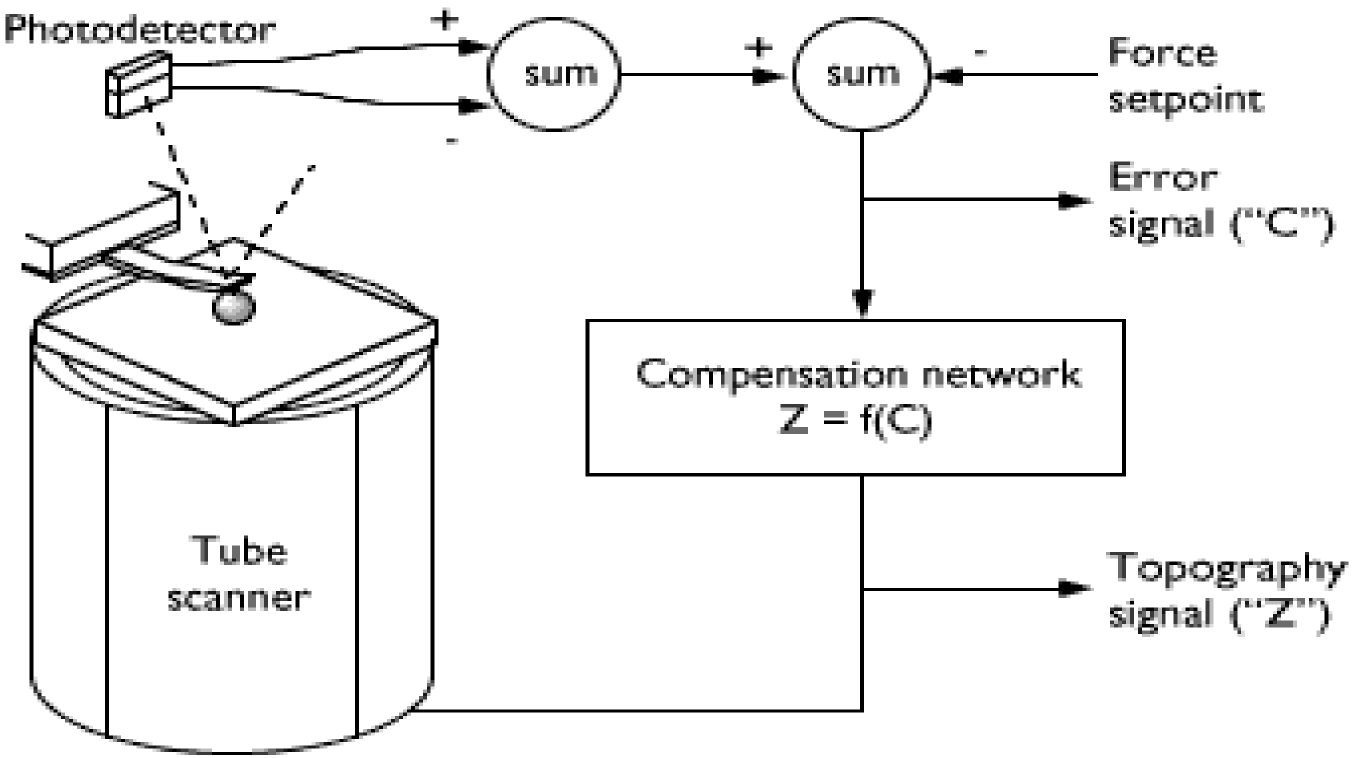
→ **How to control such local interaction
to do high precision scanning probe lithography?**

Are there any other methods (other than tunneling) to monitor the position of a sharp tip on a surface?


Position sensitive photodiode
laser light
Tip
Scanner
Feedback loop

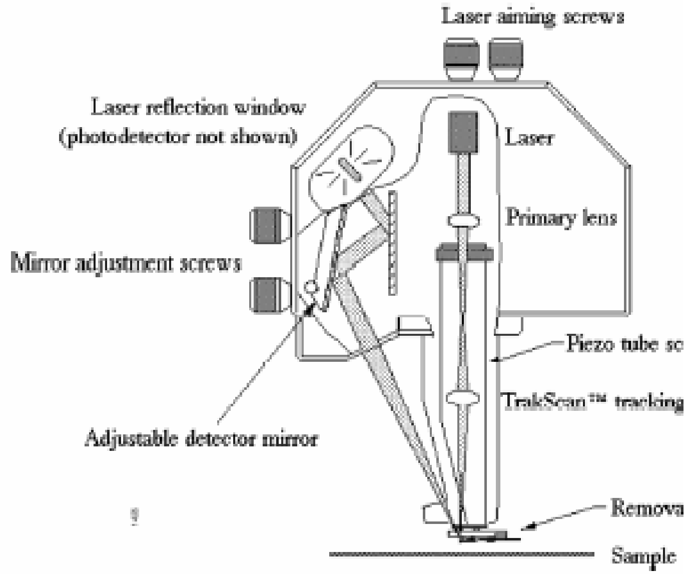

Laser
Position-
sensitive
detector
Tube
scanner

AFM also uses feedback to regulate the force on the sample

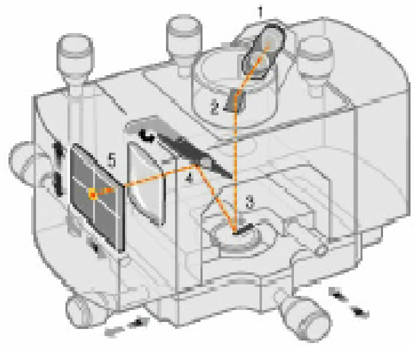


13.0 SPM Configurations

Scanned Tip SPM



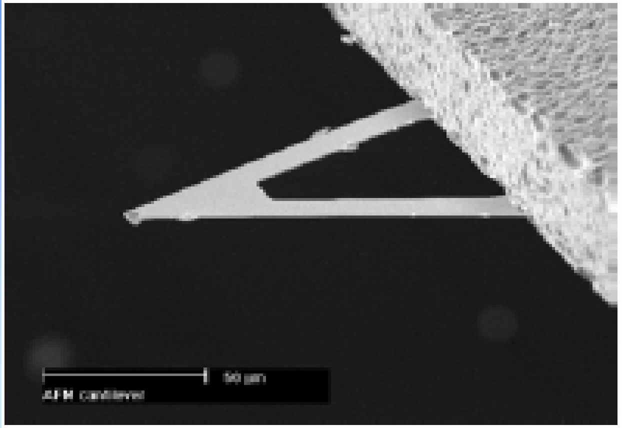
Scanned Sample SPM

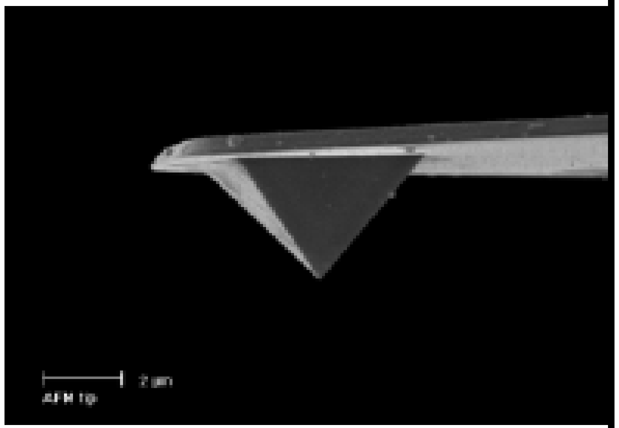


Labels:
1. Laser
2. Mirror
3. Cantileve
4. Tilt mirro
5. Photodete

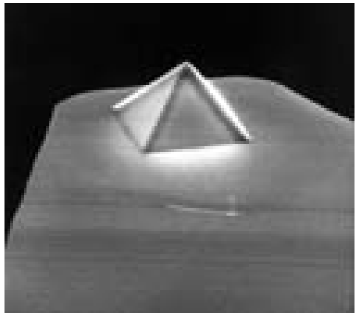
Atomic force microscopy, AFM

- The surface of the sample is scanned by a very sharp tip, which is attached to the end of the flexible cantilever
  - cantilever bends due to forces between the tip and the surface of the sample
  - sample or tip is moved by piezoelectric tube scanner

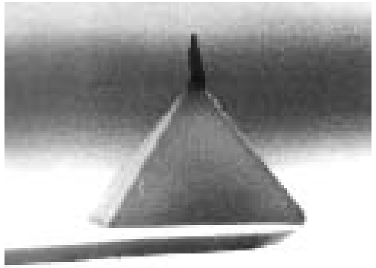




Some commercially available tips configuration



(a)



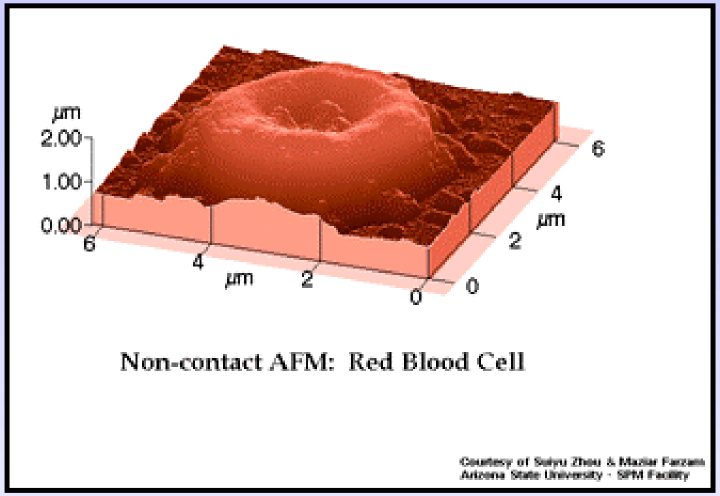
(b)

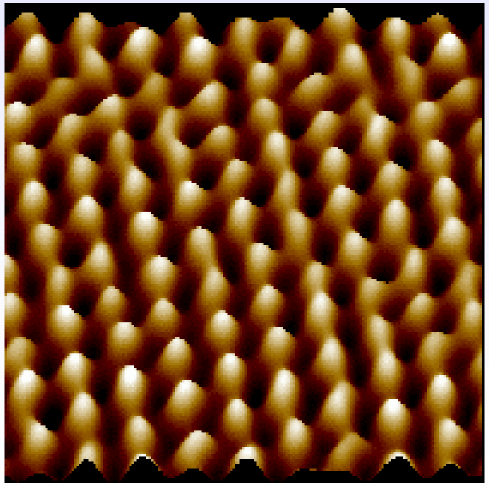
©

Three common types of AFM tip. (a) normal tip (3 µm tall); (b) supertip; (c) Ultralever (also 3 µm tall). Electron micrographs by Jean-Paul Revel, Caltech.

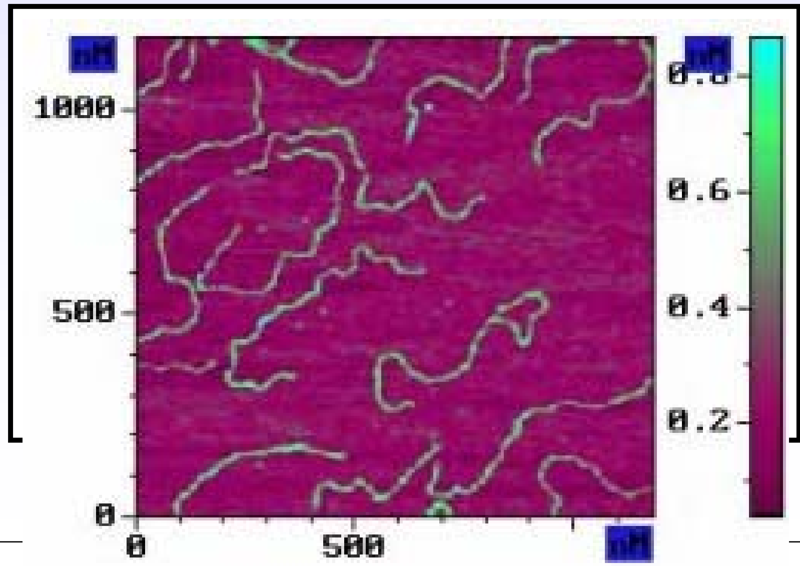
- Tips are generally evaluated by their “end radius” which limits the resolution of AFM.
- The "normal tip" (Albrecht et al., 1990) is a 3 µm tall pyramid with ~30 nm end radius.
- The electron-beam-deposited (EBD) tip or "supertip" offers a higher aspect ratio (it is long and thin, good for probing pits and crevices) and sometimes a better end radius than the normal tip.
- The "Ultralever" is based on an improved microlithography process. Ultralever offers a moderately high aspect ratio and on occasion a ~10 nm end radius.

AFM Images





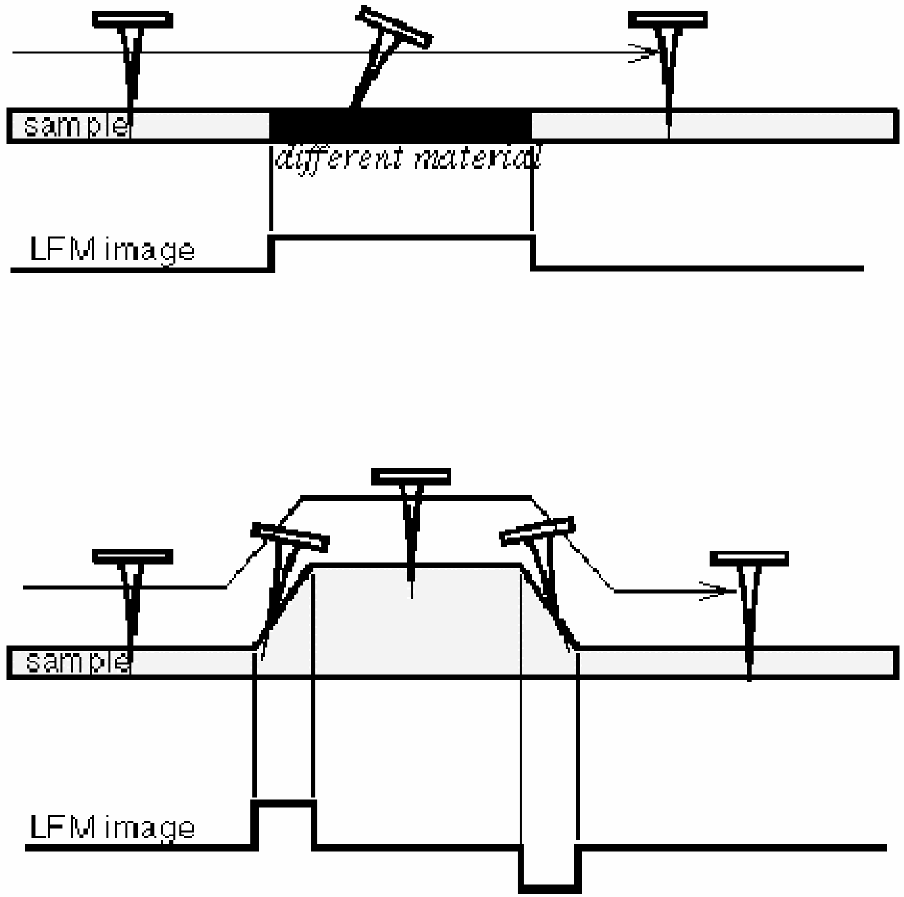
Mica atomic resolution image



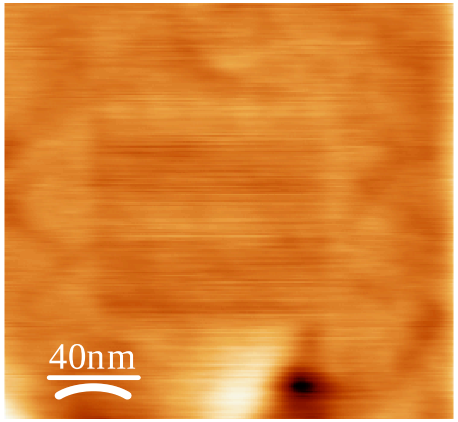
DNA

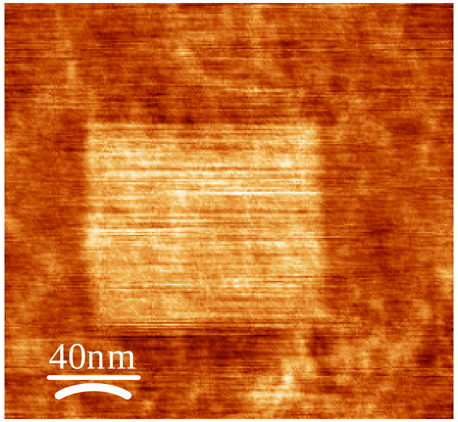
Lateral Force Microscope

- Lateral force microscopy (LFM) measures lateral deflections (twisting) of the cantilever that arise from forces on the cantilever parallel to the plane of the sample surface. LFM studies are useful for imaging variations in surface friction that can arise from inhomogeneity in surface material, and also for obtaining edge-enhanced images of any surface.
- Lateral deflections of the cantilever usually arise from two sources: changes in surface friction and changes in slope.

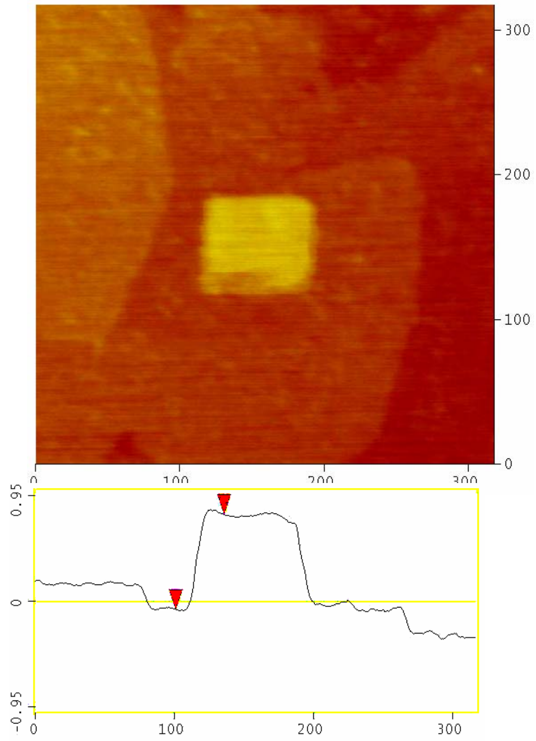


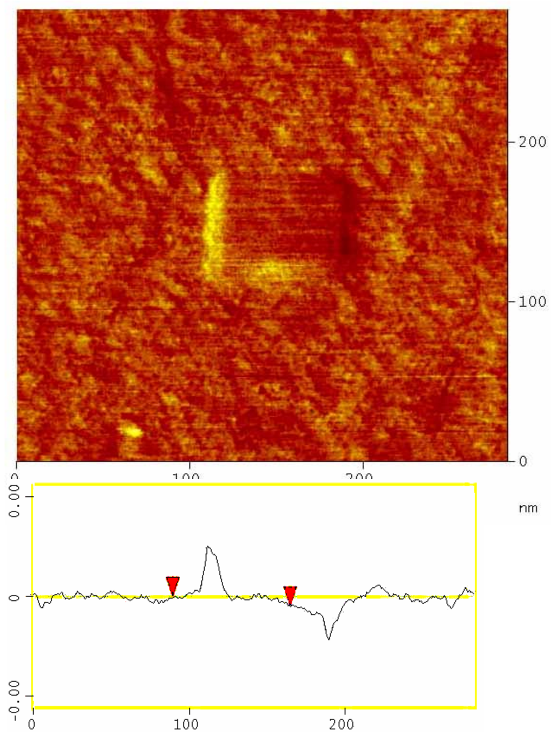
Dip Pen Nanografting





SH-(CH2)14-CF3 nanografted into
SH-(CH2)17-CH3 layers
(2000Å×2000Å) in air





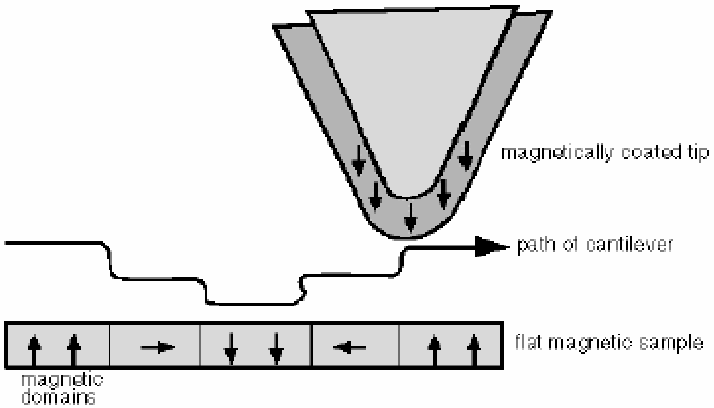
Topographic Data   Lateral Force Data

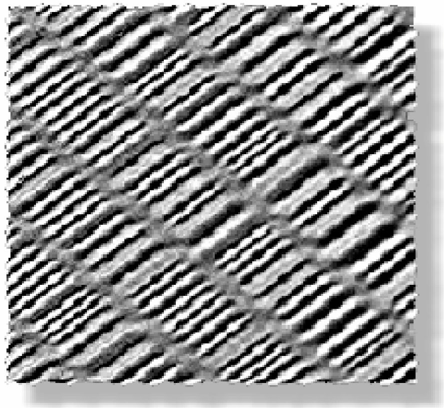
C_{18} pattern written into C_{10} matrix

Jordan Amadio(2002)

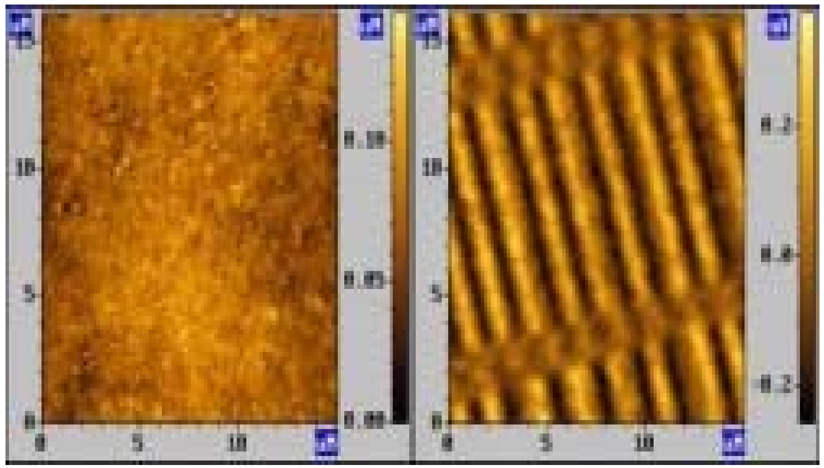
Magnetic Force Microscope

- Magnetic force microscopy (MFM) images the spatial variation of magnetic forces on a sample surface. For MFM, the tip is coated with a ferromagnetic thin film. The system operates in non-contact mode, detecting changes in the resonant frequency of the cantilever induced by the magnetic field's dependence on tip-to-sample separation. MFM can be used to image naturally occurring and deliberately written domain structures in magnetic materials.
- An image taken with a magnetic tip contains information about both the topography and the magnetic properties of a surface





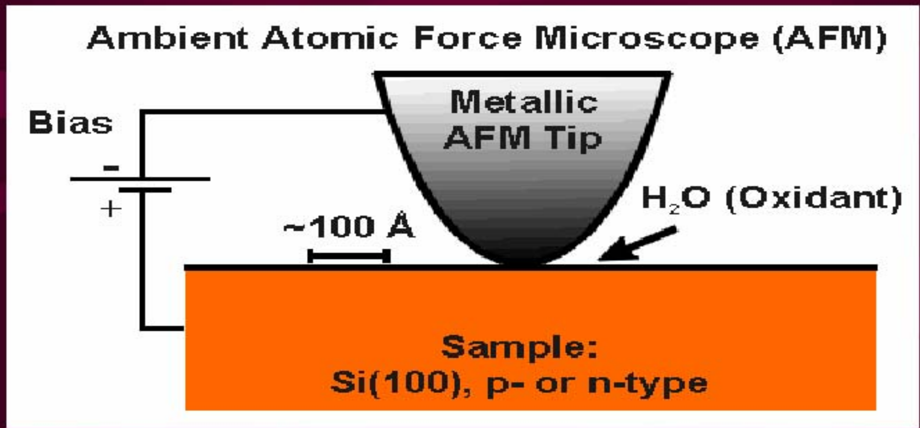
Hard-disk service. Field of view is 30 μm.



Hard disk

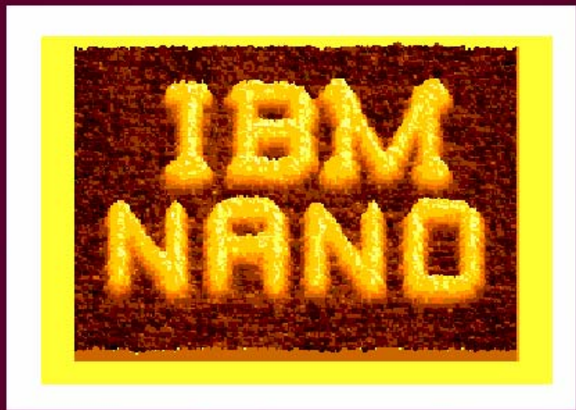
Local Oxidation

- The AFM-tip induced oxidation process is based on negatively biasing the tip with respect to the substrate under ambient conditions, which can be either a semiconductor or a metal.



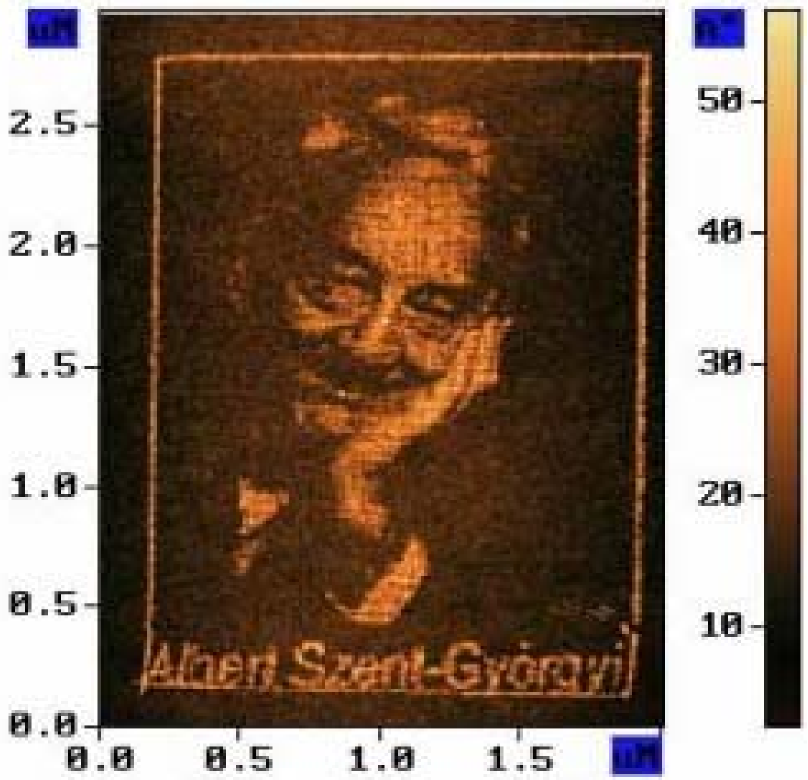
- The substrate locally oxidizes upon moving the tip in contact mode across the surface.

Example of Local Oxidation



- The atomic-force microscope (AFM) image above gives an example where oxide lines of about 20 nm width were used to define the silicon dioxide pattern "IBM NANO" on a silicon wafer.

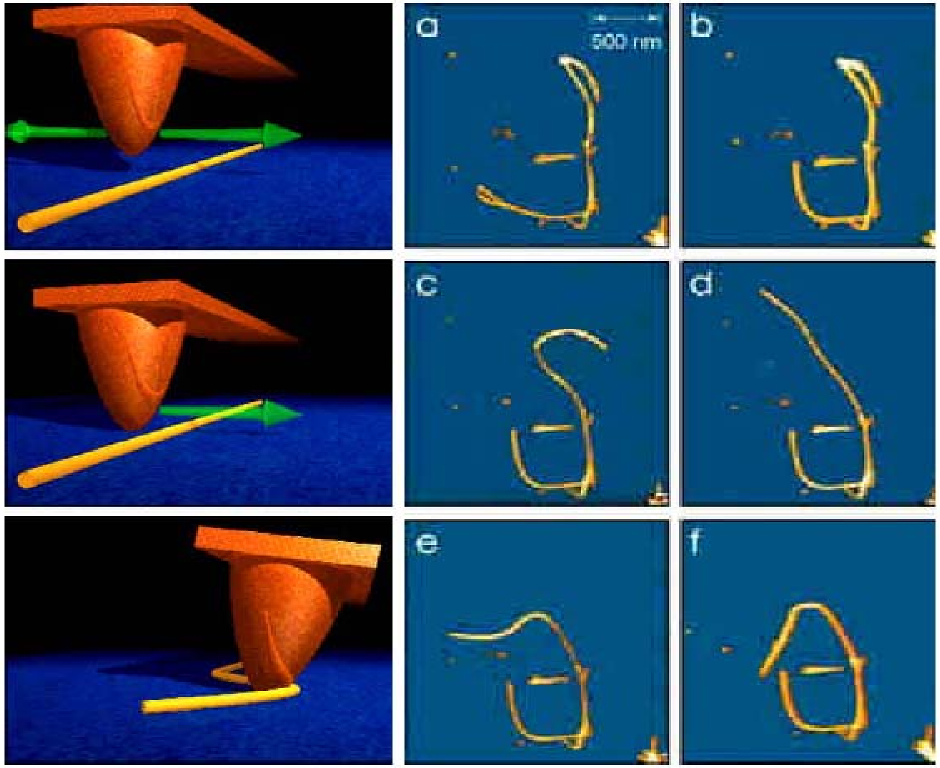
Examples of local oxidation



MANIPULATION is DIFFICULT but POSSIBLE

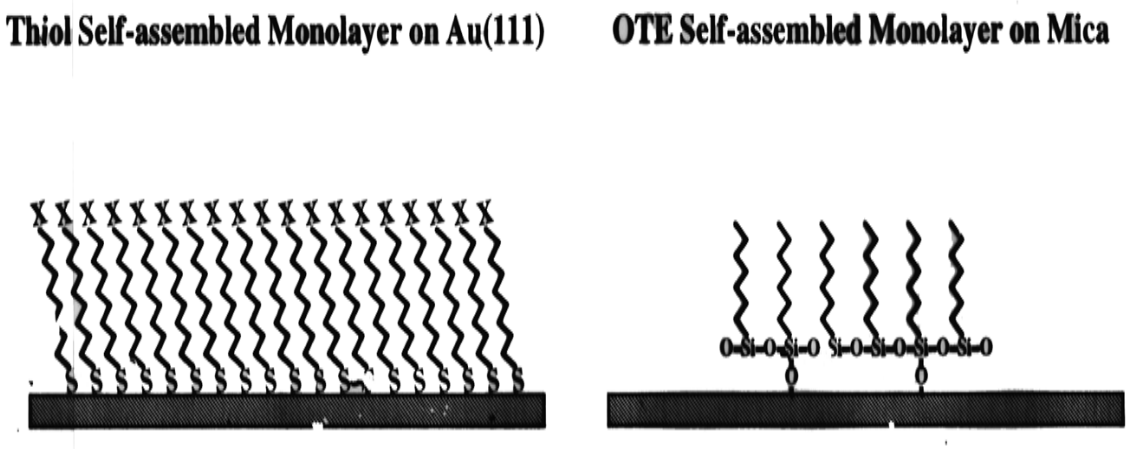
Micro Nano Manipulation

- IBM nanotube manipulation for position nanotube on transistors.
- http://www.research.ibm.com/nanoscience/nanotubes.html



CHEMICAL APPLICATIONS

A Quick Introduction of Self-Assembled Monolayers (SAMs)



Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* 1983, *106*, 4481.

Membrane-like monolayers:

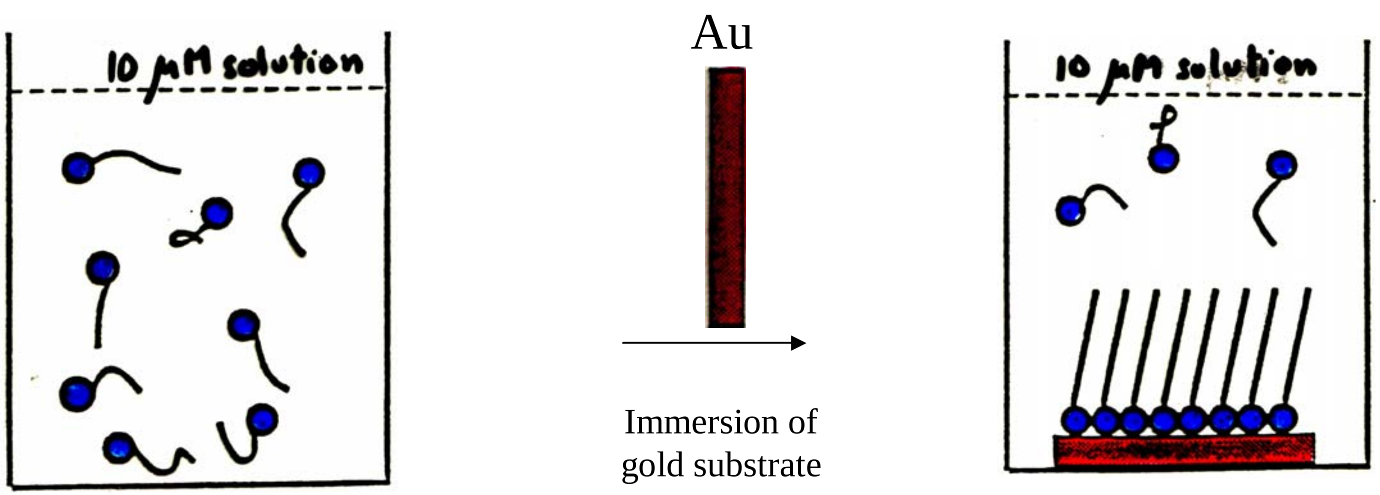
1) Langmuir 2) Langmuir-Blodgett

3) Preparation of Thiol SAMs

(Self-Assembled Monolayers) on Au(111)

Solution Deposition

We prepare a thiol monolayer by placing a clean gold(111) substrate in less than 0.1 micromolar ethanolic thiol solution for 18 hours.



Alkyl thiol: CH3(CH2)nSH: 

A Quick Introduction of Self-Assembled Monolayers (SAMs)

Bond energy

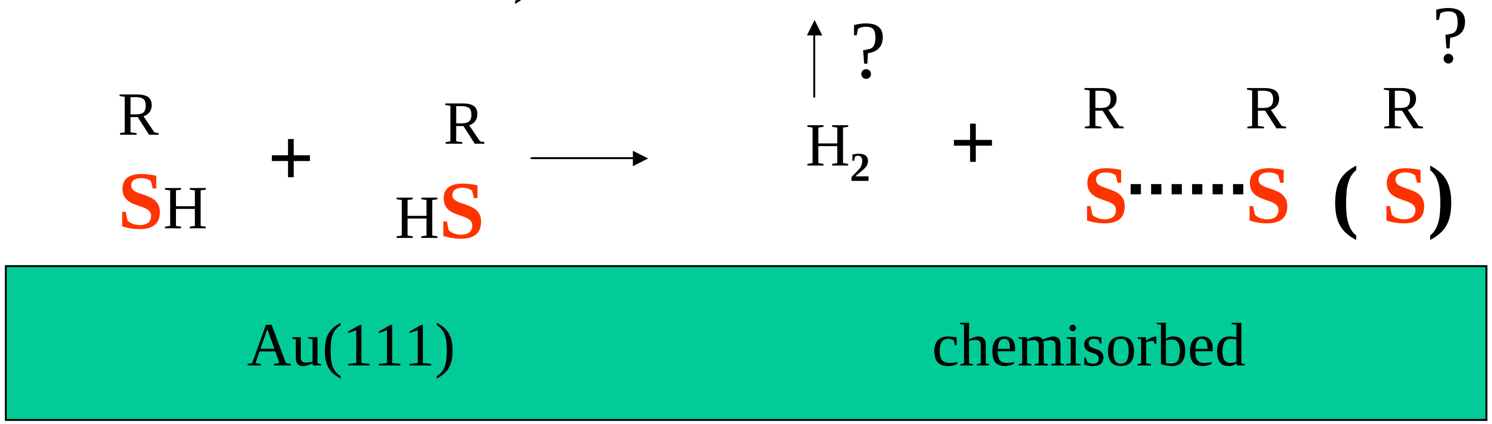
- **C-C: 145 kcal/mol**
- **C-S: 171 kcal/mol**
- **C-H: 81 kcal/mol**

- **S-Au: 40 kcal/mol**
- **van der Waals energy per CH_2 group is ~ 1.5 kcal/mol**

THE ADSORPTION of ALKYLTHIOLS on GOLD

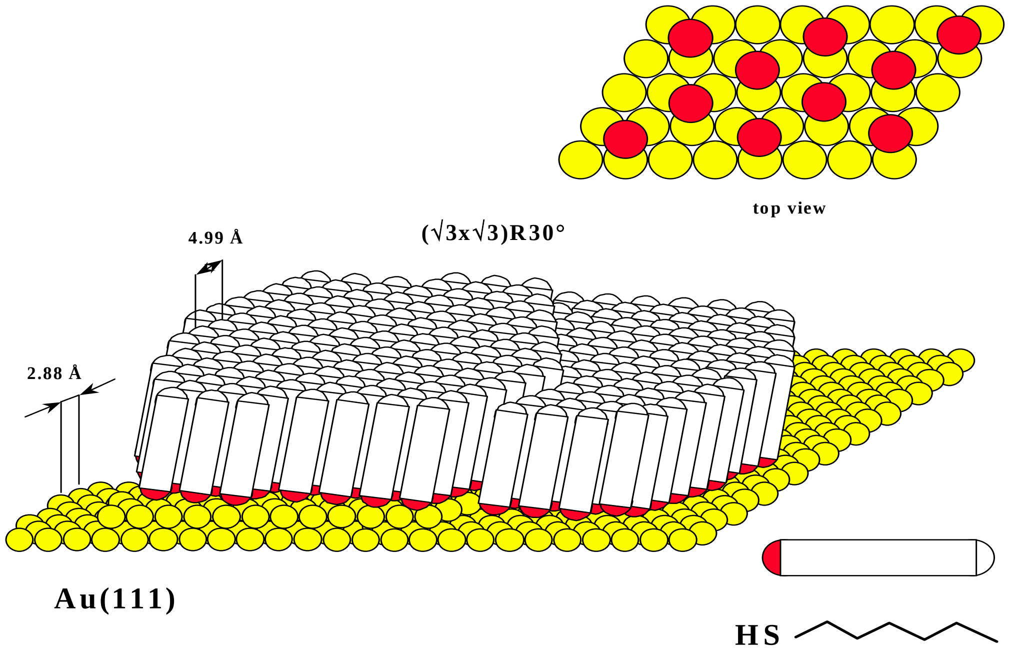
H-**S**-R thiol
R-**S**-R dialkyl sulfide
(R-**S**-**S**-R disulfide)

H-O-R alcohol
R-O-R dialkyl oxide



CH_3**SS**CH_3	sticks to gold with unit probability
CH_3**S**H	very low sticking probability
CH_3**S**CH3	does not stick

A Quick Introduction of Self-Assembled Monolayers (SAMs)



Self-assembled monolayers of alkanethiols on gold are much studied systems because:

1) Very stable and easily formed
2) Frequently used for electrode surface modification (Chemical SENSORS)
3) Model systems for interfacial electron transfer
4) Soft lithography & surface patterning (micro printing)
5) Model systems for surface passivation against corrosion (also bio passivation).
6) Model systems for study of friction
7) Colloid coating and linking for cluster-based materials
8) Suitable films for nanografting (i.e. locally induced chemistry)
9) Last but not least, SAMs have, recently, become the building blocks of a new wave of promising molecular electronic devices (FETs, switches etc).

During the last 10 years we have dealt extensively, using X-rays, atom diffraction and SPM, with issues like:

1) Structure

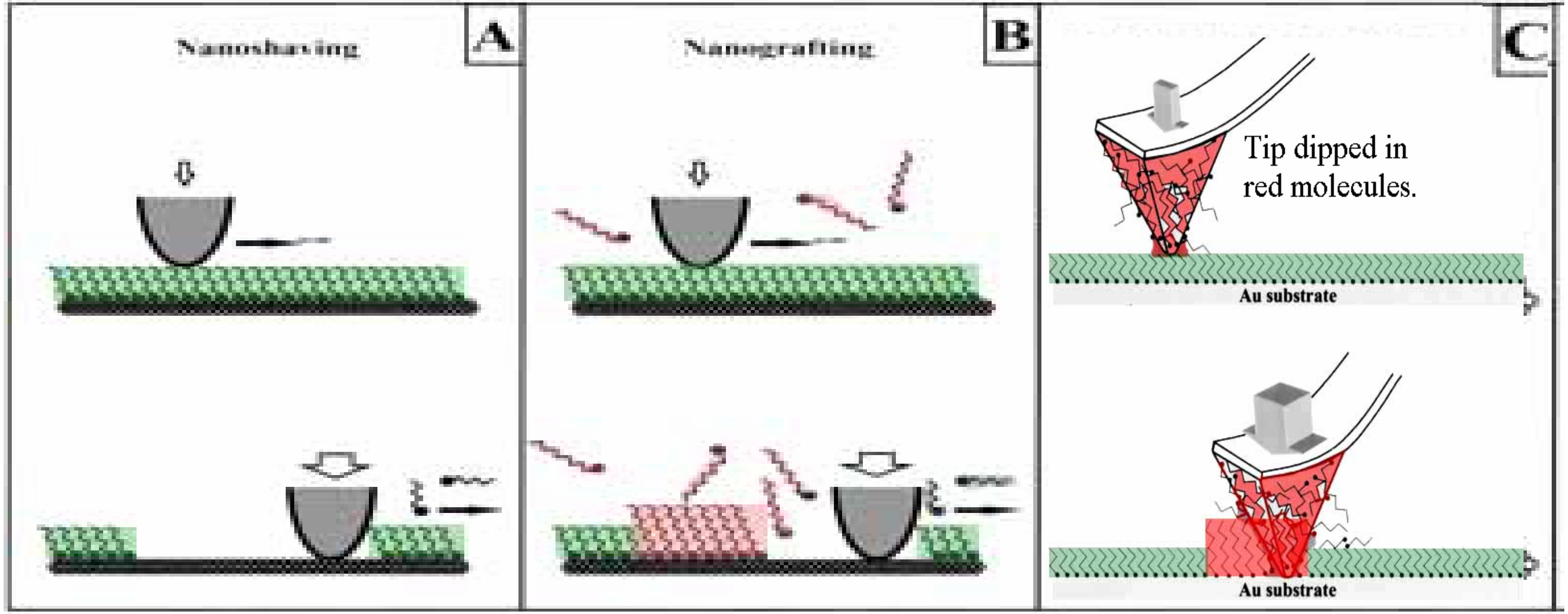
2) Kinetics of growth

3) Manipulation at the nanoscale

The third topic is the focus of today's talk.

Surface Manipulation

Three powerful methods to manipulate the chemical composition of surfaces on the nanoscale.



Nanoshaving | Nanografting | Dip Pen Nanografting

These techniques have been introduced in 1997 by Gang-Yu Liu At Wayne State University. She is now at the U. of C. Davis.

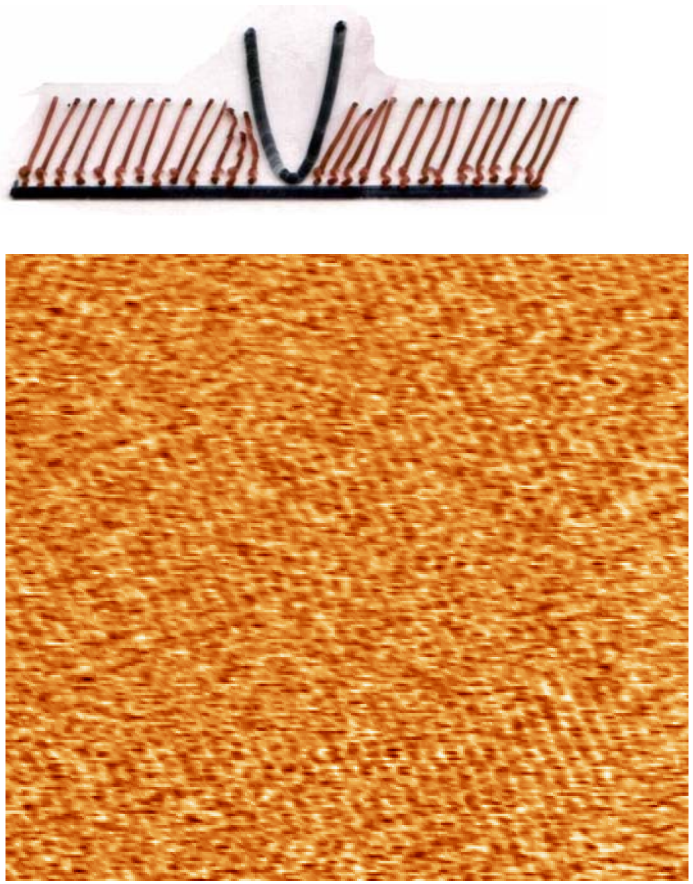
This method is similar to Mirkin's but it is less affected by molecule diffusion and hence has 10 times higher resolution.

G.Y.Liu Acc. Chem. Res. 2000

How do we know how much force to use?

High Force 20nN

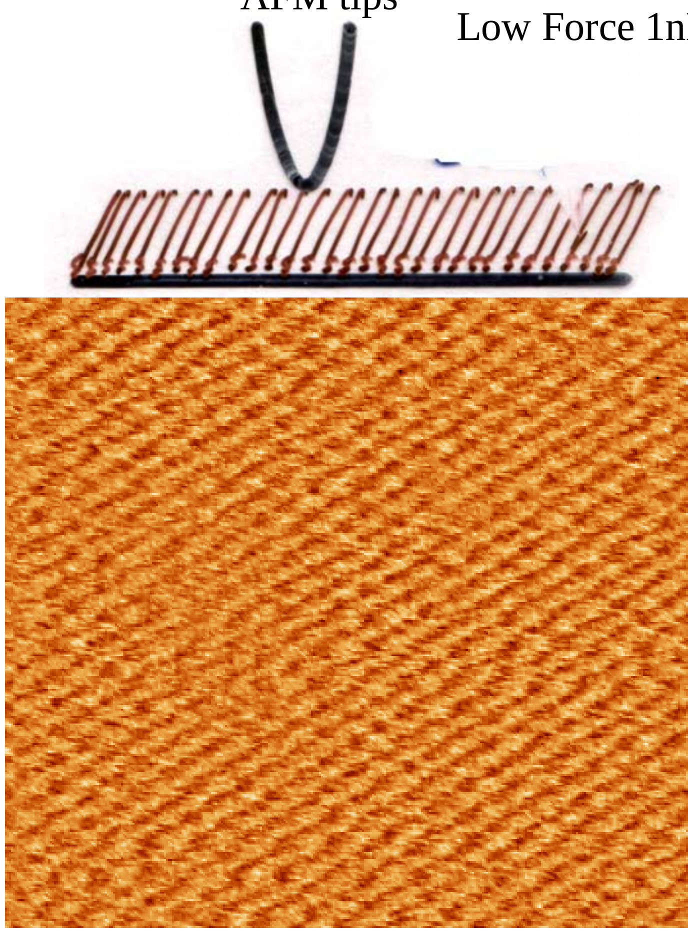
AFM tips



Atomic resolution image of
gold(111) (100 Å × 100 Å)

AFM tips

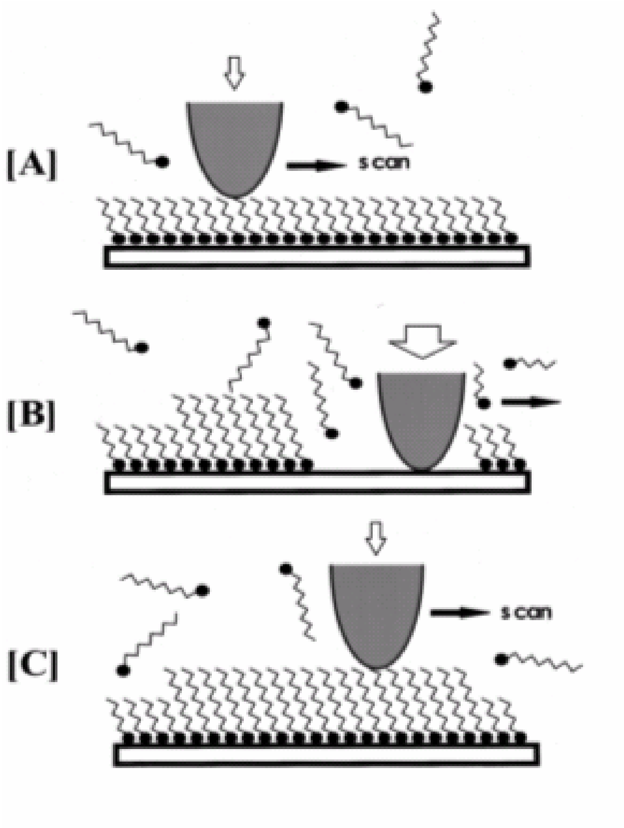
Low Force 1nN

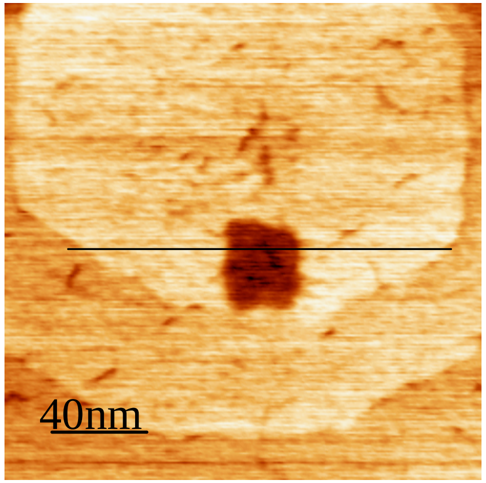


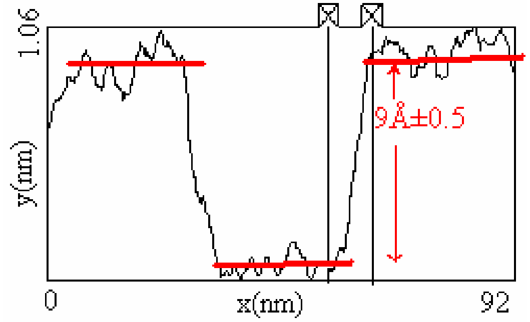
Molecular resolution image of
C18 (100 Å × 100 Å)

BASIC NANOGRAFTING

In solution:

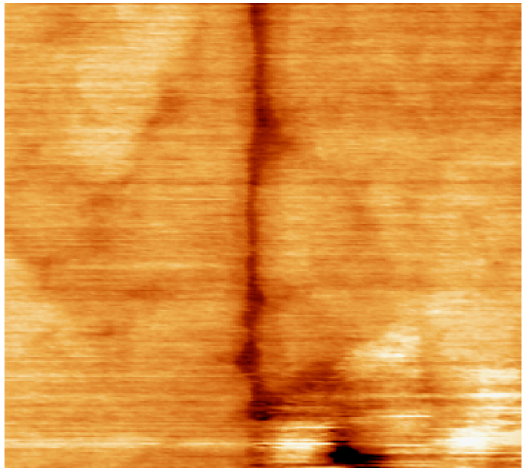






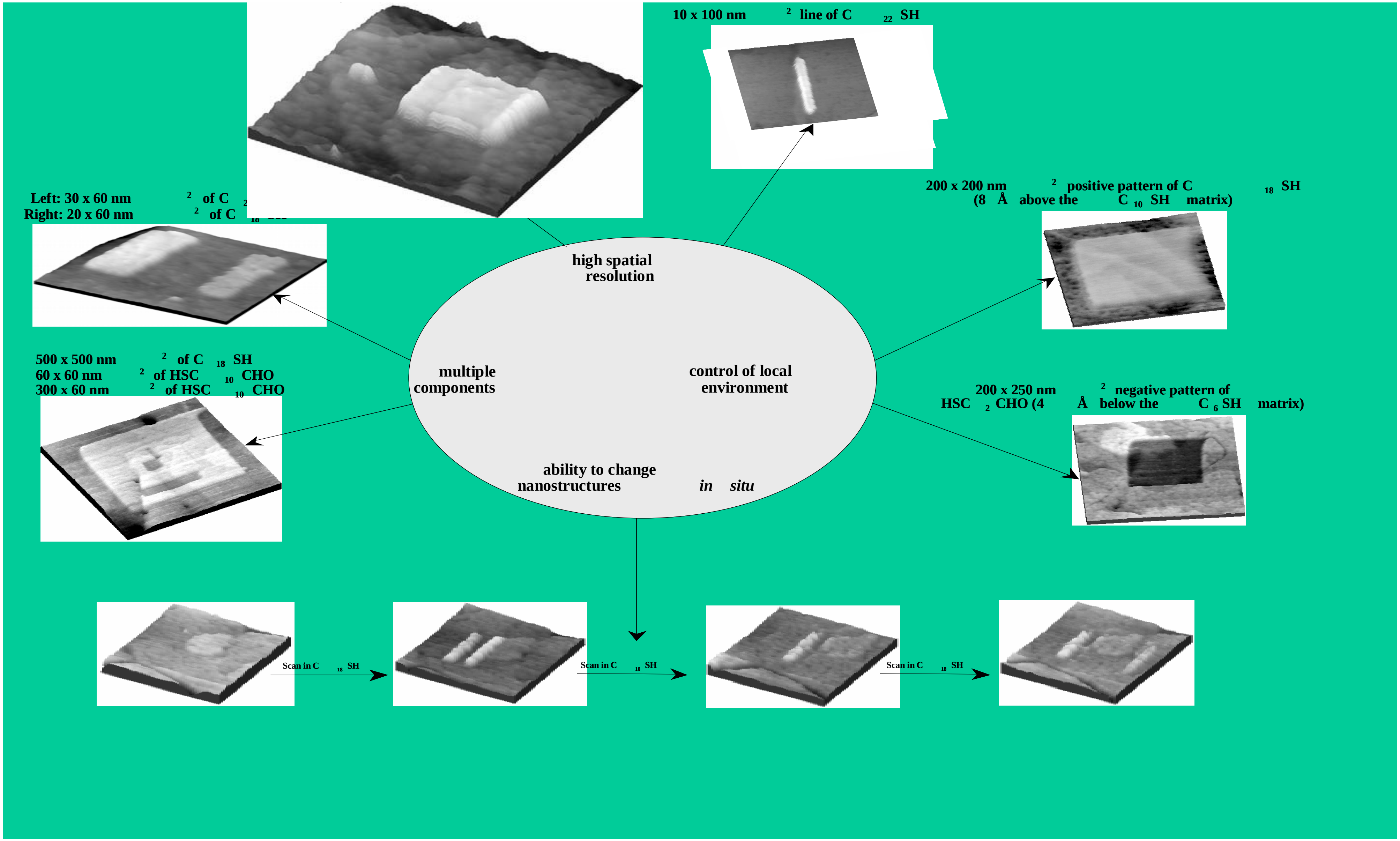
Expected height difference: 8.7Å

C_{10} nanografted into a C_{18} SAM (400 Å × 400 Å)

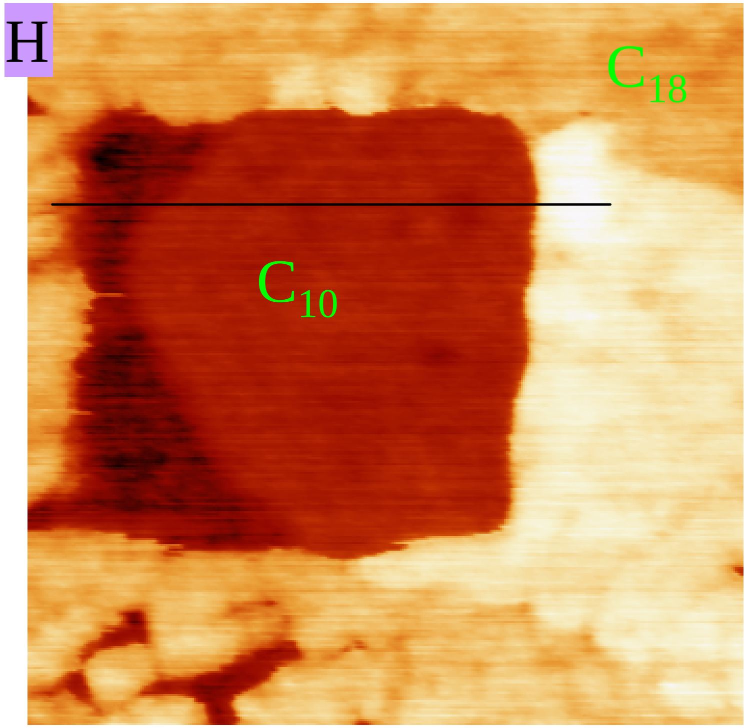


A 70 Å “line” of C_{10} nanografted into a C_{18} SAM (800 Å × 800 Å)

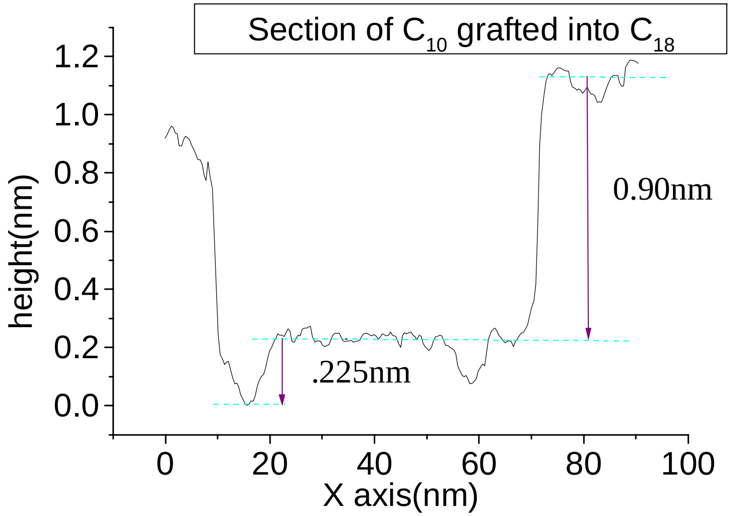
Example nanostructures of organic molecules

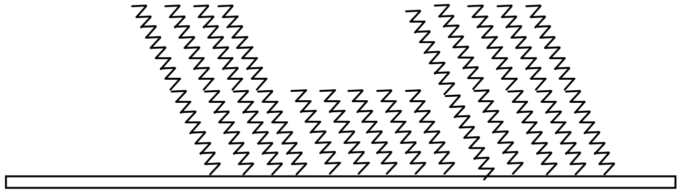


An Example of Nanografting



C_{10} grafted into C_{18} (100nm×100nm)
and the corresponding height measurement



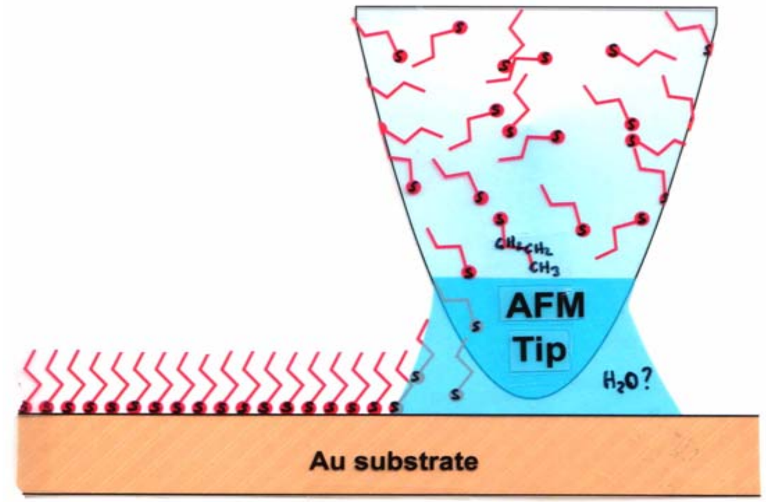


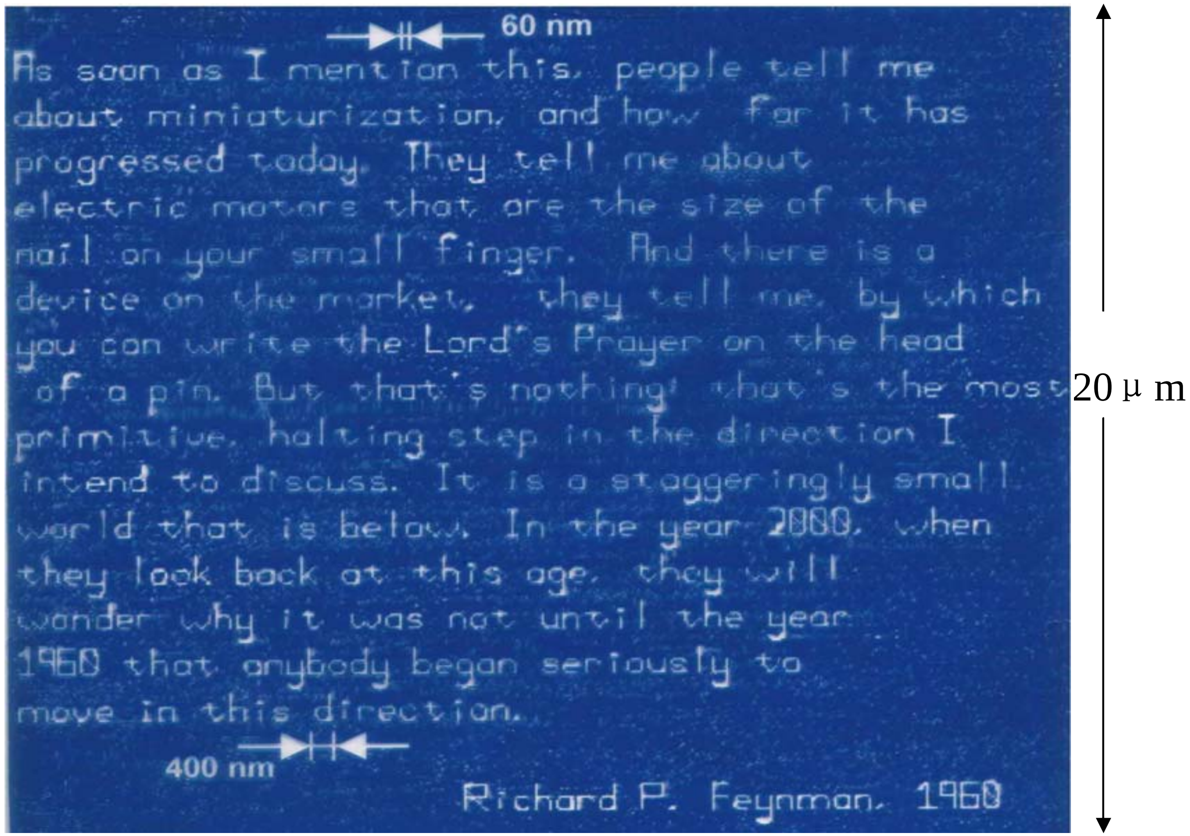
Calculated height measurement between C_{10} and C_{18} is 0.86 nm.

(Ying Hu 2002)
Princeton

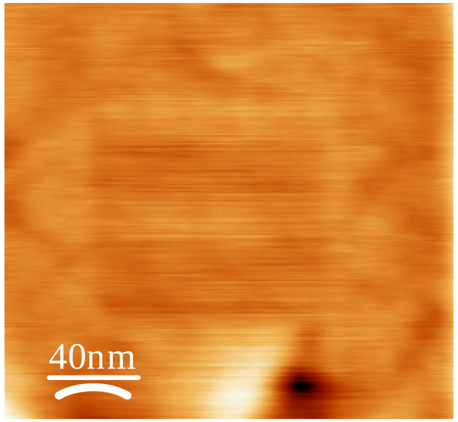
Dip-Pen Nanolithography

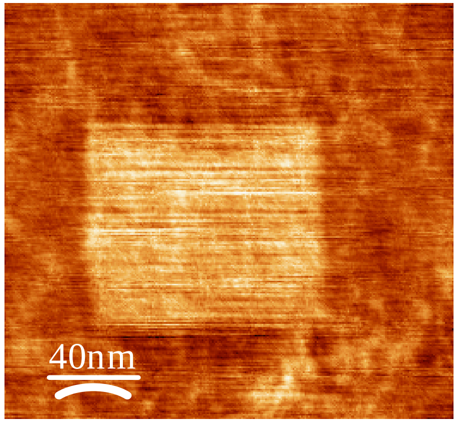
C.Mirkin and Coll. Science, 2000



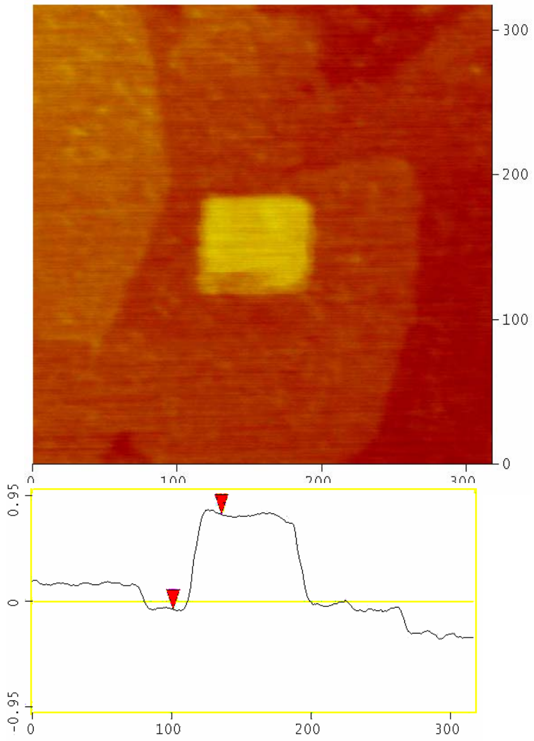


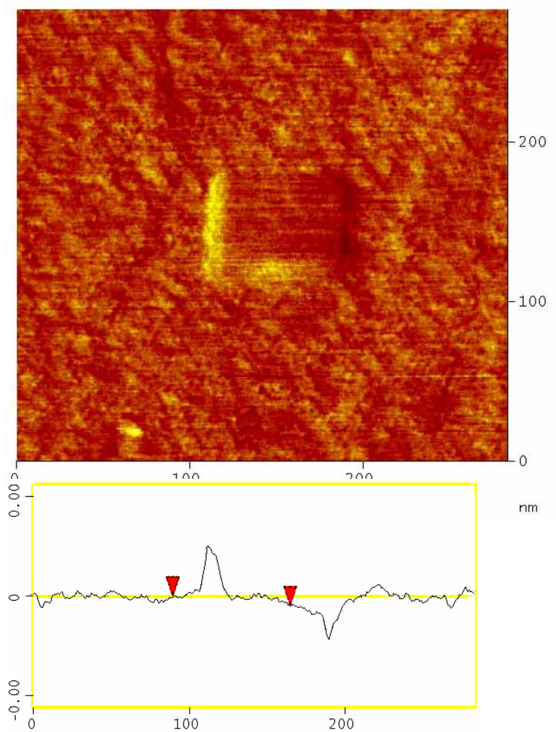
Dip Pen Nanografting





SH-(CH2)14-CF3 nanografted into
SH-(CH2)17-CH3 layers
(2000Å×2000Å) in air





Topographic Data   Lateral Force Data

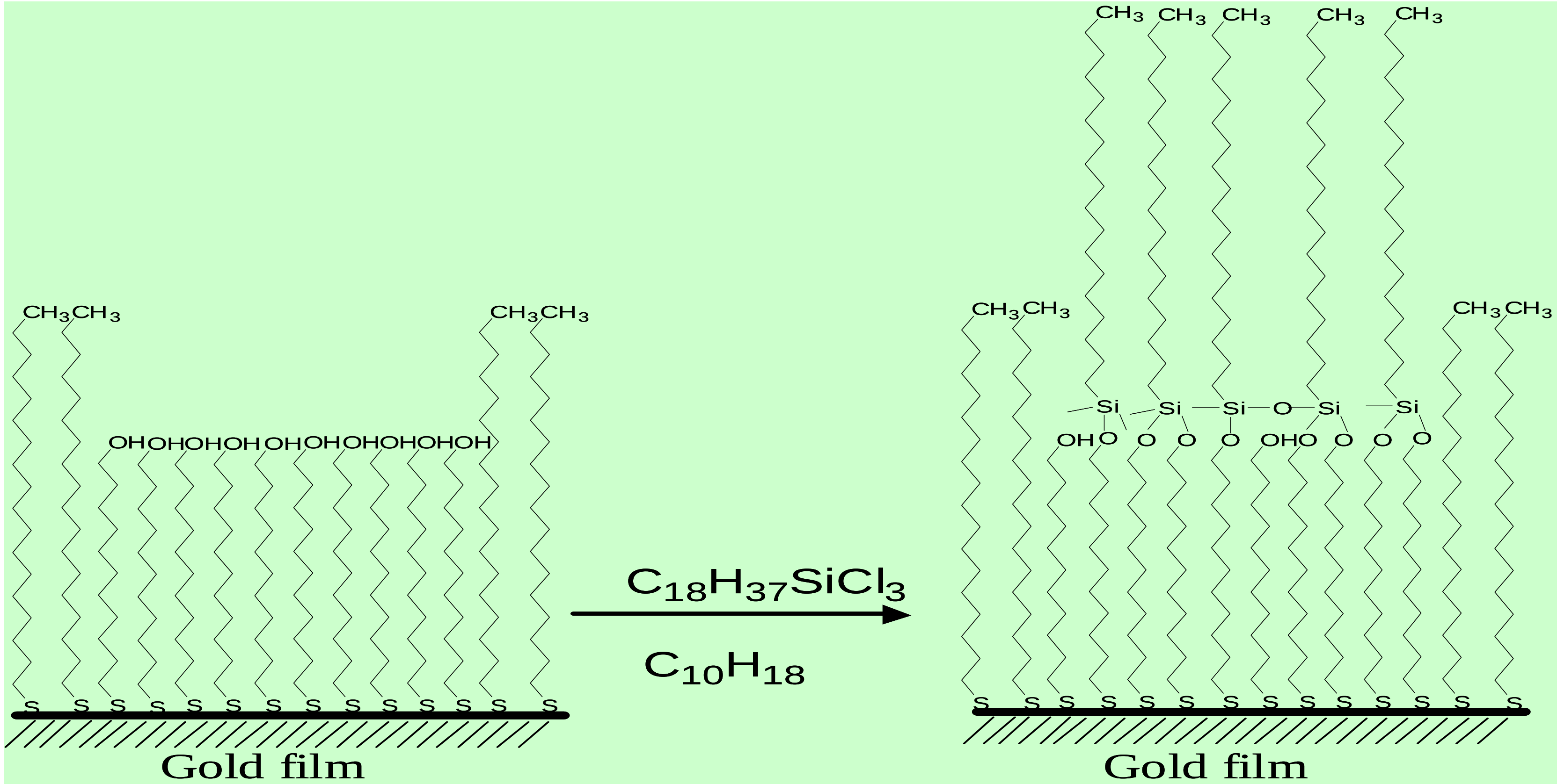
C_{18} pattern written into C_{10} matrix

Jordan Amadio(2002)

Construction of 3D Nanostructures

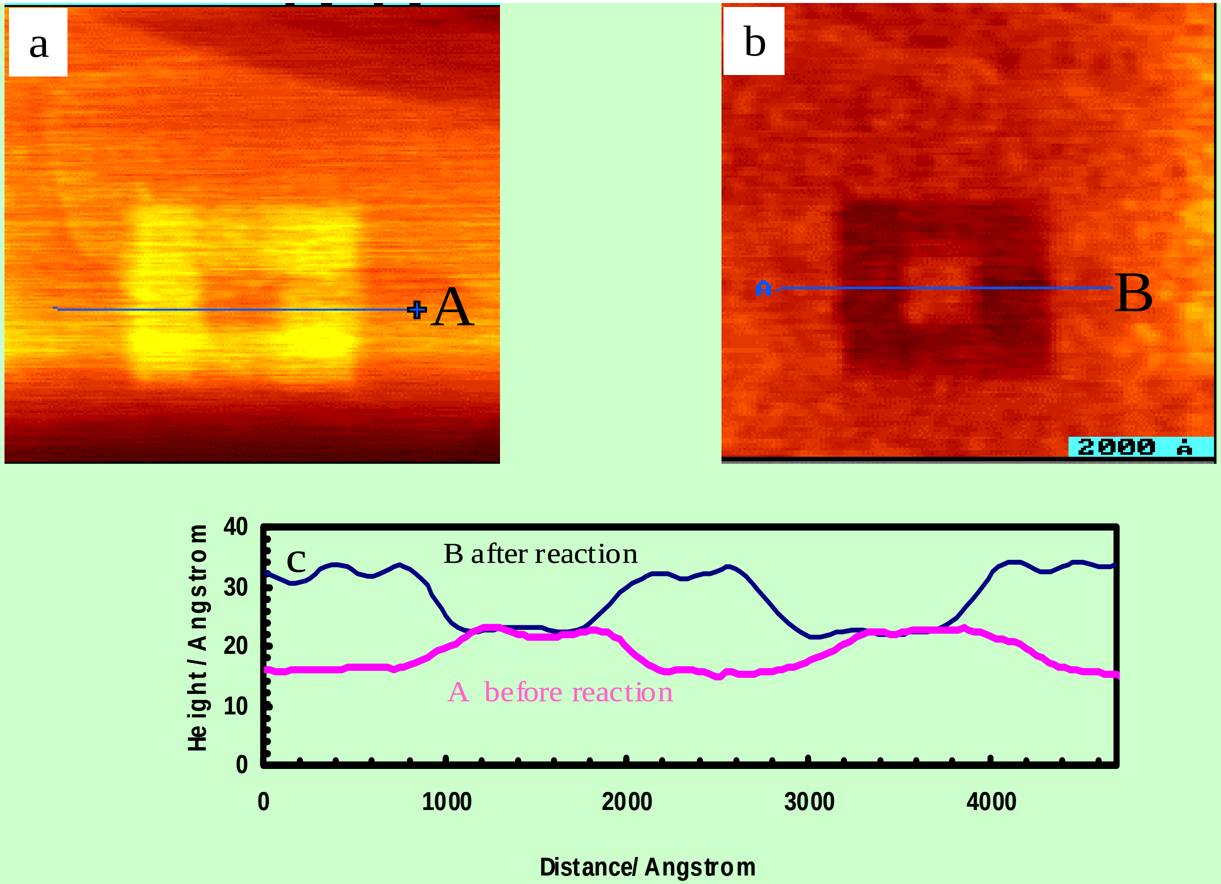
Pattern transfer via surface reactions

Construction of 3D Nanostructures



Reaction of surface -OH groups with octadecyltrichlorosilane ($C_{18}H_{37}SiCl_3$)in decahydronaphthalene($C_{10}H_{18}$)

Construction of 3D Nanostructures



AFM images (a, b) and height-distance plots (c) before (a) and after (b) reaction of the surface hydroxyl groups with 11 mM octadecyltrichlorosilane in decahydronaphthalene