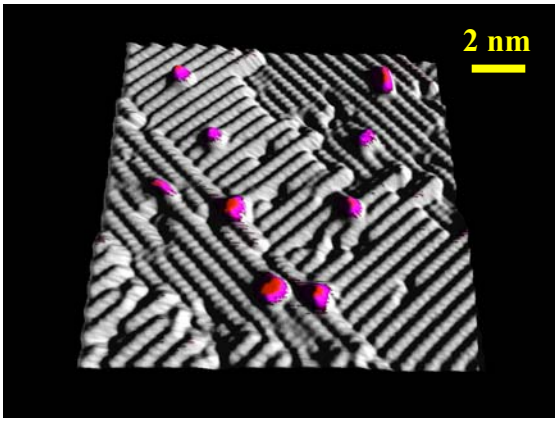
Scanning Probe Lithography



M. C. Hersam, *et al.*, *Nanotechnology*, **11**, 70 (2000).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Scanning Tunneling Microscopy Nanofabrication

Many nanofabrication schemes have been developed with STM (spatial resolution down to the single atom level):

(1) Initially demonstrated by Eigler in 1989
("IBM" written with atoms at cryogenic temperatures)

(2) Room temperature atom removal from Si(111) by Avouris

(3) Field evaporation of gold

(4) Electron stimulated desorption of hydrogen from Si(100)

Department of Materials Science and Engineering, Northwestern University

Tunable Bond Formation with STM

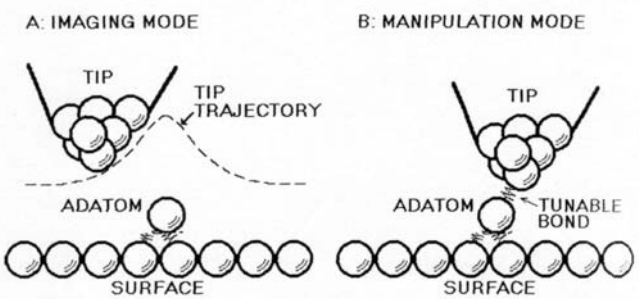


FIGURE 2. (A) In the imaging mode the tip is stabilized far enough above the surface so that the interaction between the tip and the adatom is negligible. (B) In the manipulation mode the tip is brought close enough to the adatom to drag the adatom along the surface. The force exerted on the adatom by the tip is due to the partially formed chemical bond between the tip and the adatom.

G. Timp, *Nanotechnology*, Chapter 11

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Sliding Adatoms with STM

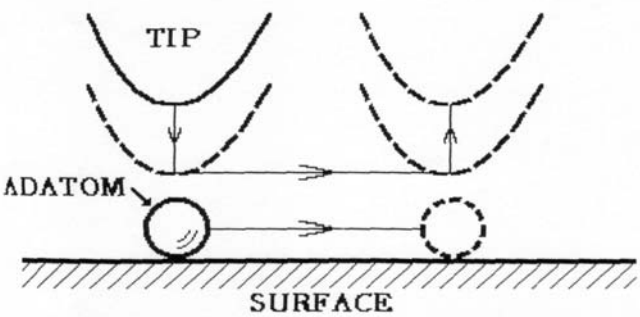
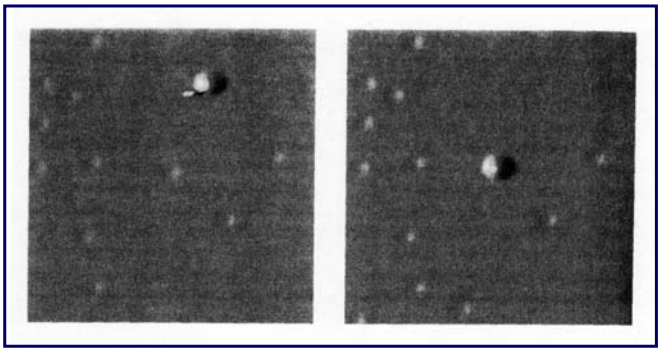


FIGURE 3. Schematic of the sliding process. The tip is placed above the adatom and then lowered to an empirically determined height at which the attractive interaction between the tip and the adatom is sufficient to pull the adatom along the surface. Once the adatom is moved to its final location, the tip is raised back to the height used for imaging, effectively terminating the tip-adatom interaction.

G. Timp, *Nanotechnology*, Chapter 11

Department of Materials Science and Engineering, Northwestern University

The First Atom Moved with STM



Xenon on platinum → requires a defect to prevent tip-induced motion under normal scanning conditions

G. Timp, *Nanotechnology*, Chapter 11

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

STM Manipulation of Xenon on Nickel

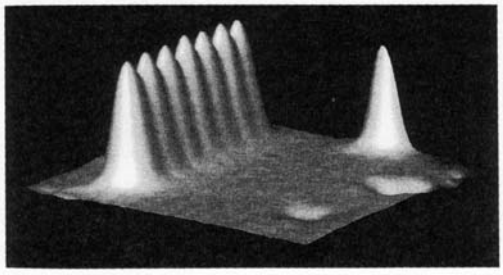


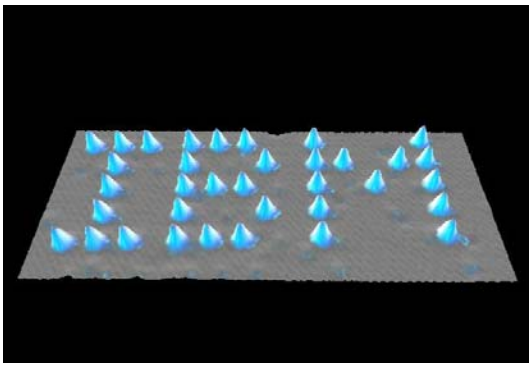
FIGURE 5. A row of seven xenon atoms constructed with the STM. The xenon atoms are spaced apart every other atom of the underlying nickel surface. The xenon atom cannot be packed together any tighter and remain in a single row. From building structures like this we learn about the strength of the xenon-xenon interaction relative to the strength of the in-plane interaction between the xenon atoms and the underlying nickel atoms.

G. Timp, *Nanotechnology*, Chapter 11

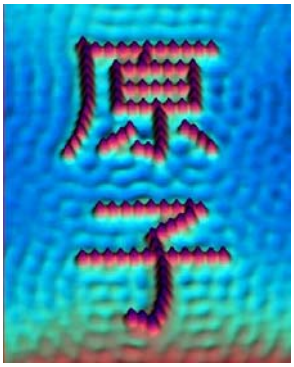
Department of Materials Science and Engineering, Northwestern University

Nanograffiti

Kanji for atom:



Xenon atoms on Nickel (110)

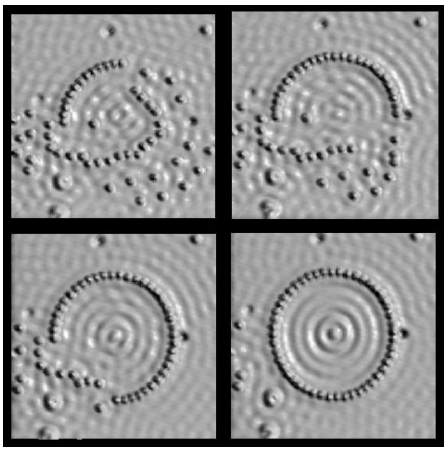


Fe atoms on Cu(111)

Don Eigler, IBM Alamden, http://www.almaden.ibm.com/vis/stm/atomo.html

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Quantum Corrals



Fe atoms on Cu(111)

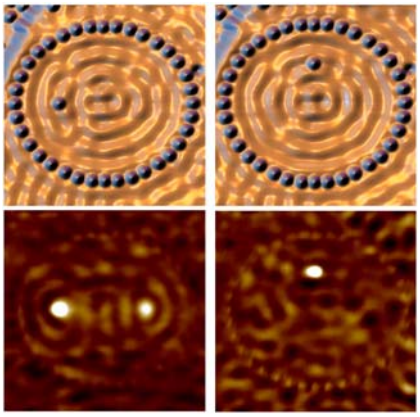
Don Eigler, IBM Alamden, http://www.almaden.ibm.com/vis/stm/atomo.html

Department of Materials Science and Engineering, Northwestern University

Quantum Mirage (Kondo Resonance)

Topography:

dI/dV:

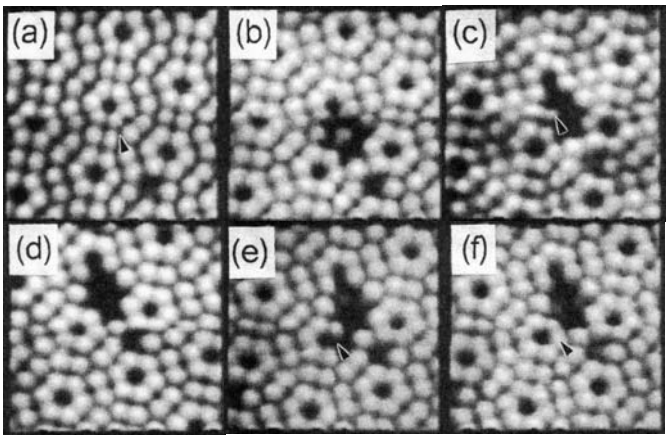


Co atoms on Cu(111)

Don Eigler, IBM Alamden, http://www.almaden.ibm.com/vis/stm/atomo.html

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Room Temperature Manipulation of Si(111)



C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*

Department of Materials Science and Engineering, Northwestern University

Field Evaporation of Gold

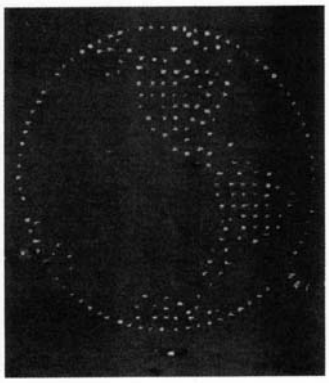
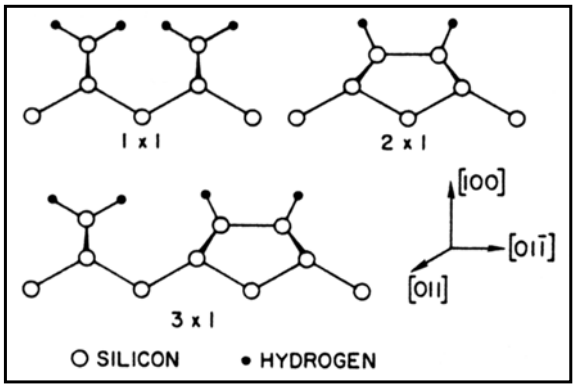


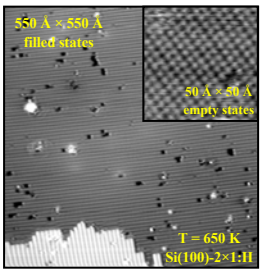
Plate 31. "It's a Small World": A miniature map of the Western Hemisphere. By applying a voltage pulse between a gold tip and a gold surface, a mound of 100–200 Å in diameter and 10–20 Å in height is formed. The location of the mound can be precisely controlled. By programming the positions of the mounds, a gold map is constructed. The diameter of the map is about 1 μm, giving the map a scale of about 10 trillion to 1. For the deposition process, see Mamin, Guenter, and Rugar (1990) for details. Original image courtesy of H. J. Mamin.

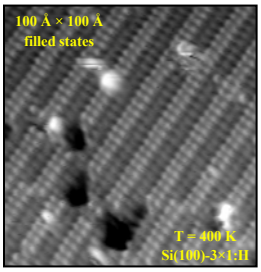
C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Hydrogen Passivated Si(100)

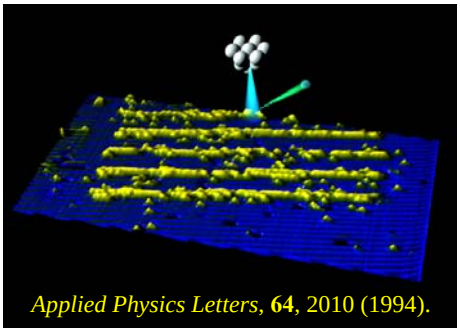


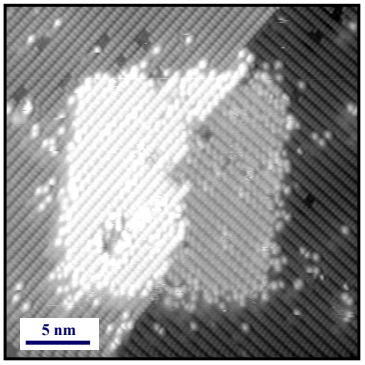




Department of Materials Science and Engineering, Northwestern University

UHV STM Electron Stimulated Desorption

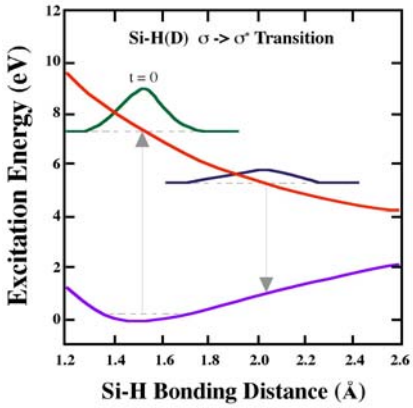


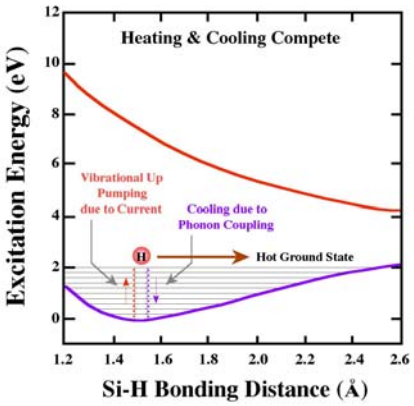


- Imaging conditions: -2 V (sample bias), 0.1 nA (tunneling current)
- Patterning conditions: 5 V (sample bias), 2 nA (tunneling current)
- Dangling bonds have enhanced density of states
- Strong chemical contrast between the clean and passivated areas

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

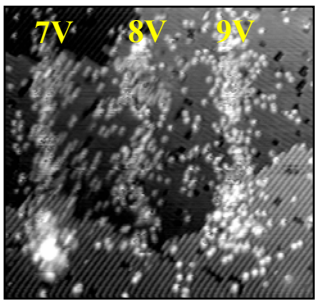
Hydrogen Desorption Mechanisms

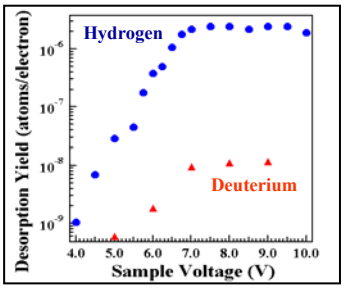




Department of Materials Science and Engineering, Northwestern University

Electron Stimulated Desorption Isotope Effect



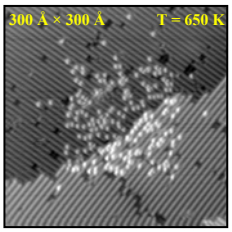


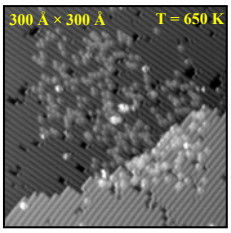
- **Deuterium has a much lower ESD yield than hydrogen.**
- **Desorption conditions exist where all of the hydrogen and none of the deuterium is removed from the surface.**
- **Deuterating CMOS devices leads to longer device lifetimes.**

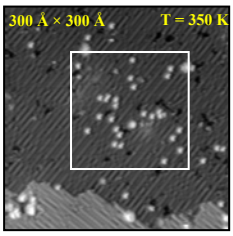
Ph. Avouris, *et al.*, *Chem. Phys. Lett.*, **257**, 148 (1996).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Direct Measurement of D:H Ratio

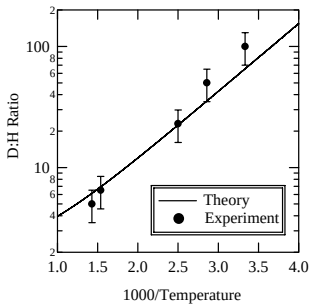






Reducing the thermal budget of CMOS processing should lead to greater deuterium incorporation and longer device lifetimes.

Passivation at 650 K ⇒ D:H Ratio ~ 5
Passivation at 350 K ⇒ D:H Ratio ~ 50

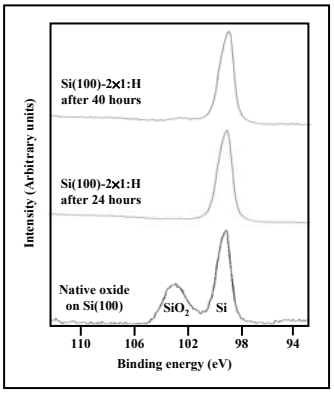


Statistical thermodynamics model confirms experimental results.

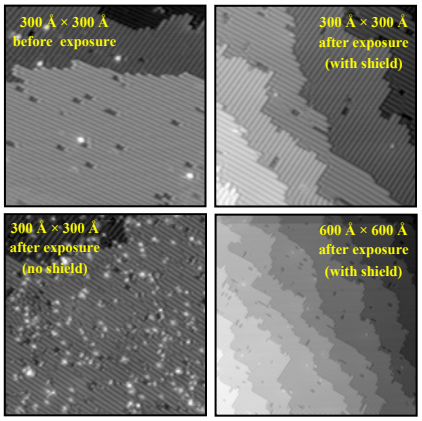
M. C. Hersam, *et al.*, *Appl. Phys. Lett.*, **80**, 201 (2002).

Department of Materials Science and Engineering, Northwestern University

Robustness of Si(100)-2×1:H



XPS results after ambient exposure

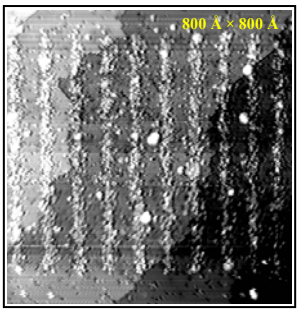


M. C. Hersam, *et al.*, *Appl. Phys. Lett.*, **78**, 886 (2001).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

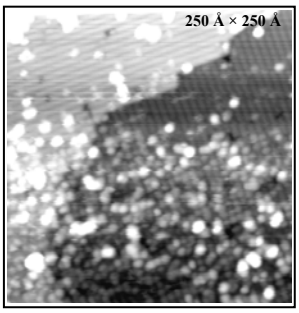
Selective Chemistry on Patterned Areas

Oxidation



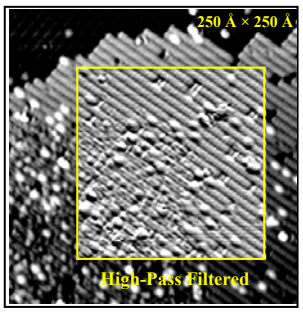
Pattern exposed to molecular oxygen

Metallization



Pattern exposed to amine stabilized alane Al precursor

Nitridation

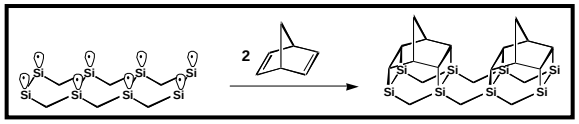


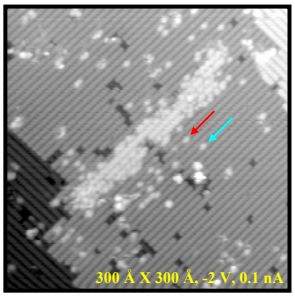
Pattern exposed to ammonia

Applied Surface Science, **132**, 221 (1998).

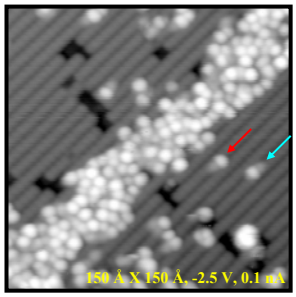
Department of Materials Science and Engineering, Northwestern University

Norbornadiene on Patterned Si(100)

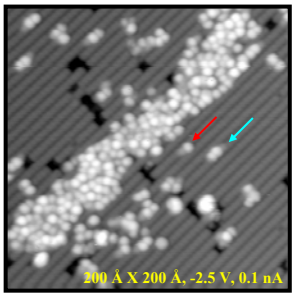




Filled states image of a depassivated line



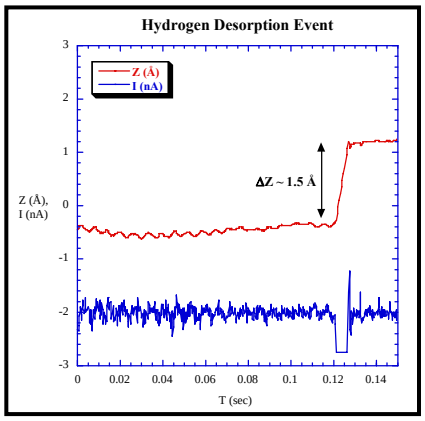
Filled states image after first norbornadiene dose

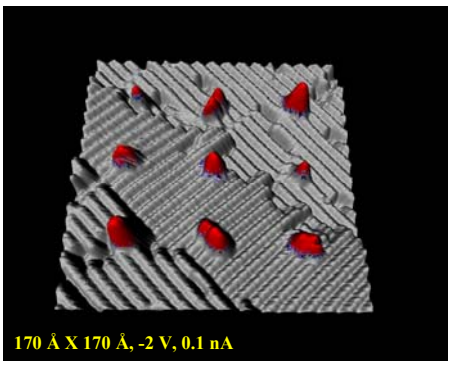


Filled states image after second norbornadiene dose

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Feedback Controlled Lithography



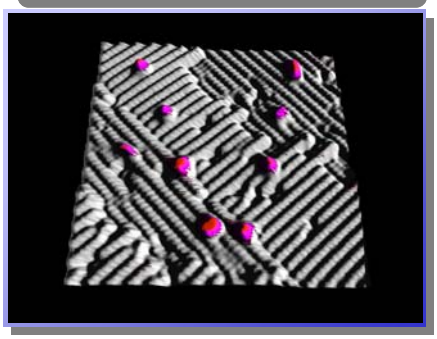


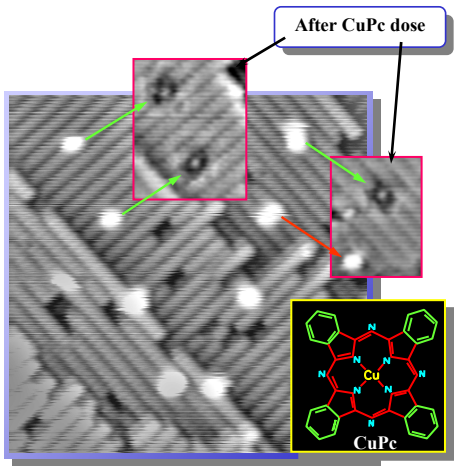
M. C. Hersam, *et al.*, *Nanotechnology*, **11**, 70 (2000).

Department of Materials Science and Engineering, Northwestern University

Patterning Individual Molecules with FCL

Use FCL to create template of Si dangling bonds



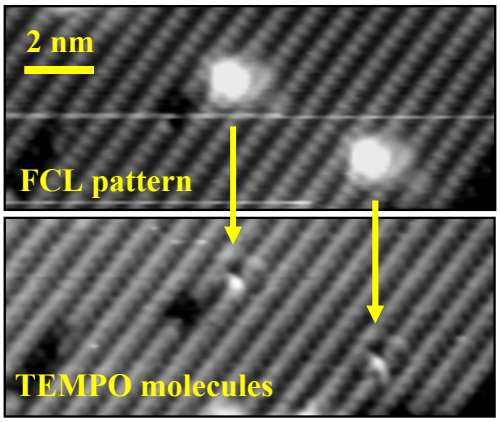


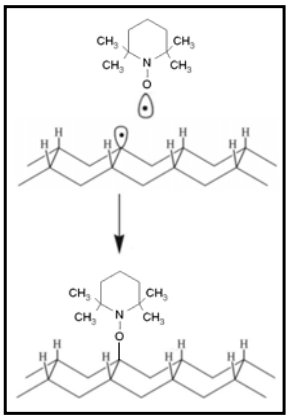
M. C. Hersam, *et al.*, *J. Vac. Sci. Technol. A*, **18**, 1349 (2000).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

FCL Patterned TEMPO Molecules

TEMPO - (2,2,6,6-tetramethyl-1-piperidinyloxy)

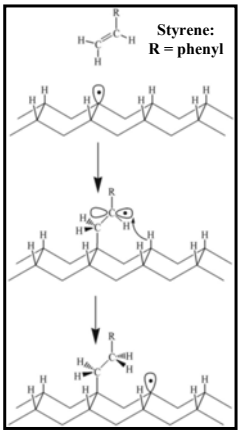


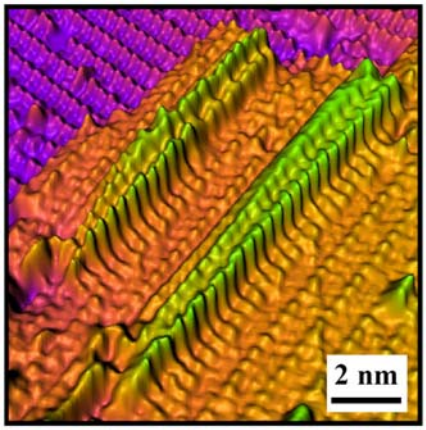


Surface Science, **559**, 16 (2004).

Department of Materials Science and Engineering, Northwestern University

Self-Directed Growth of Styrene Chains from Individual Dangling Bonds

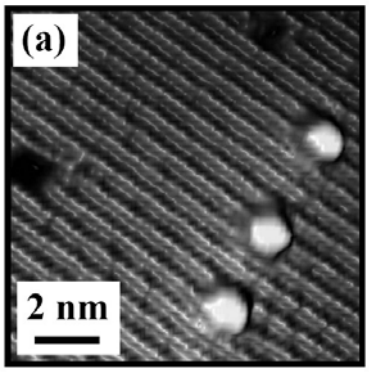


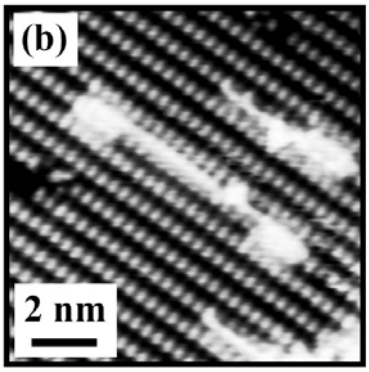


Nature, **406**, 48 (2000).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Patterning Styrene Chains with FCL



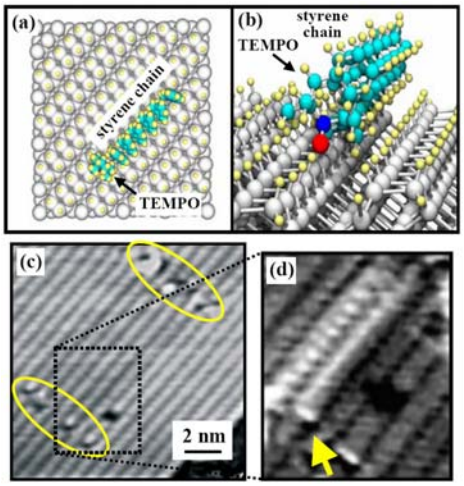


- Chain position can be controlled with FCL
- Chain growth direction and chain length is not controlled

Applied Physics Letters, **85**, 2619 (2004).

Department of Materials Science and Engineering, Northwestern University

Heteromolecular Nanostructure Fabrication



Multi-step FCL

↓

Pre-patterned TEMPO molecules constrain styrene chain growth

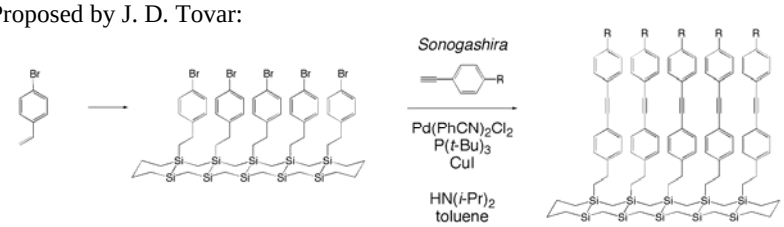
↓

1-D heteromolecular organosilicon nanostructures

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Pathway to Further Organic Complexity: Organohalide Cross Coupling Strategies

Proposed by J. D. Tovar:



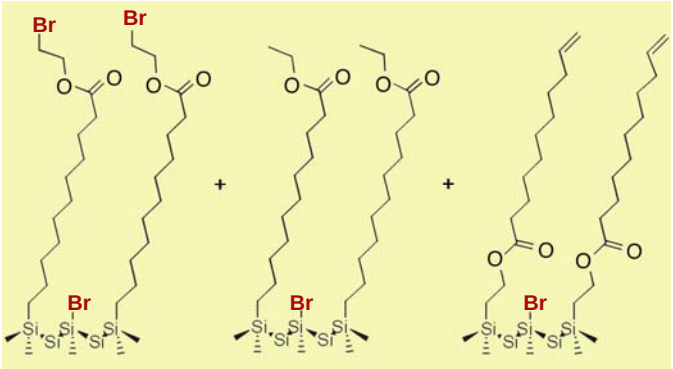
The facile synthesis of phenyl acetylenes should allow for a variety of chemically modified surfaces

(R = conjugated aromatics, peptides, receptor sites)

For room temperature Sonogashira coupling of aryl bromides, see:
Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729-1731.

Department of Materials Science and Engineering, Northwestern University

Undecanoic acid 2-bromo-ethyl ester on Si(111):H



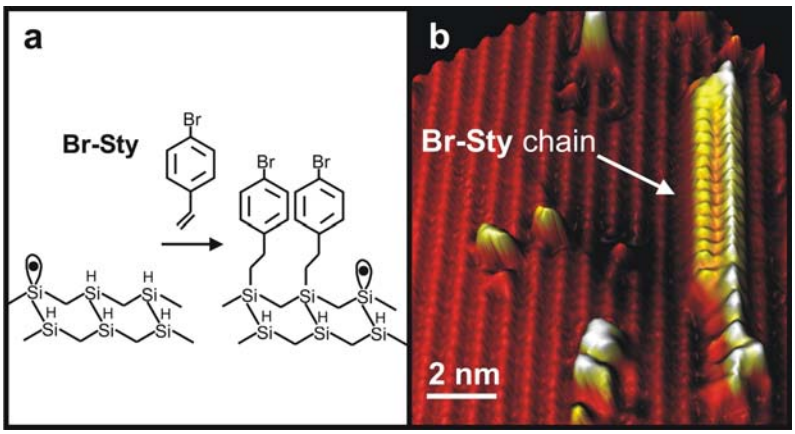
≤ 0.1 ML ≥ 0.25 ML ≤ 0.15 ML

Quantification of binding chemistry with XPS, XSW, XRR, SIMS, and AFM

Langmuir, **20**, 6252 (2004).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

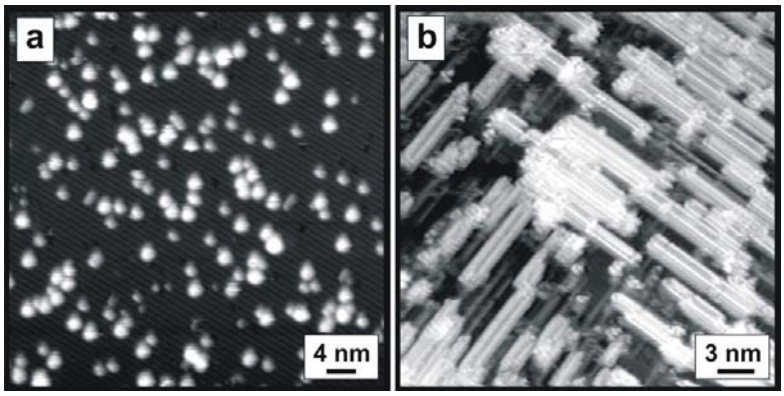
4-Bromostyrene on Si(100)-2×1:H



Chemical Physics, **326**, 144 (2006).

Department of Materials Science and Engineering, Northwestern University

Large Area Coverage of Molecular Chains

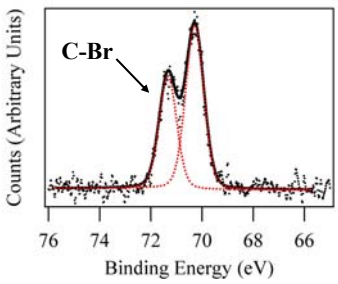


4-Bromostyrene molecular chains can be grown over the entire surface via thermally generated dangling bonds

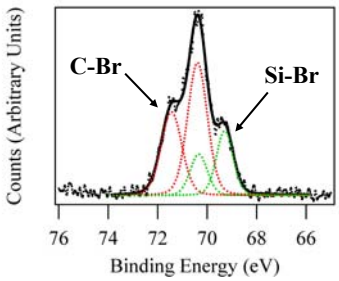
ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Confirming Chemistry with XPS

X-ray Photoelectron Spectra:



4-Bromostyrene chains on Si(100)-2×1:H

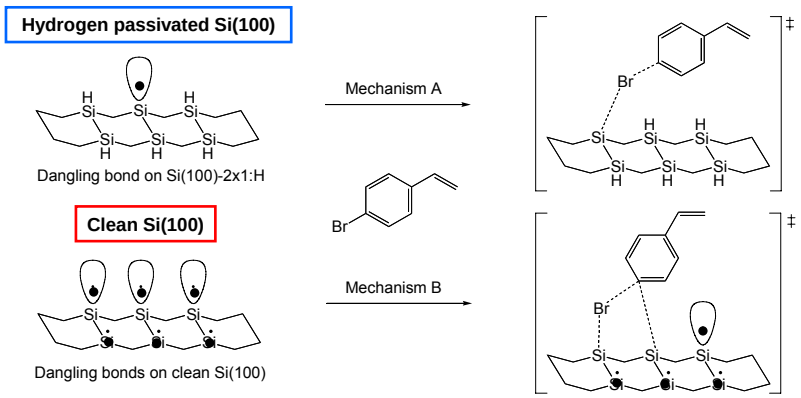


4-Bromostyrene molecules on clean Si(100)-2×1

Hydrogen terminated silicon surface ensures molecular adsorption in the desired orientation

Department of Materials Science and Engineering, Northwestern University

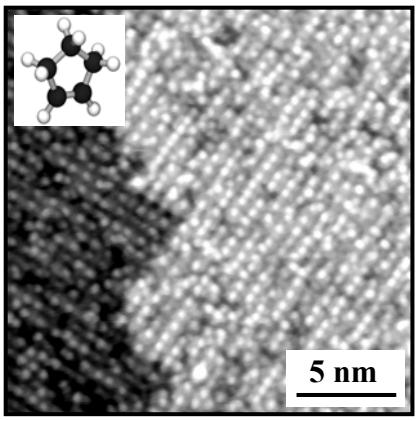
Proposed Reaction Mechanism

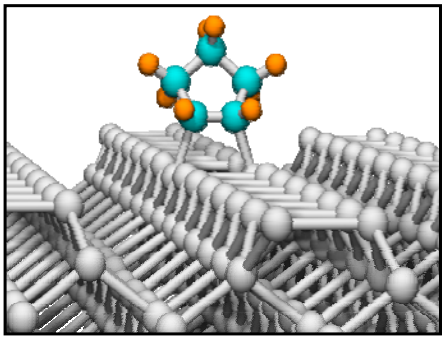


Chemical Physics, **326**, 144 (2006).

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Exploring Organic Resists for FCL



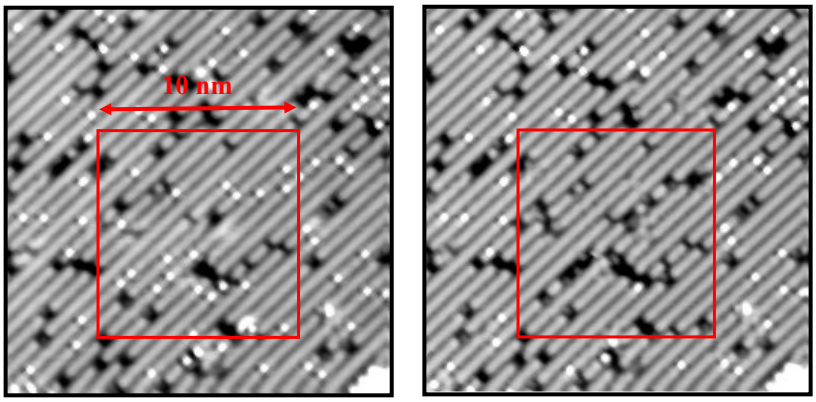


Cyclopentene on Si(100)

- Cyclopentene forms a well-ordered monolayer on Si(100)

Department of Materials Science and Engineering, Northwestern University

Desorption of Cyclopentene from Si(100)



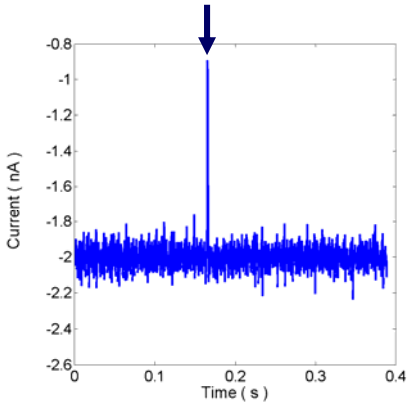
- Patterning conditions: -3.8 V, 1 nA, 1 nm/sec, 50 lines/box

Physical Review Letters, **97**, 187601 (2006).

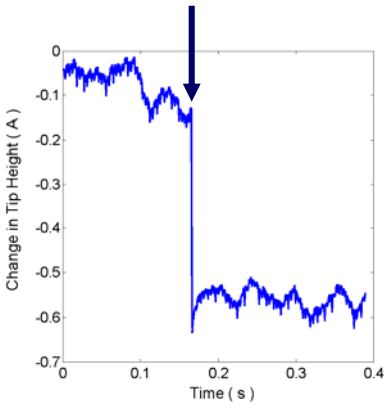
ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

FCL of Cyclopentene on Si(100)

Magnitude of tunneling current drops upon desorption of cyclopentene



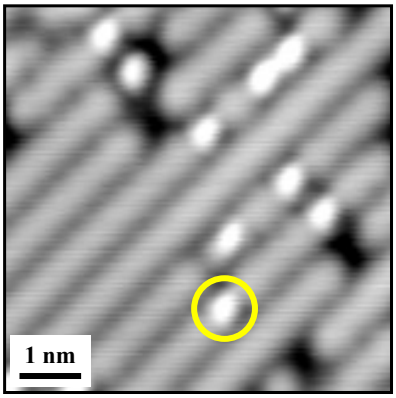
Tip moves towards the surface upon desorption of cyclopentene



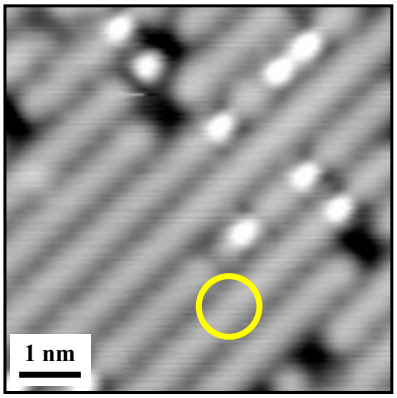
Department of Materials Science and Engineering, Northwestern University

Single Molecule FCL

Before FCL:



After FCL:



- Individual cyclopentene molecules can be desorbed with FCL

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Atomic Force Microscopy Nanofabrication

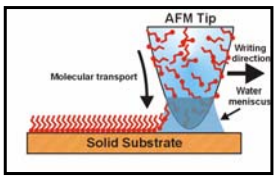
Many nanofabrication schemes have been developed with AFM (generally, spatial resolution is approximately 10 nm):

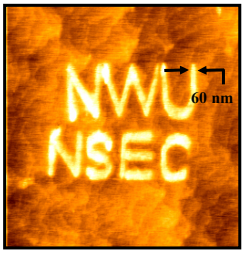
(1) Dip-pen nanolithography

(2) Scratching, pushing

(3) Electrochemistry

(4) Tip-induced oxidation

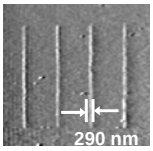




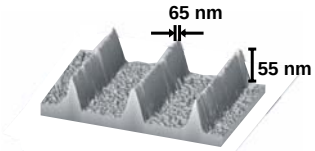
Department of Materials Science and Engineering, Northwestern University

Dip Pen Nanolithography

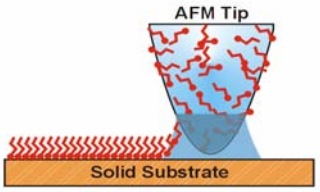
Conducting Polymers

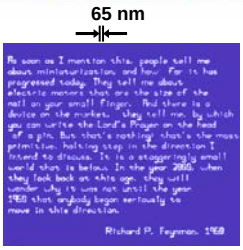


Sol Gel Templates

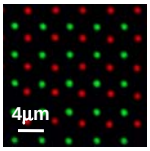


Silicon Nanostructures

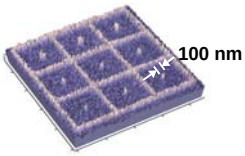




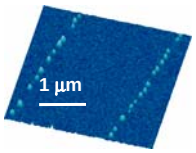
Small Organic Molecules



DNA Nanoarrays



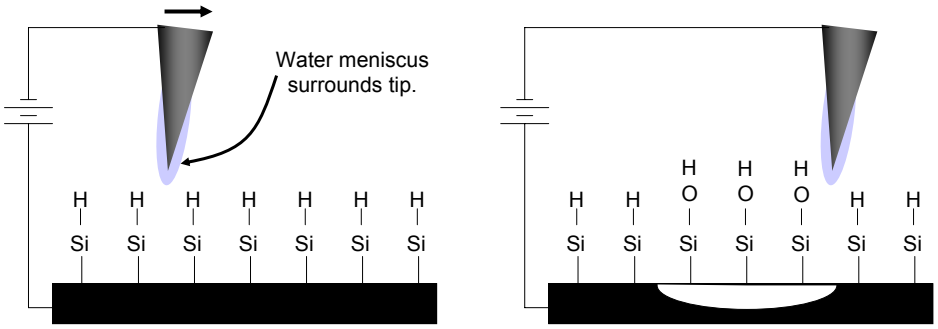
Protein Nanoarrays



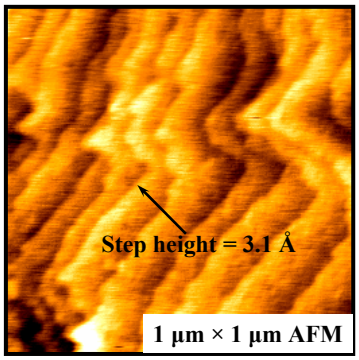
Single Nanoparticle Lines

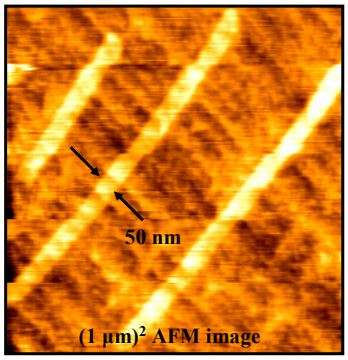
Field Induced Oxidation (FIO)

- Locally anodize the Si(111):H surface using conductive AFM
- Hydroxyl termination provides nanoscale chemical contrast



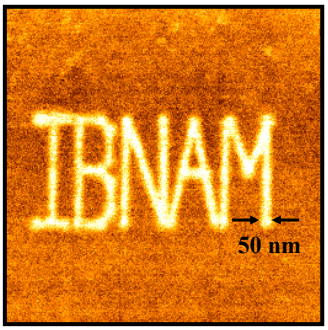
Nano Oxidation of Silicon with Conductive AFM

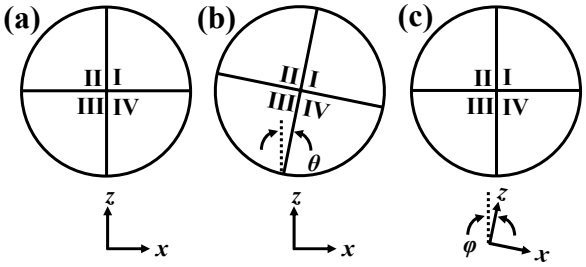




- Oxide nanopatterns achieved via local anodization of Si(111):H
- Spatial resolution limited to ~10 nm.

Lateral Force Microscopy



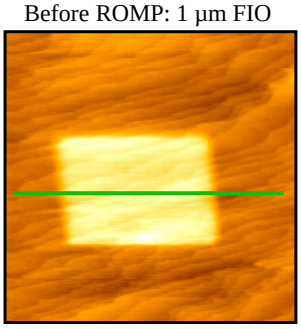


- Chemical contrast monitored via frictional force.
- Care must be taken to extract quantitative LFM data.

M. W. Such, D. E. Kramer & M. C. Hersam, *Ultramicroscopy*, 99, 189 (2004).

Selective Polymerization Chemistry

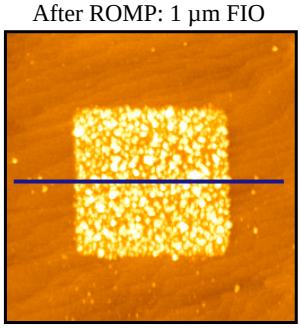
Before ROMP: 1 µm FIO



2 µm x 2 µm

7 V
Sample
Bias

After ROMP: 1 µm FIO



2 µm x 2 µm

ROMP = Ring Opening Metathesis Polymerization

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

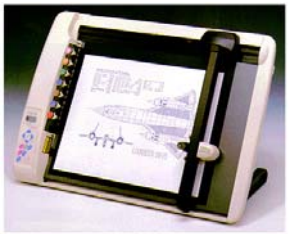
Serial Nature of DPN and SPL

- 1. "Despite its usefulness in research, single-probe DPN is a slow process and not suitable for industrialization."
- 2. "[DPN has]…a patterning time of 100 years/cm^2."
- 3. "At writing speeds of a few micrometers per second it is very hard to envision an industrial fabrication process based on these approaches, no matter how revolutionary the final device can be."
- 4. "The serial nature of SPL results in a low sample throughput…. [SPL] is probably restricted to research applications."
- 5. "…SPL patterning is expensive and difficult to adapt to large-scale patterns.

1. Bullen, D.; Liu, C. *Sensors and Actuators a-Physical* **2006**, *125*, 504.
2. Schwartz, P. V. *Langmuir* **2002**, *18*, 4041.
3. Stellacci, F. *Advanced Functional Materials*. **2006**, 15-16.
4. Whitesides et al., *Chemical Reviews*. **2005**, 105, 1171-1196.
5. Langer, R. et al., *Nano Lett.* **2006**, ASAP

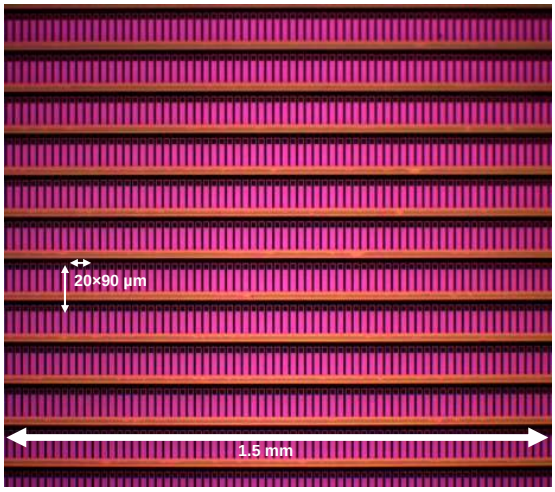
Department of Materials Science and Engineering, Northwestern University

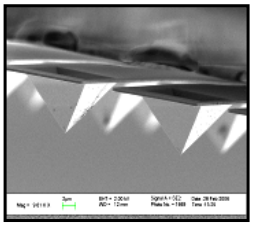
The Evolution of the Pen

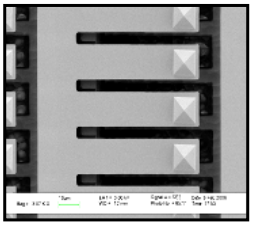
Quill	Fountain	Ball-Point	Multi-Pen Plotter
			
4000 years old	125 years old	65 years old	25 years old

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

MegaScriptor (5.5×10^4 tips/cm^2)

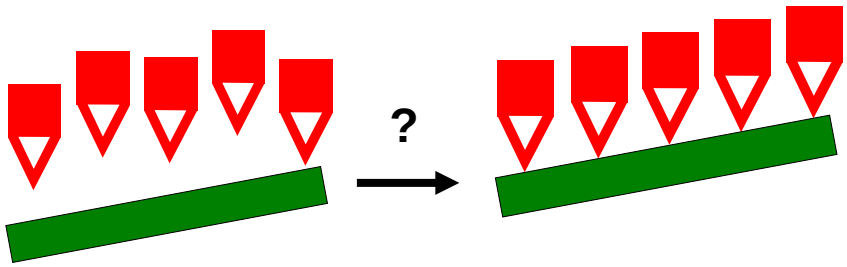






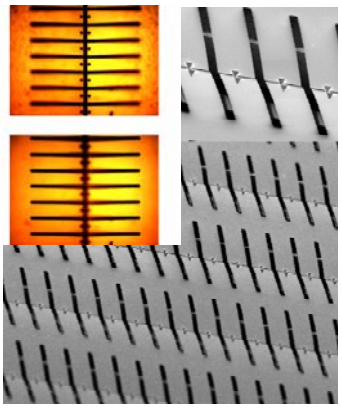
Department of Materials Science and Engineering, Northwestern University

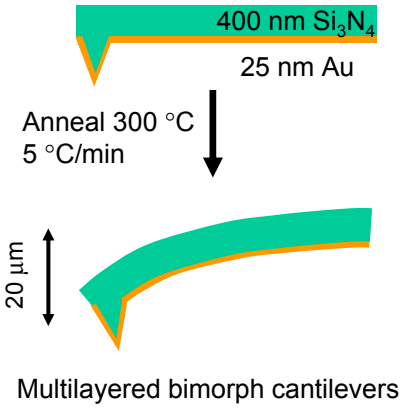
Alignment of Probe Arrays with Substrate



For parallel patterning, all 55,000 probes need to be in contact with the surface concurrently.

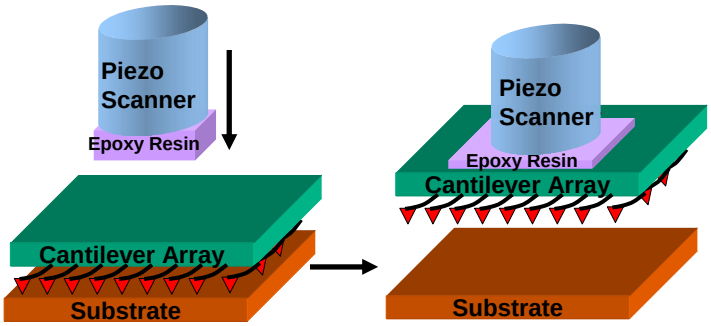
Bending Cantilevers





Cantilevers bent toward the substrate increase the chance of probe contact without cantilever contact.

Aligning 55,000 Probes with the Substrate

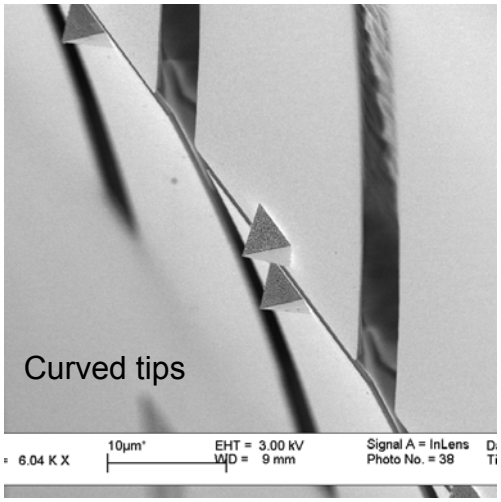


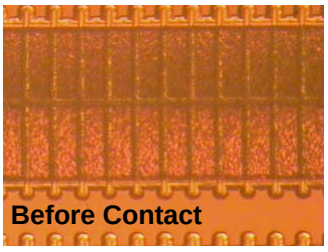
Alignment Protocol

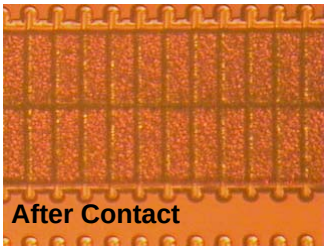
- Rest the pen array on a sacrificial substrate using its own weight (~100 mg or 20 nN/tip).
- Lock the position of the pen array with respect to the piezo scanner head by taking advantage of the malleability of the epoxy.

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Monitoring Tip-Substrate Contact

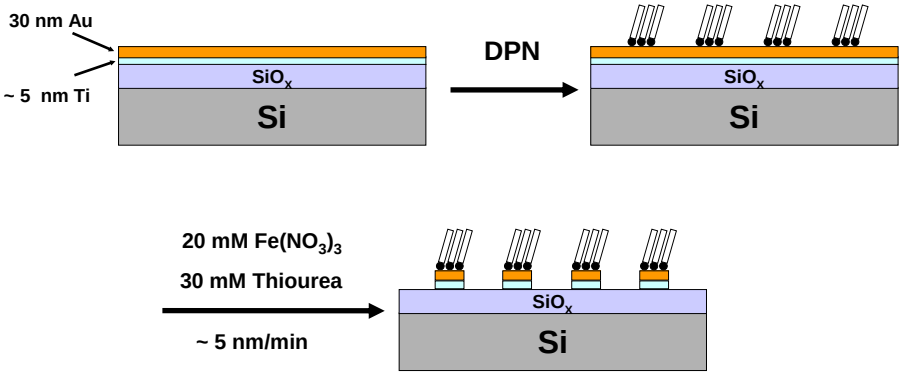






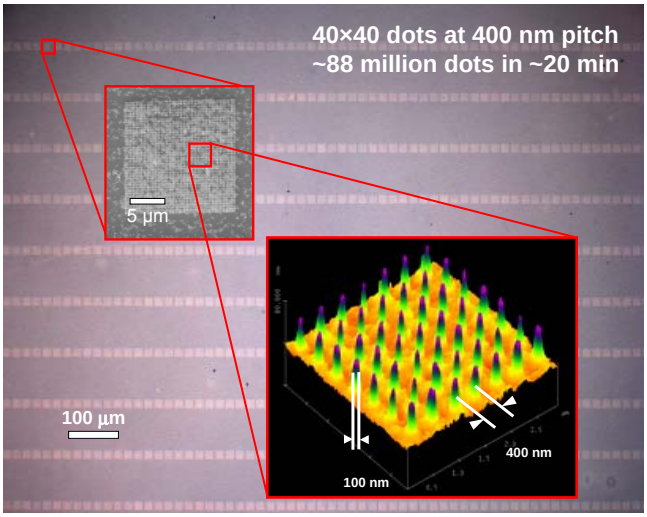
Department of Materials Science and Engineering, Northwestern University

Pattern Evaluation



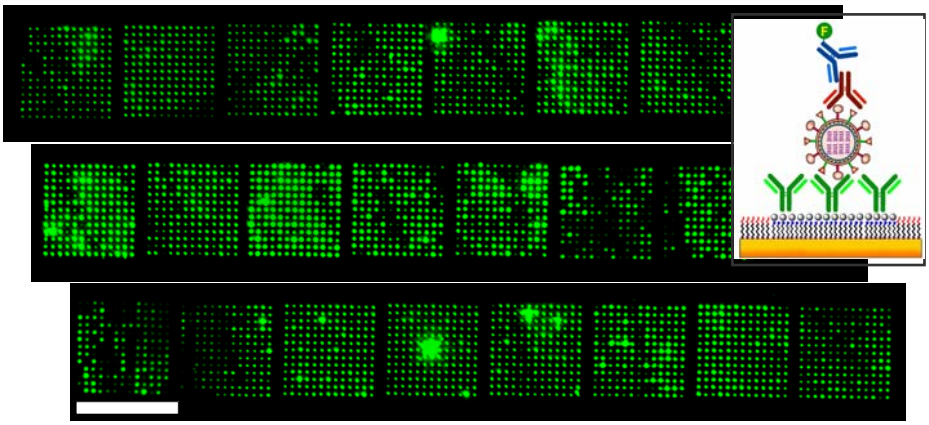
ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE

Massively Parallel Patterning



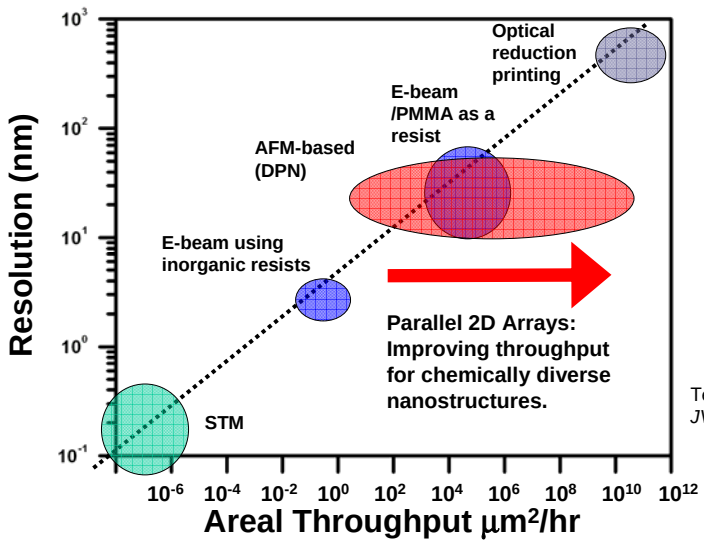
Department of Materials Science and Engineering, Northwestern University

Functional Oriented Antibody Arrays



35 µm

ROBERT R. McCORMICK SCHOOL OF ENGINEERING AND APPLIED SCIENCE



Tennant et al., **2003**, *JVST A* 21, S207.

Department of Materials Science and Engineering, Northwestern University