ME597/PHYS57000
Fall Semester 2009
Lecture 26

Scanning Probe Nanolithography

- STM – early work
- Arranging atoms with a tip
- Local Oxidation Lithography (Electrochemical)
- Dip Pen Lithography
- Nanografting

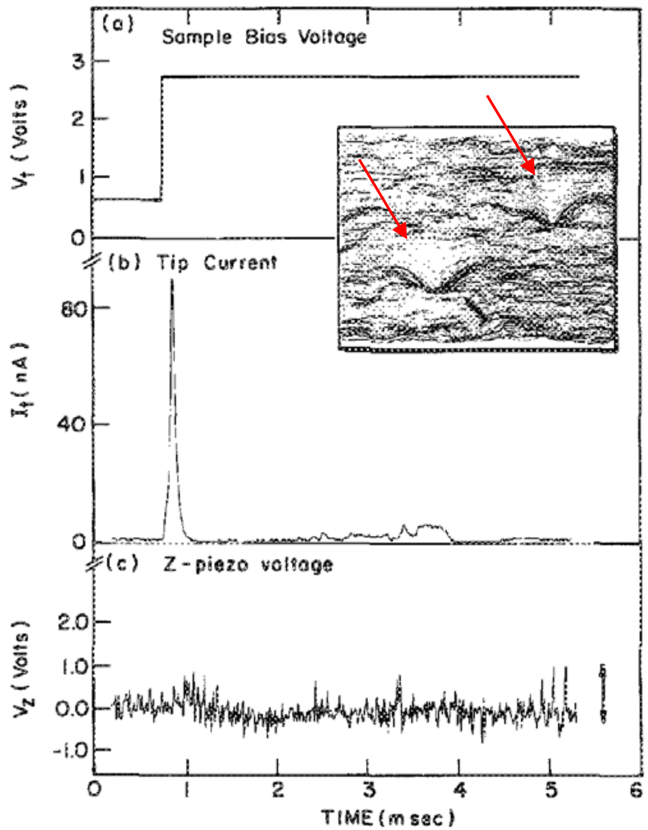
Recent Topical Review:
Garcia, Martinez and Martinez, Chem. Soc. Rev. **35**, 29 (2006)
Rosa and Liang, J. Phys.: Condens. Matter **21**, 483001 (2009)

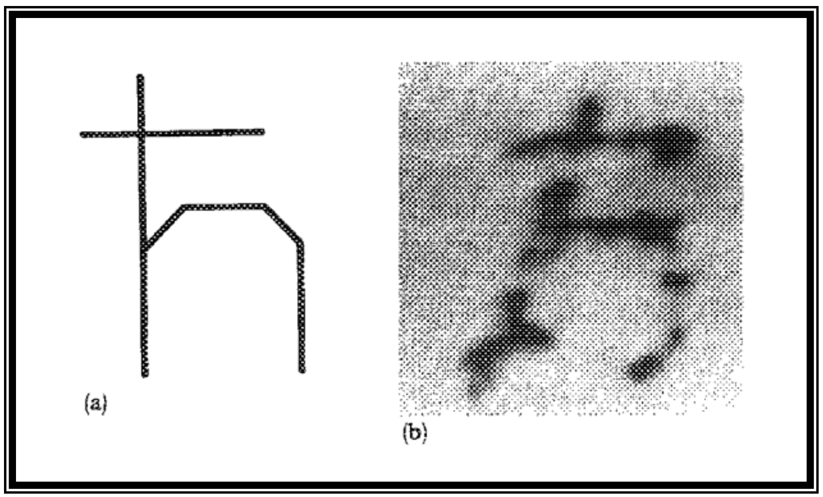
STM-based Results

Writing nanometer-scale symbols in gold using the scanning tunneling microscope

Y. Z. Li, L. Vazquez,[a] R. Piner, R. P. Andres,[b] and R. Reifenberger
Department of Physics, Purdue University, West Lafayette, Indiana 47907

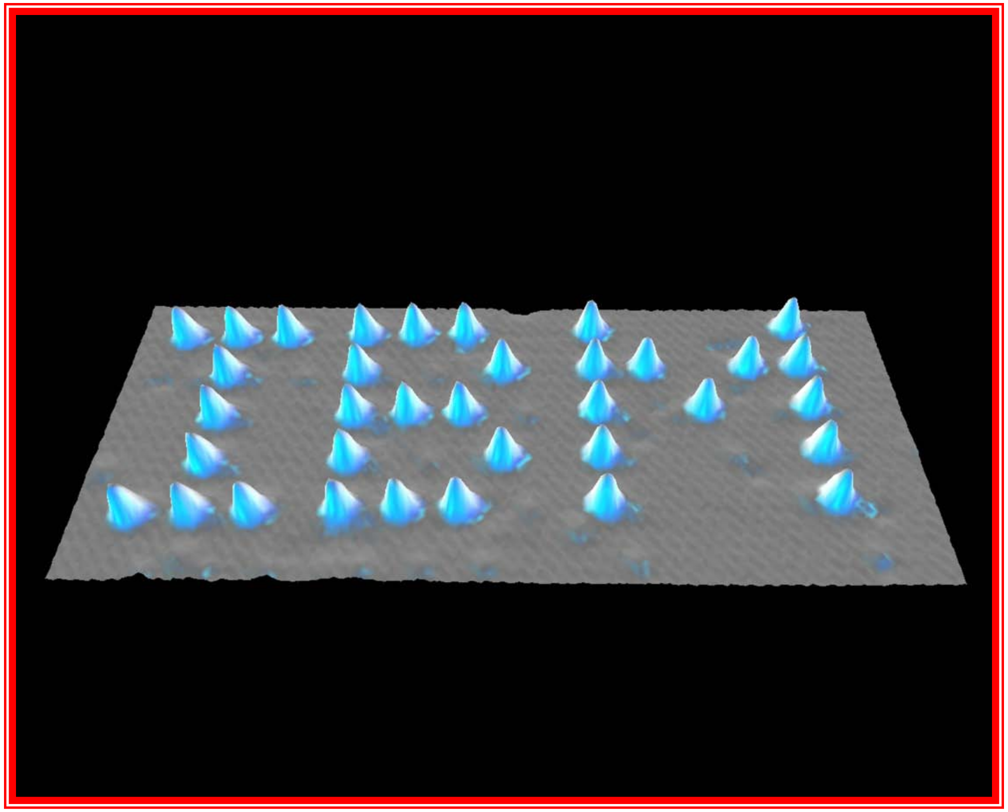
(Received 5 December 1988; accepted for publication 30 January 1989)





65 nm x 40 nm x 2 nm

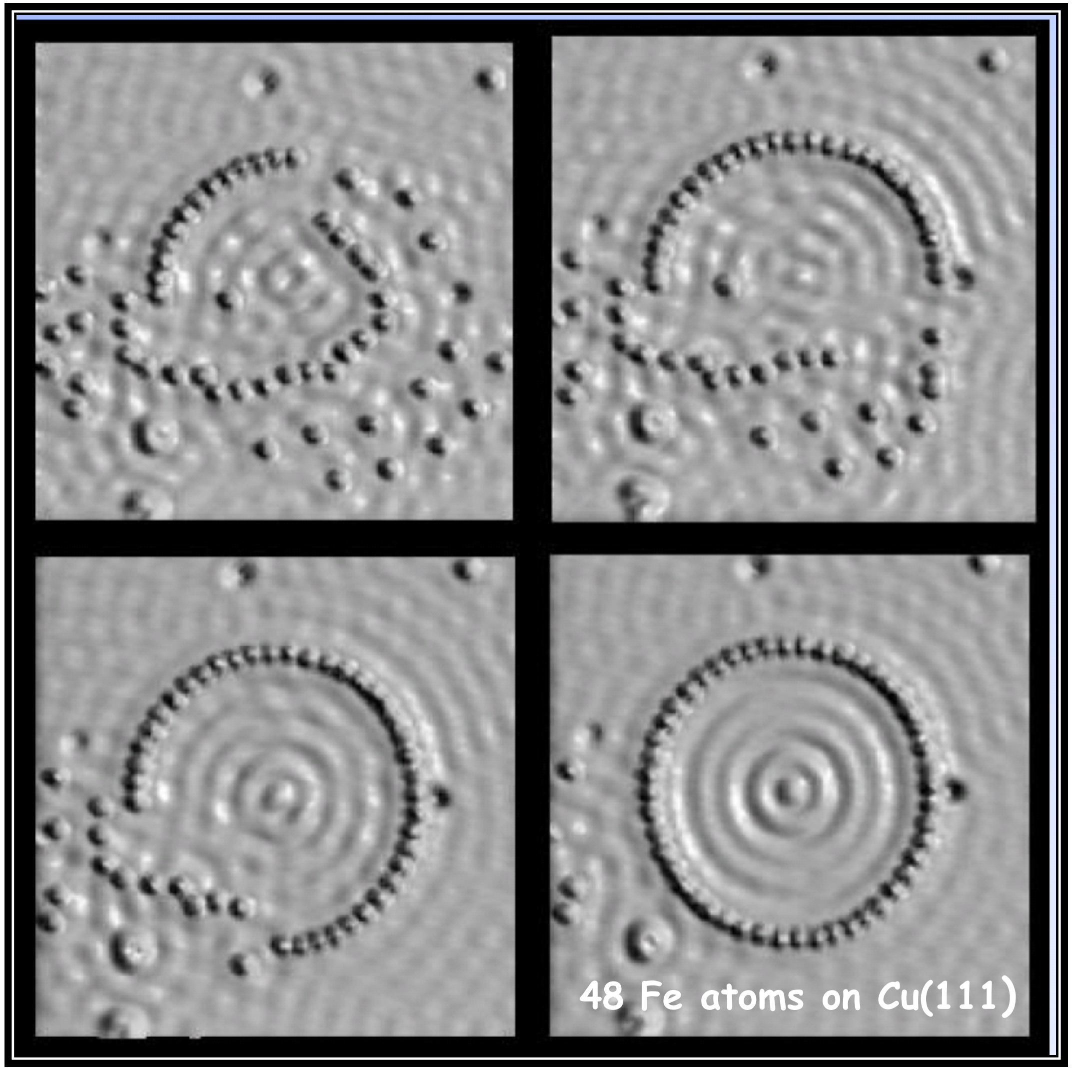
D. Eigler moves and controls position of an individual Xe atom (1989)



35 Xenon atoms on Ni(110)

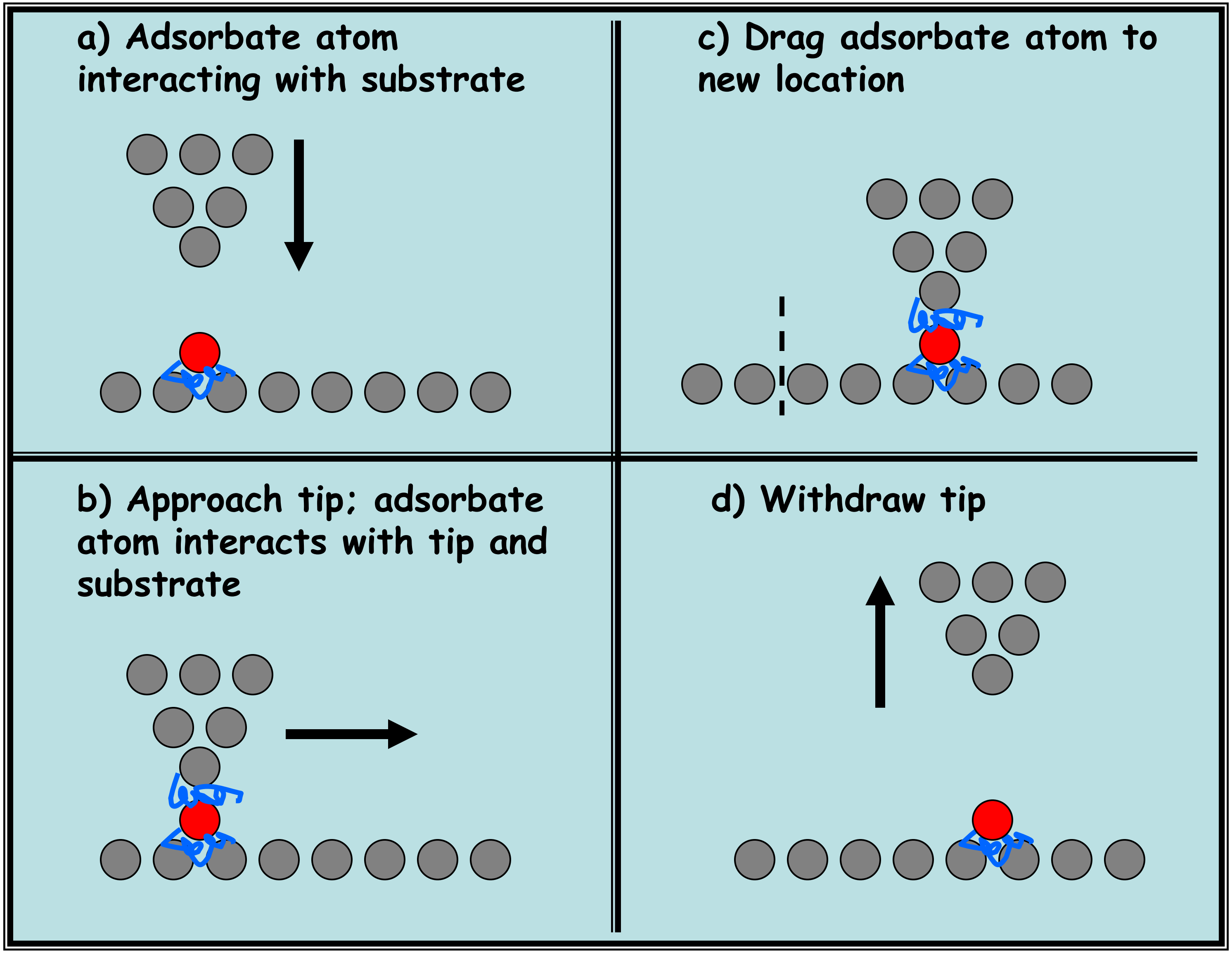
D.M. Eigler and E.K. Schweizer, Nature 344, 524 (1990).

An atomic pencil!



Crommie et al., Science **262**, 218 (1993)

Physical Mechanism



Local Oxidation Lithography

Early Work:

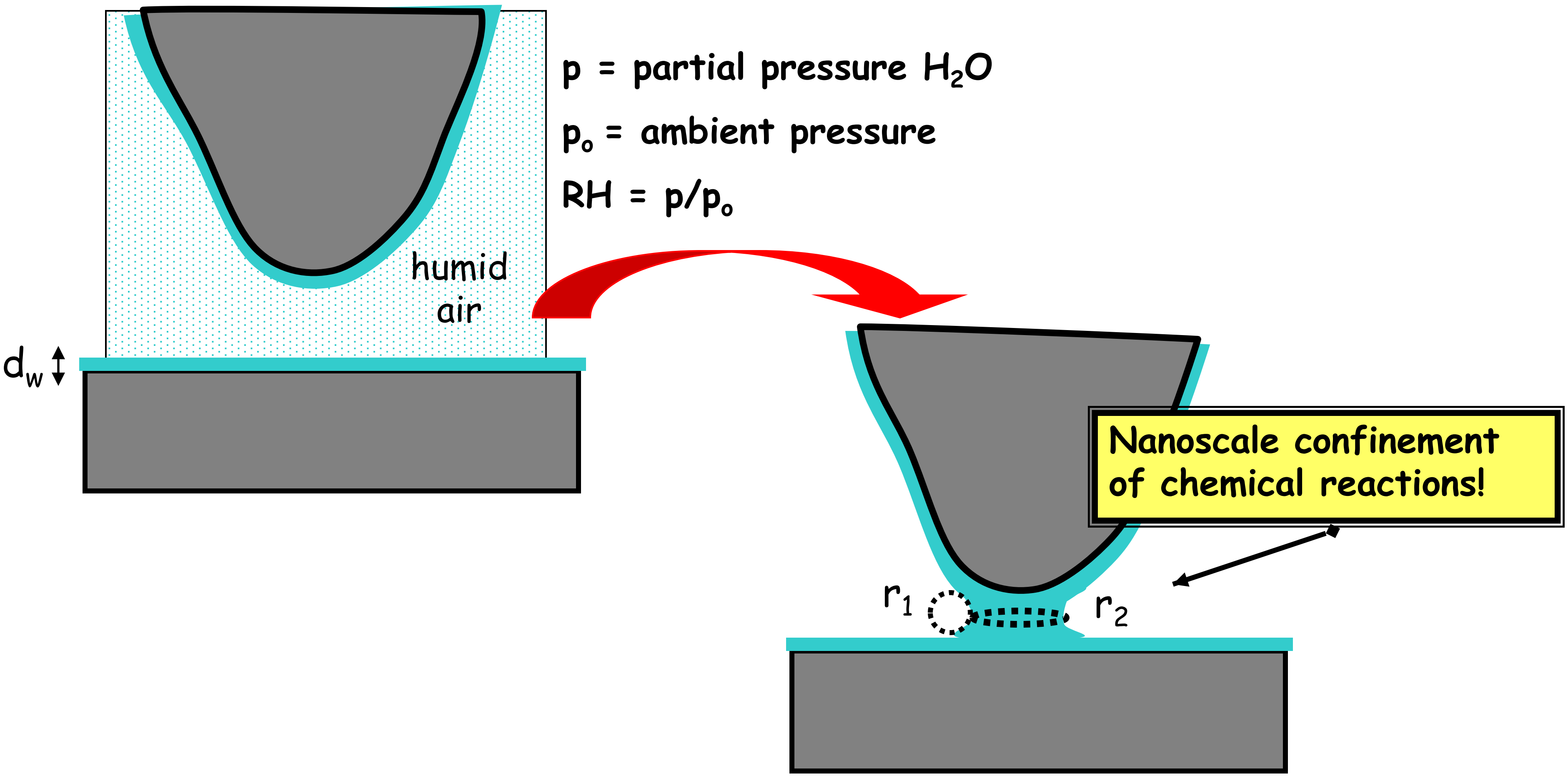
J. Dagata et al. Appl. Phys. Lett. **56**, 2001 (1990).

H.C. Day and D.R. Allee, Appl. Phys. Lett. **62**, 2691 (1993).

E.S. Snow et al, Appl. Phys. Lett. **72**, 3071 (1998).

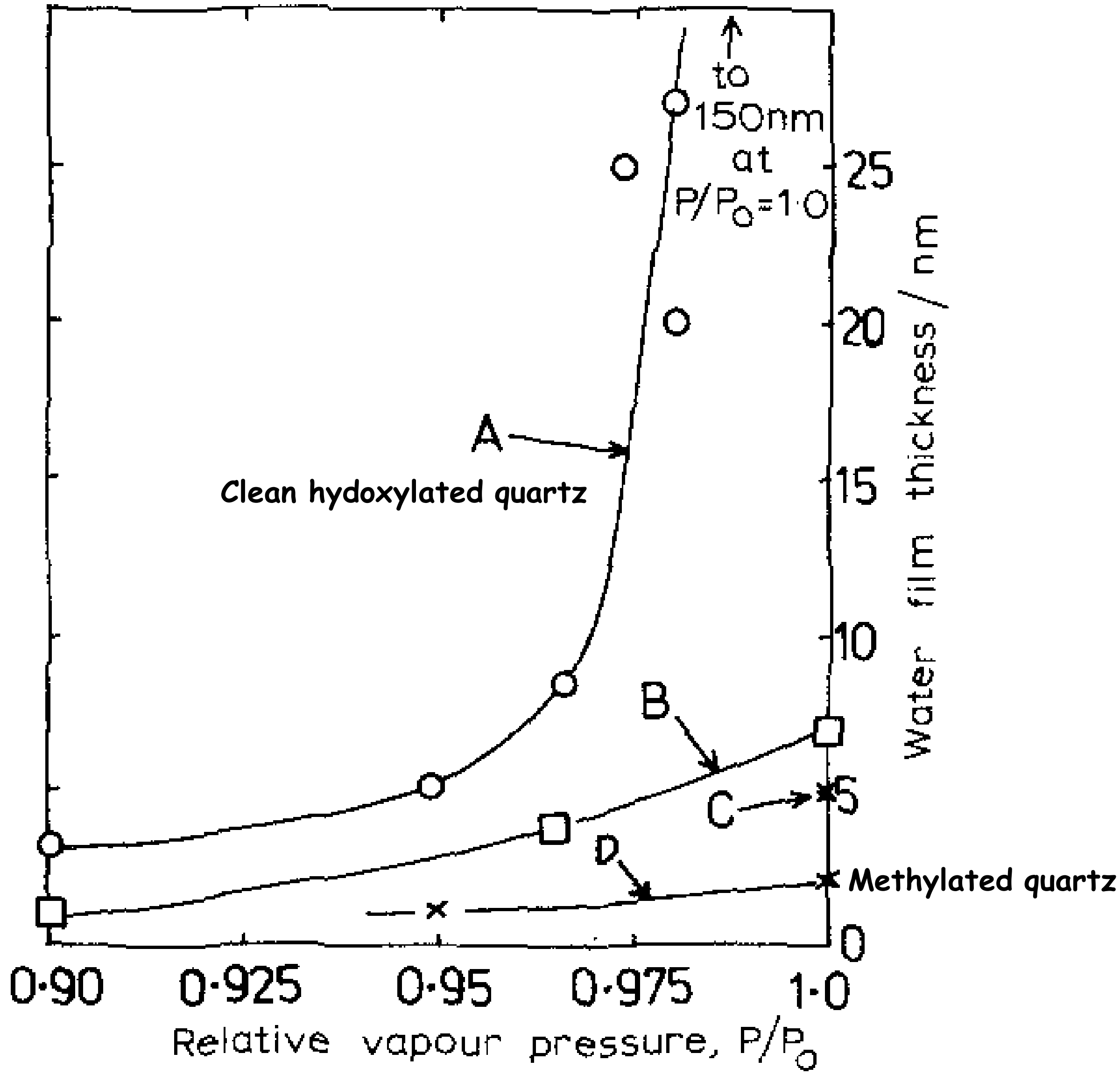
R. Held, et. al., Appl. Phys. Lett. **73**, 262 (1998).

Scanning Under Ambient Conditions



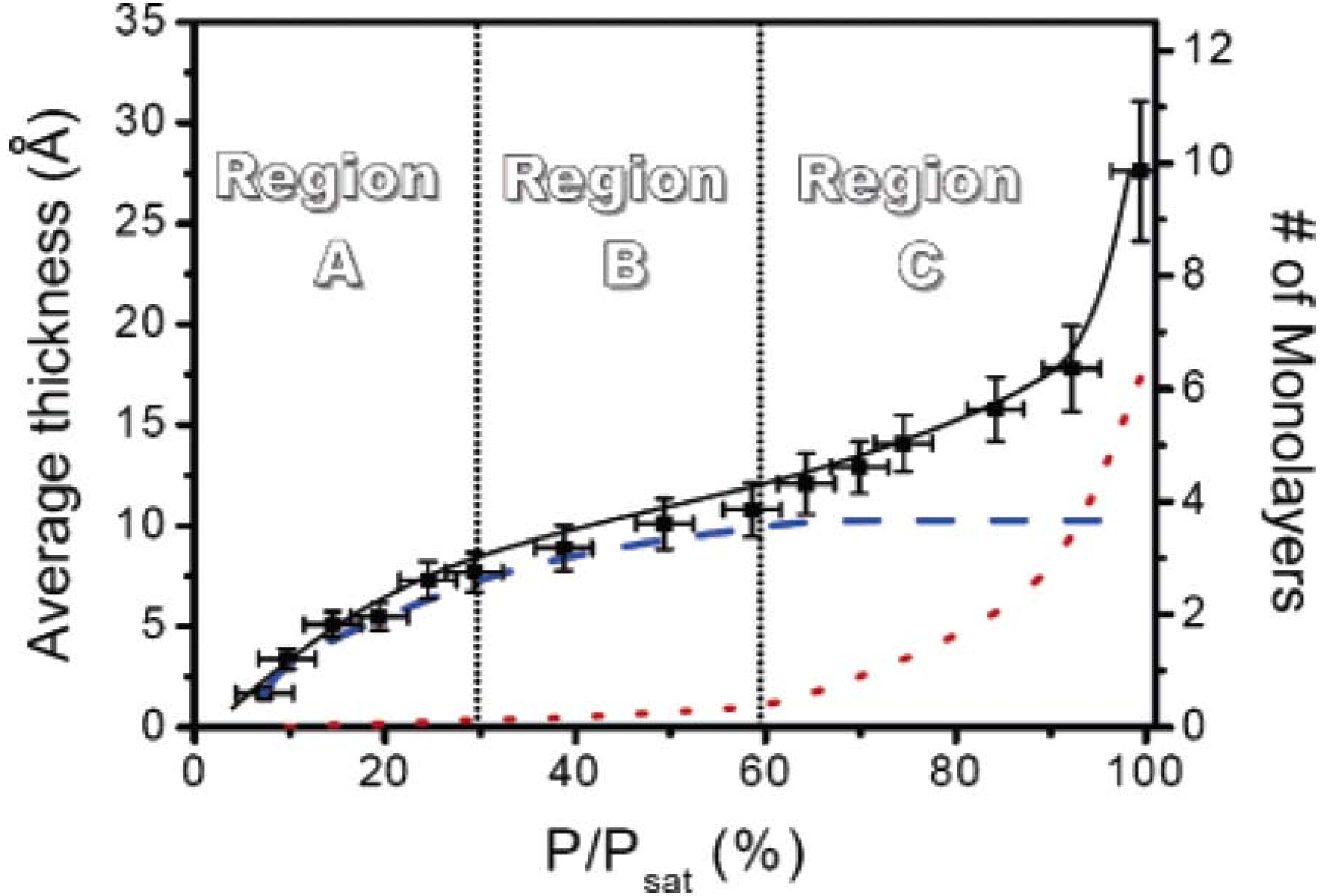
Upon approach, a water neck forms. Due to surface tension, an additional force is required to pull the tip from the substrate. The additional force depends on the shape (r_1,r_2) of the water meniscus.

Water layer adsorbed on quartz at room temperature



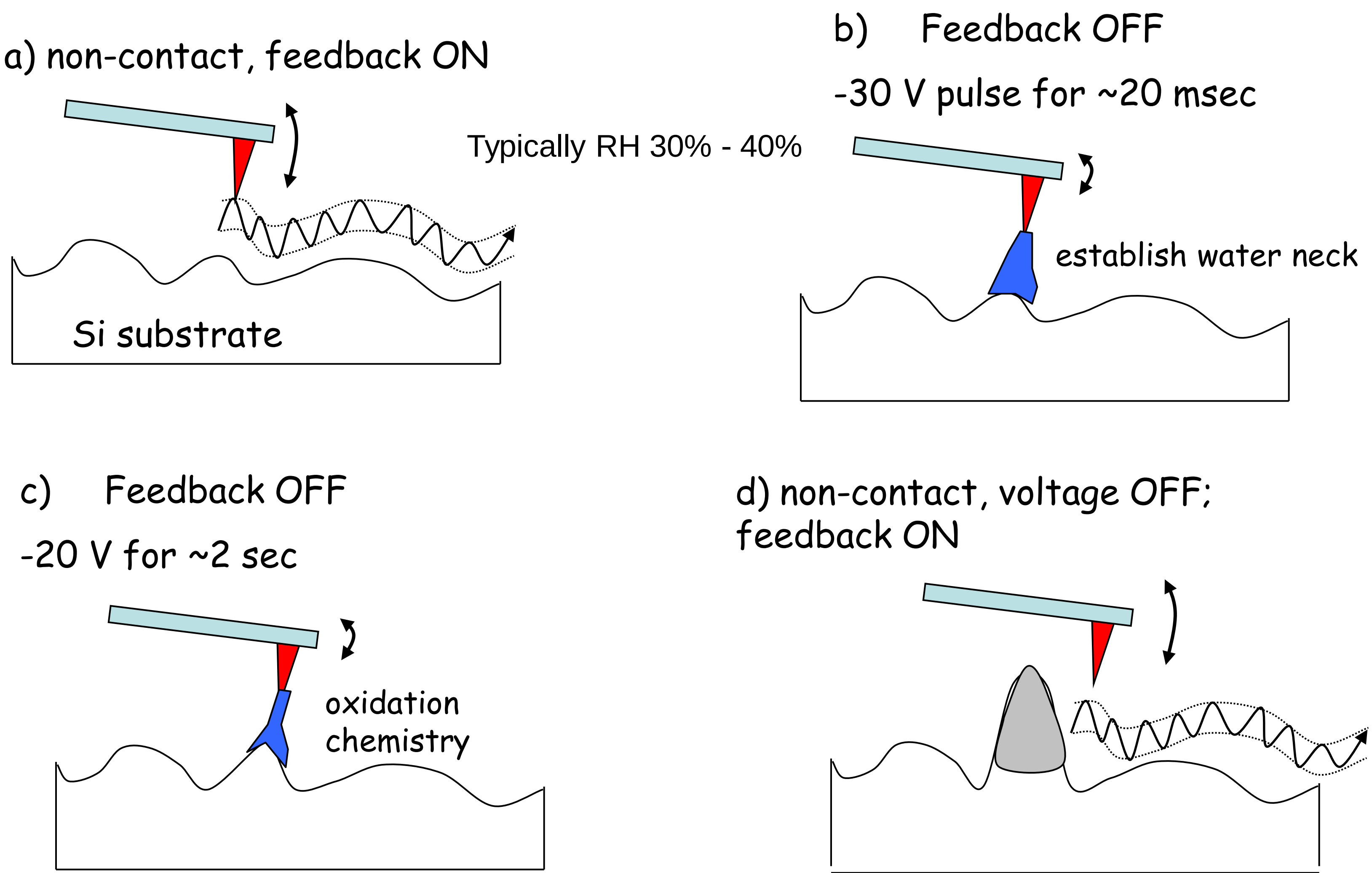
Pashley and Kitchener, J. Colloid and Interface Sci., 71, 491 (1979).

Water layer adsorbed on SiO_2 at room temperature



Asay and Kim, J. Phys. Chem B **109**, 16761 (2005).

SPM Oxidation Lithography - Schematic



Local Chemistry at the Tip

1. Si rapidly reacts with oxygen to form passivating layer of SiO_2

2. Water vapor also oxides Si; (gaseous O_2 is not required)

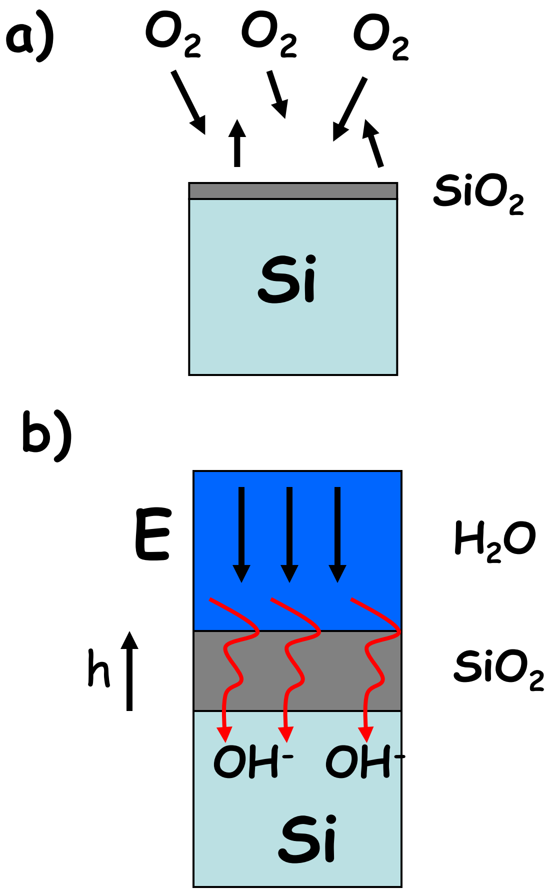
3. Large electric field dissociates water

4. OH^- diffuses through SiO_2 faster than O_2, allowing the oxide to grow

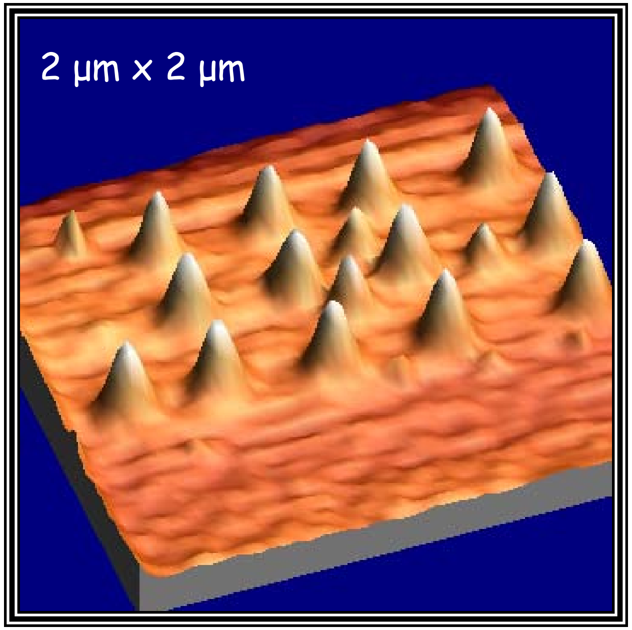
$$Si + O_2 \rightarrow SiO_2$$

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

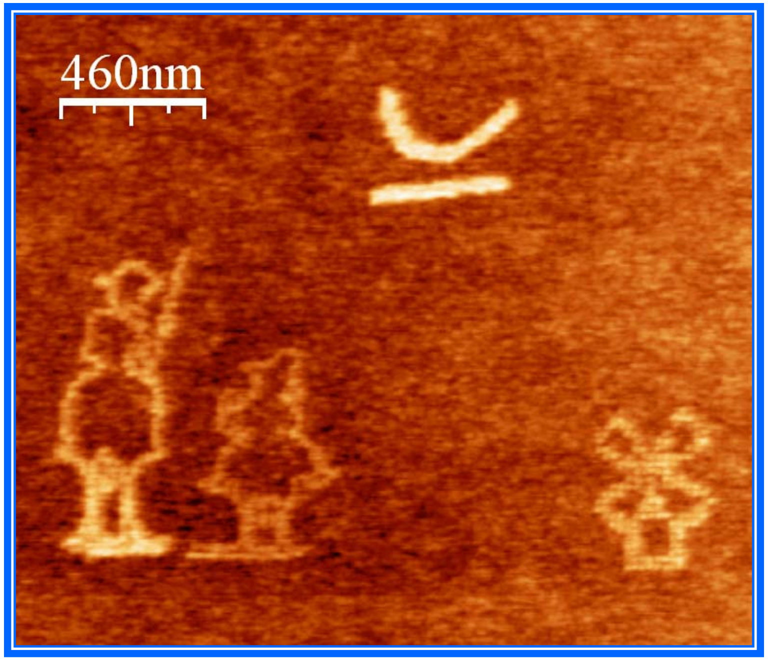
$$H_2O \xrightarrow{\text{large } \vec{E}} OH^- + H^+$$



Examples - Local Oxidation Lithography

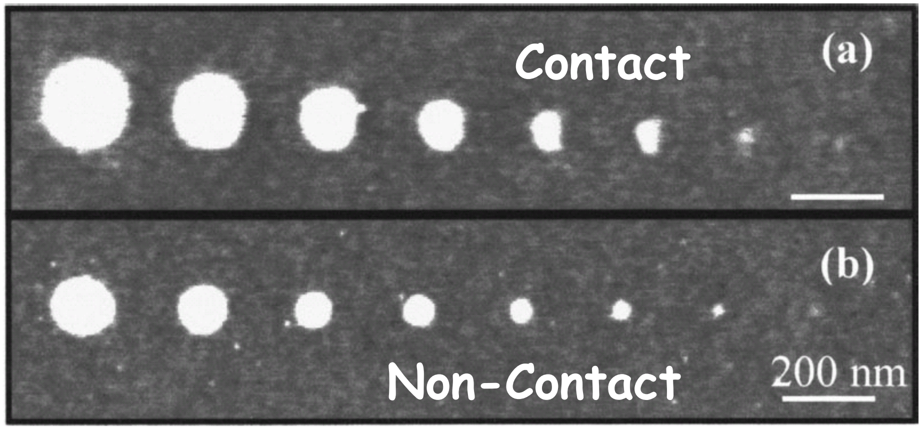


S.W. Howell, Sandia National Labs



P. Ares, *Nanotec Electronica*

Minimum Feature Size



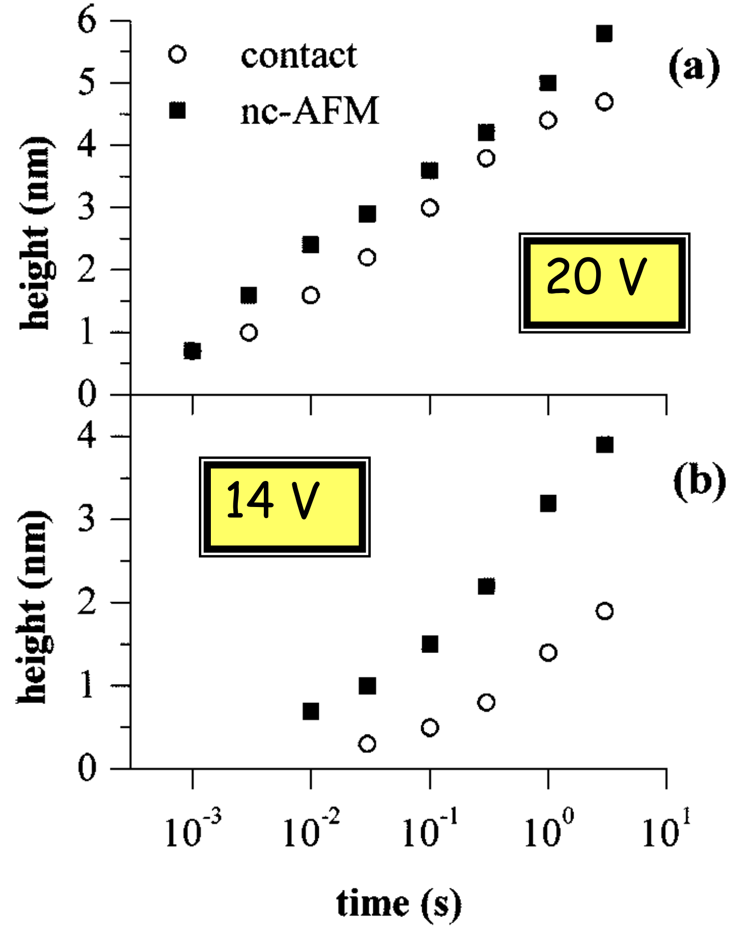
Estimating the height:

$$h \sim \left(\frac{t}{t_o}\right)^{\gamma}$$

γ ~ 0.1-0.3

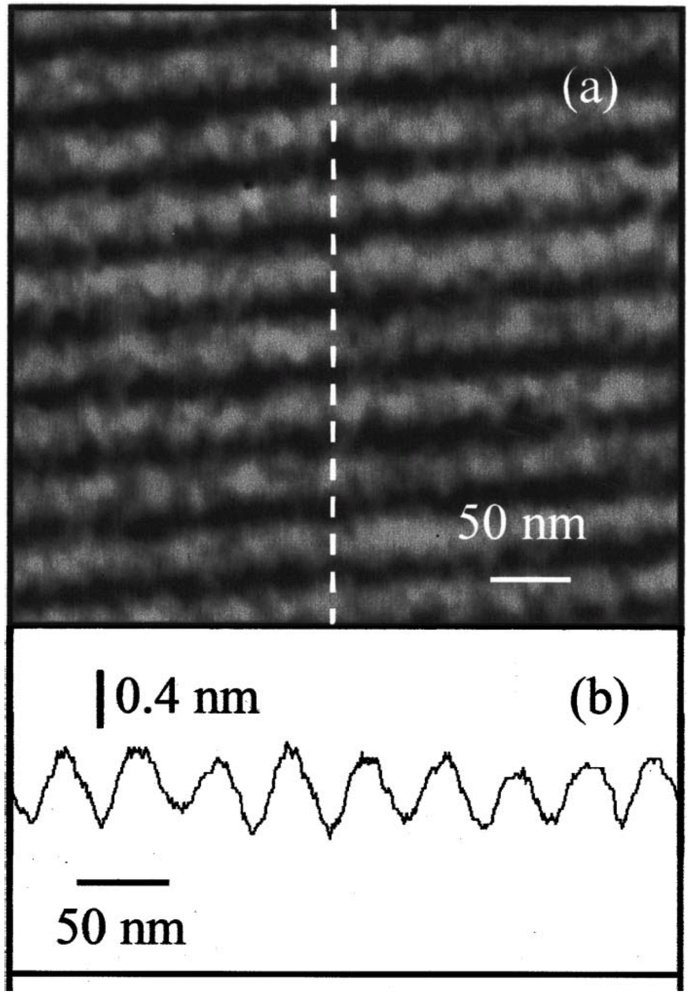
t ~ 0.005 - 1 s

RH 36%



Tello and Garcia, Appl. Phys. Lett. **79,** 424 (2001).

Line widths



SUMMARY
Local Oxidation enables fabrication of

a) Dielectric barriers

b) Masks for selective etching

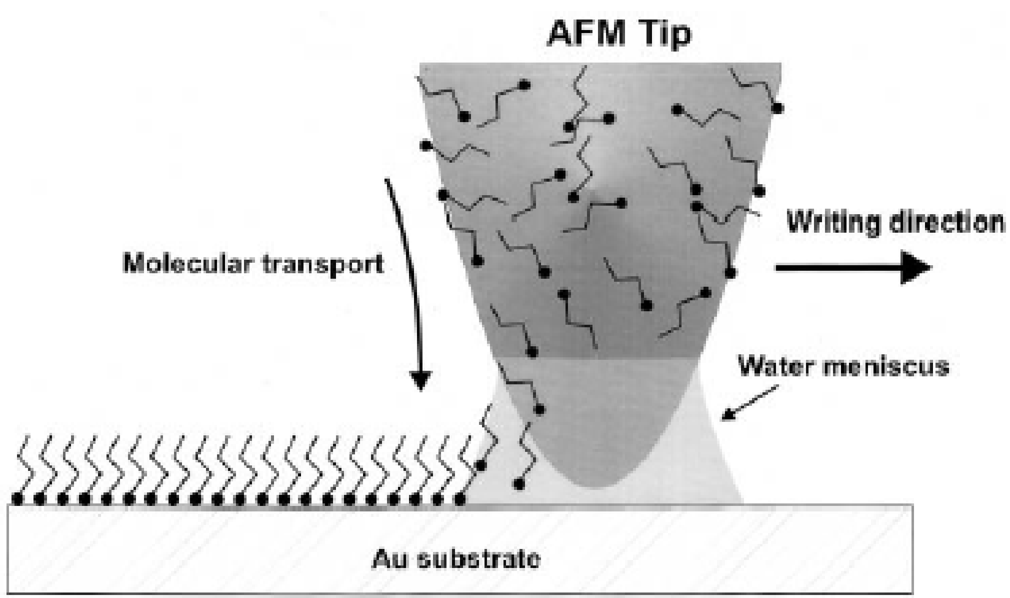
c) Templates

Tello and Garcia, J. Appl. Phys. **92**, 4075 (2002)

Chemical Writing

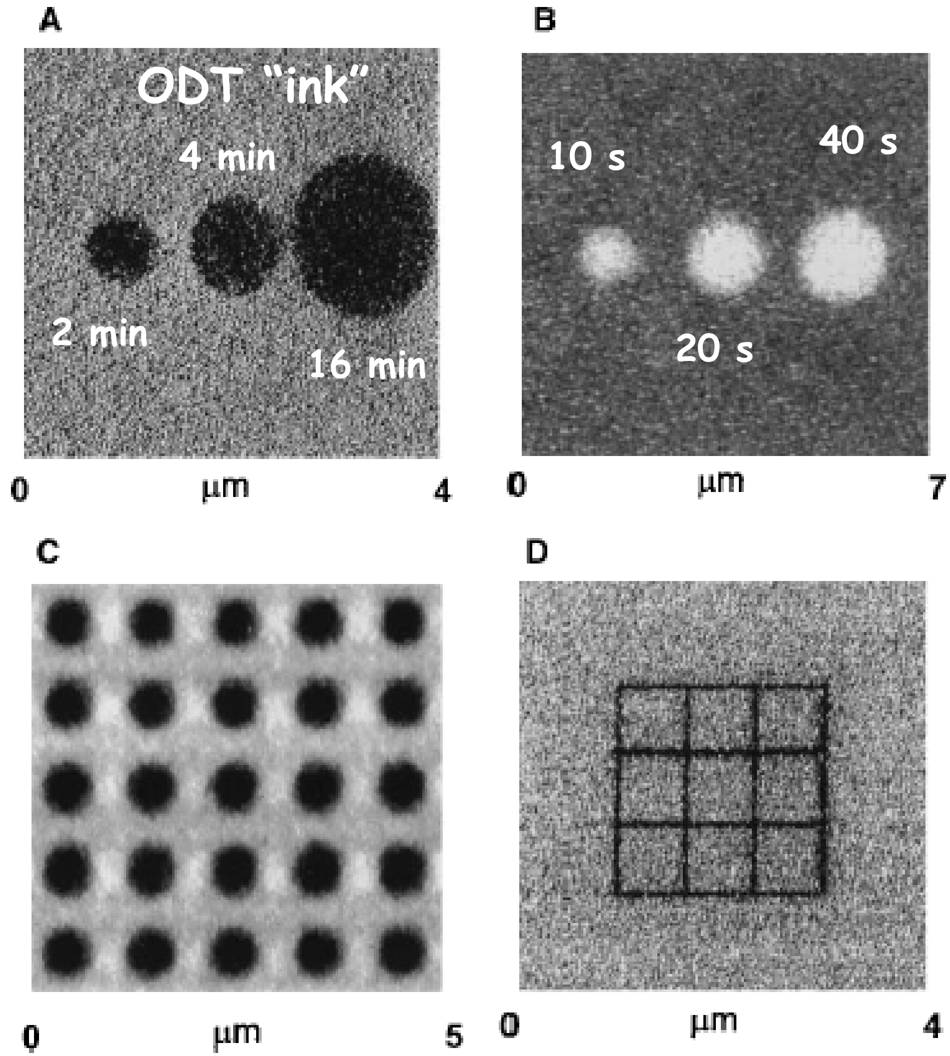
"Dip-Pen" Nanolithography

Richard D. Piner, Jin Zhu, Feng Xu, Seunghun Hong,
Chad A. Mirkin*



Nanolithography with Molecules

Lateral force images of Au substrate; RH 35%



16-mercapto-hexadecanoic acid "ink"

Piner, Zhu, Xu, Hong, Mirkin, Science **283**, 661 (1999)

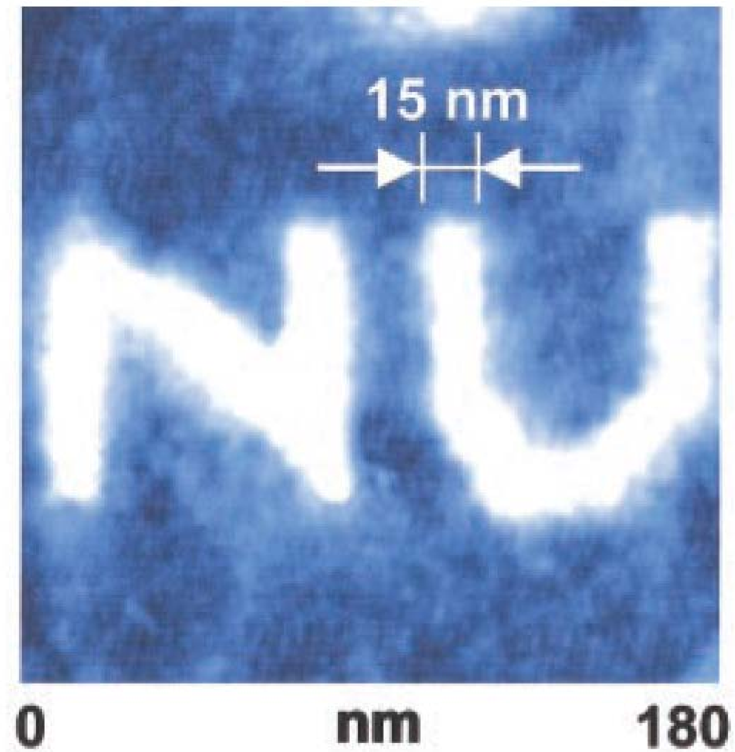
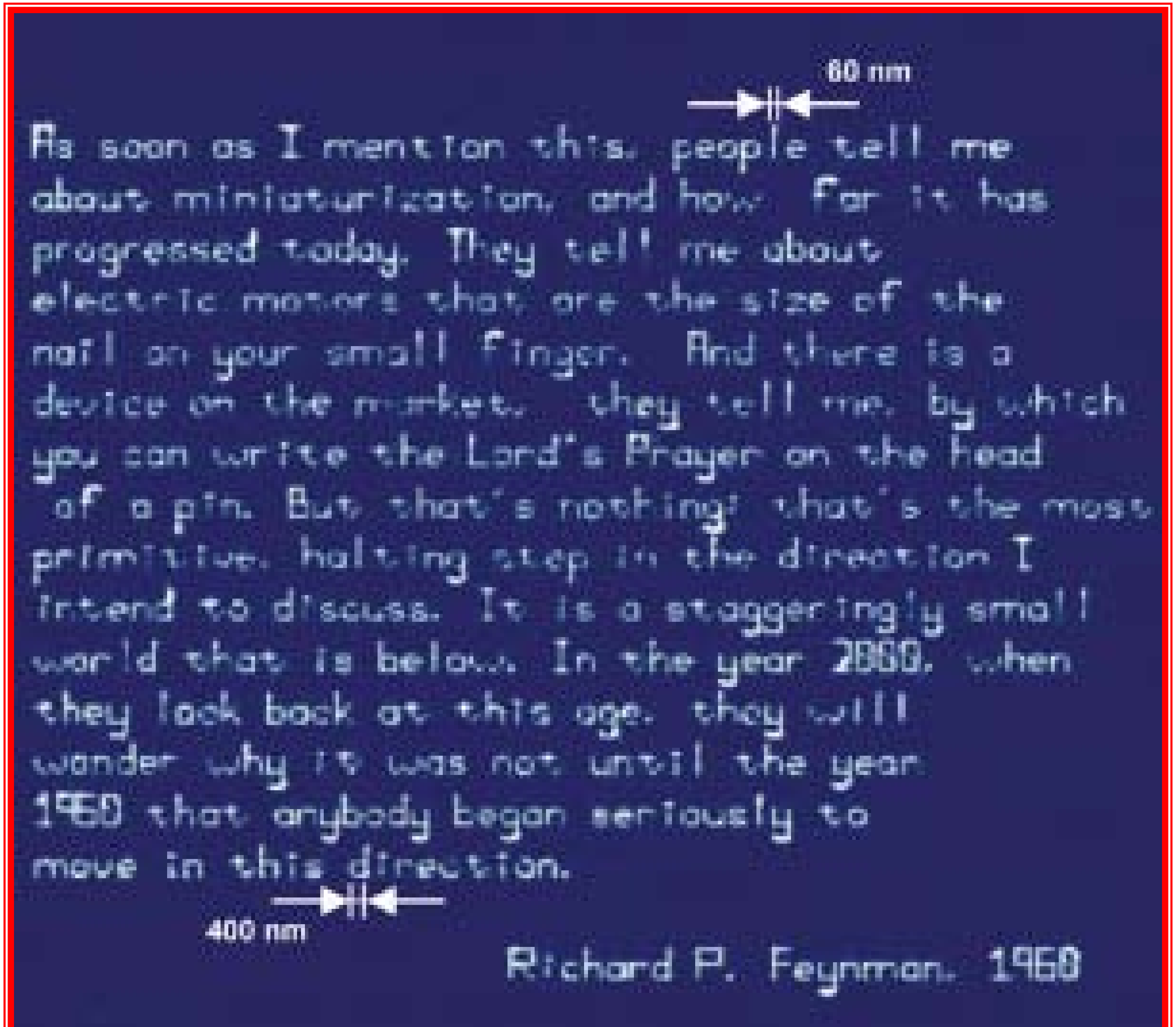


Fig. 1. Nanoscale molecular letters written on an Au(111) surface with MHA molecules by DPN.

Hong, Zhu, Mirkin, Science **286**, 523 (1999)

115 words in 10 minutes



S. Hong

Nanografting

Early Work:

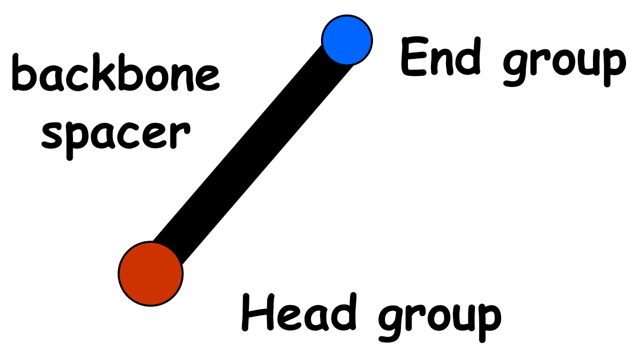
S. Xu and G.Y. Liu, "Nanometer-scale fabrication by simultaneous nanoshaving and molecular self-assembly", *Langmuir* 13, 127–29 (1997).

Self-Assembled Monolayers

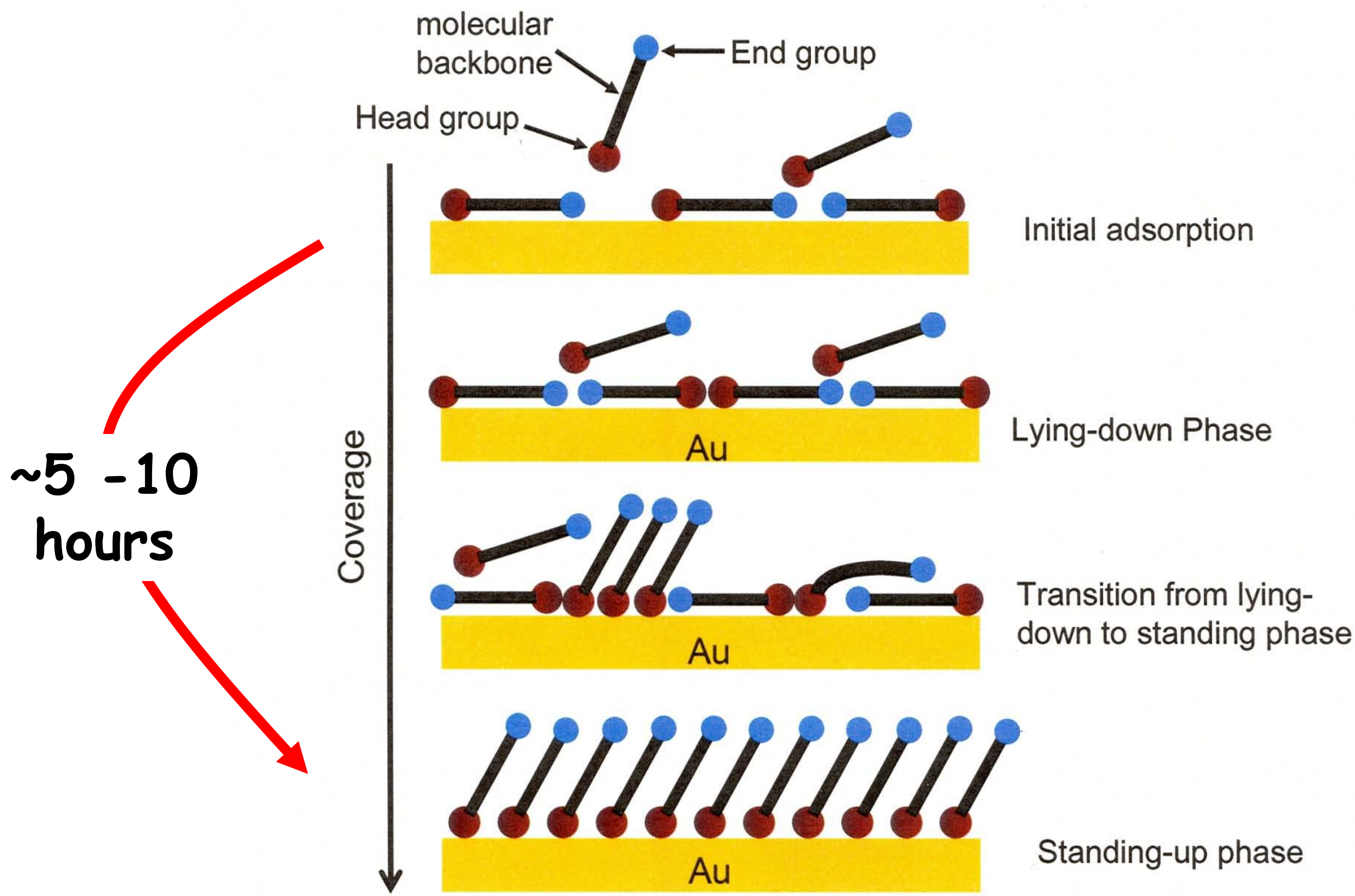
Self-Assembled Monolayers (SAMs) are ordered molecular assemblies formed by the adsorption of an active surfactant onto a solid surface.

Early Work: R.G. Nuzzo and D.L. Allara, J. Am. Chem. Soc. **105**, 4481 (1983).

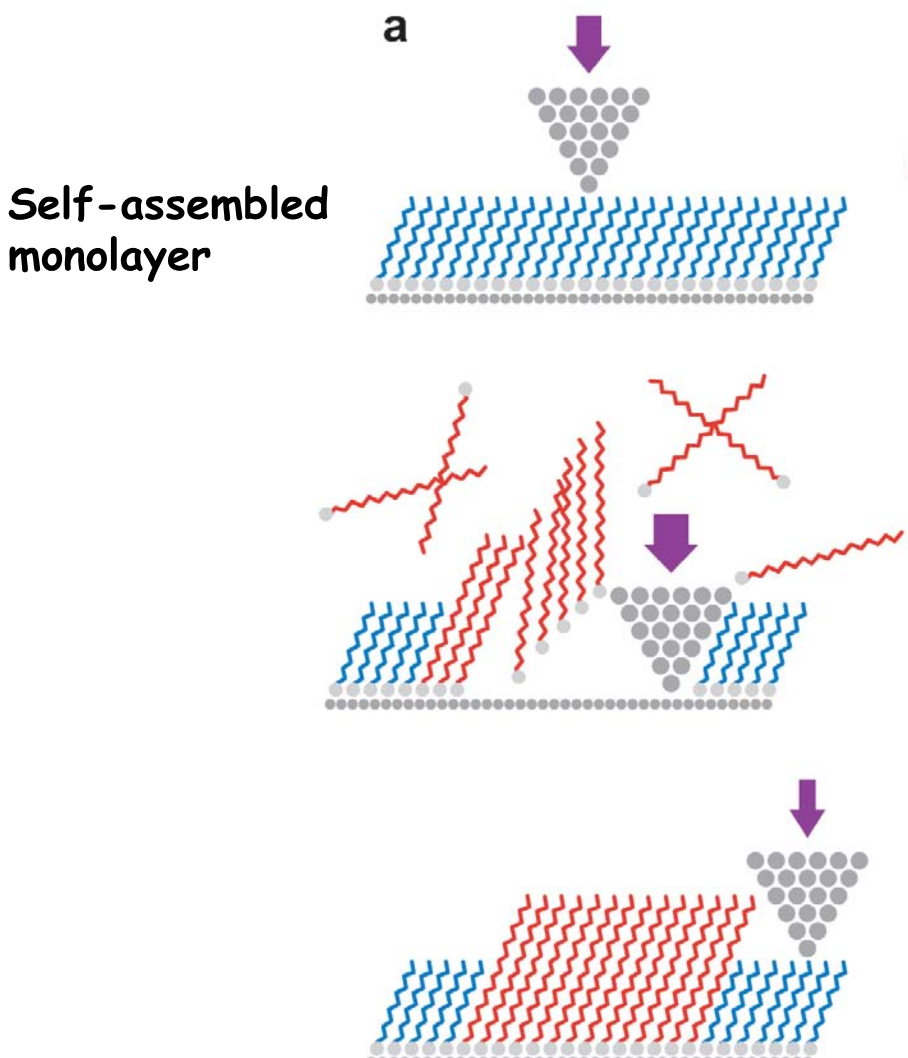
Molecules that can form a SAM (schematic):



The Self-Assembly Process

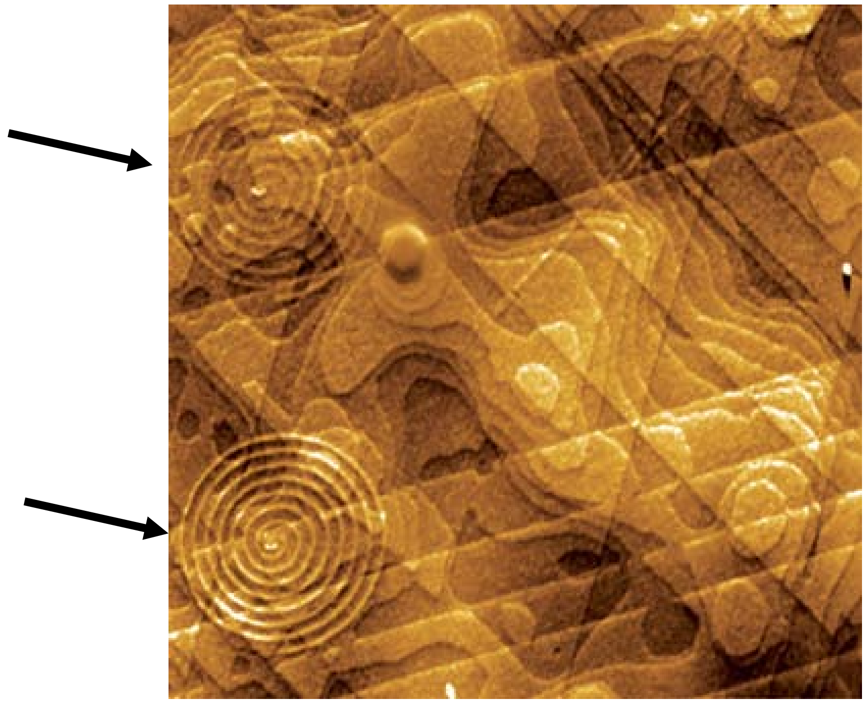


Nanografting



Liu, et al., Annu. Revs. Phys. Chem. **59**, 367 (2008).

Nanografting Thiols on Au

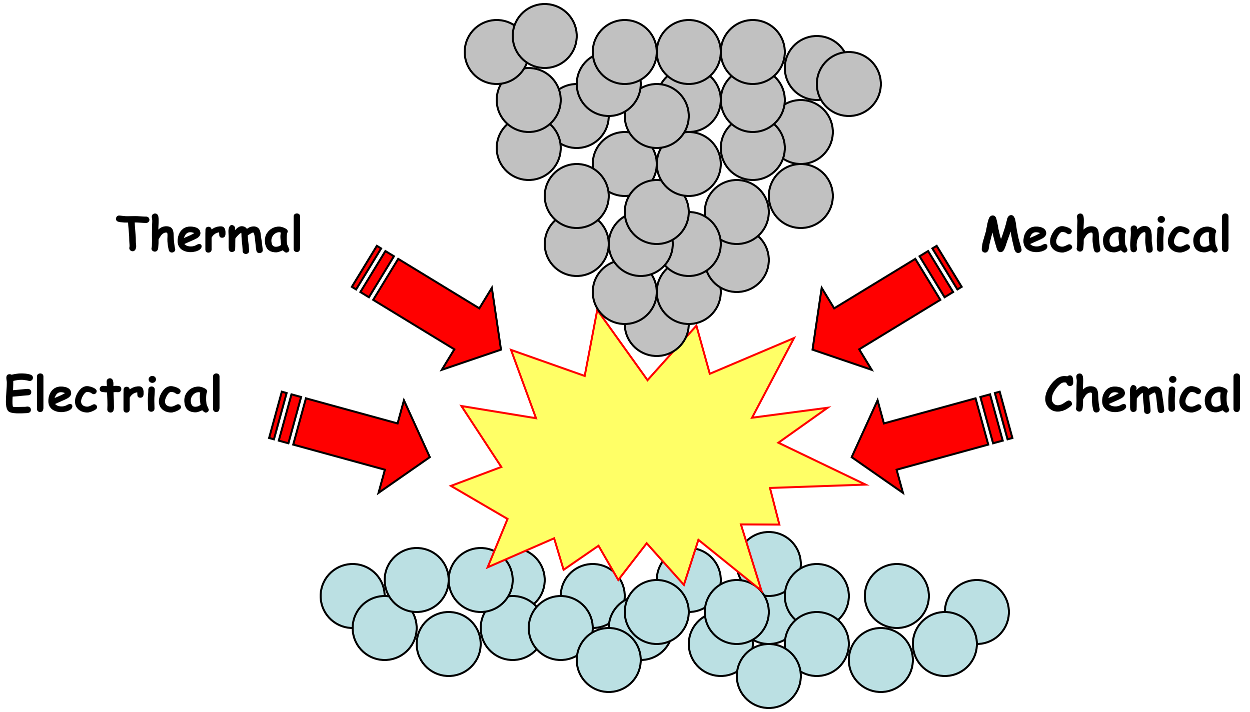


1.5 µm x 1.5 µm

Two nanografted spirals, 620 nm in diameter, with average line spacing of 40 nm, average line-widths (FWHM) of 15 nm, and average heights of 0.15 nm. Mono-atomic steps in Au(111) are clearly present.

http://www.azonano.com/details.asp?ArticleId=2385

Summary
Mechanisms to Modify Surfaces



Garcia, Martinez and Martinez, Chem. Soc. Rev. **35**, 29 (2006)