# 25 Years of Scanning Probe Microscopes:

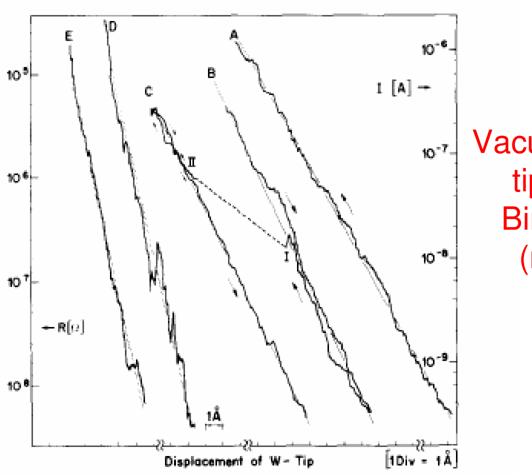
## How Instrumental Developments Revolutionized Surface Science and Nanotechnology

Frank Ogletree
Molecular Foundry
Imaging and Manipulation Facility

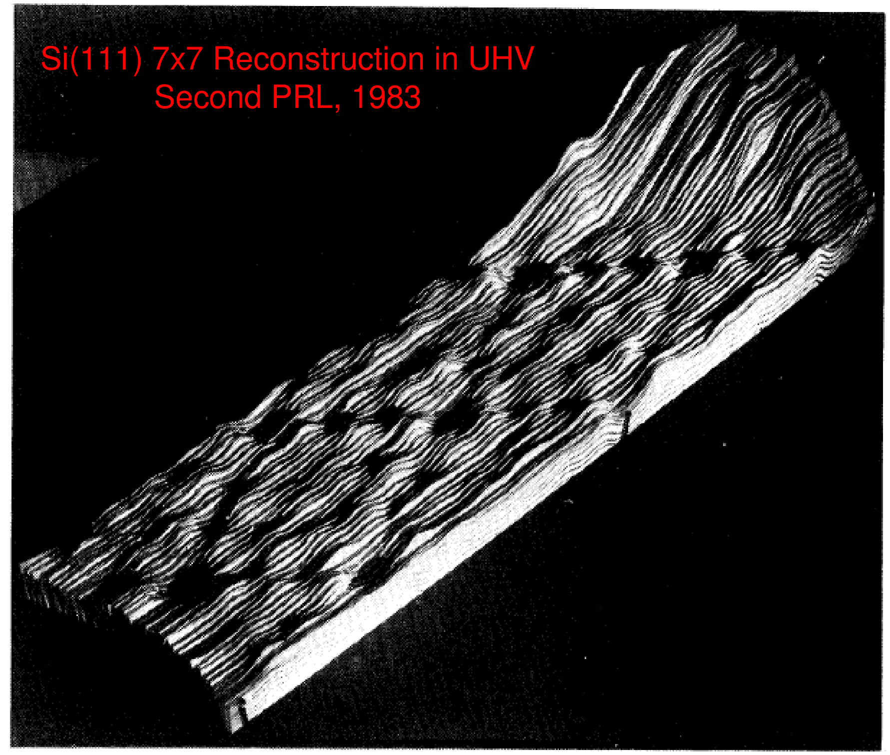
BERKELEY LAB

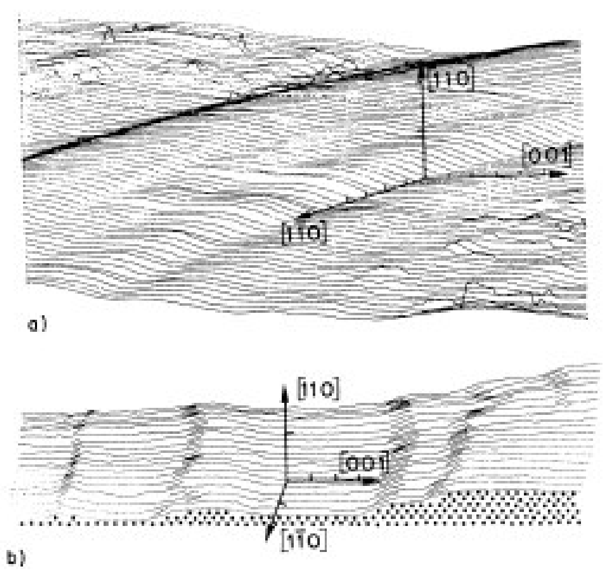
# Invention of the STM, 1981

## Gerd Binnig & Heine Rohrer, IBM Rüshlikon



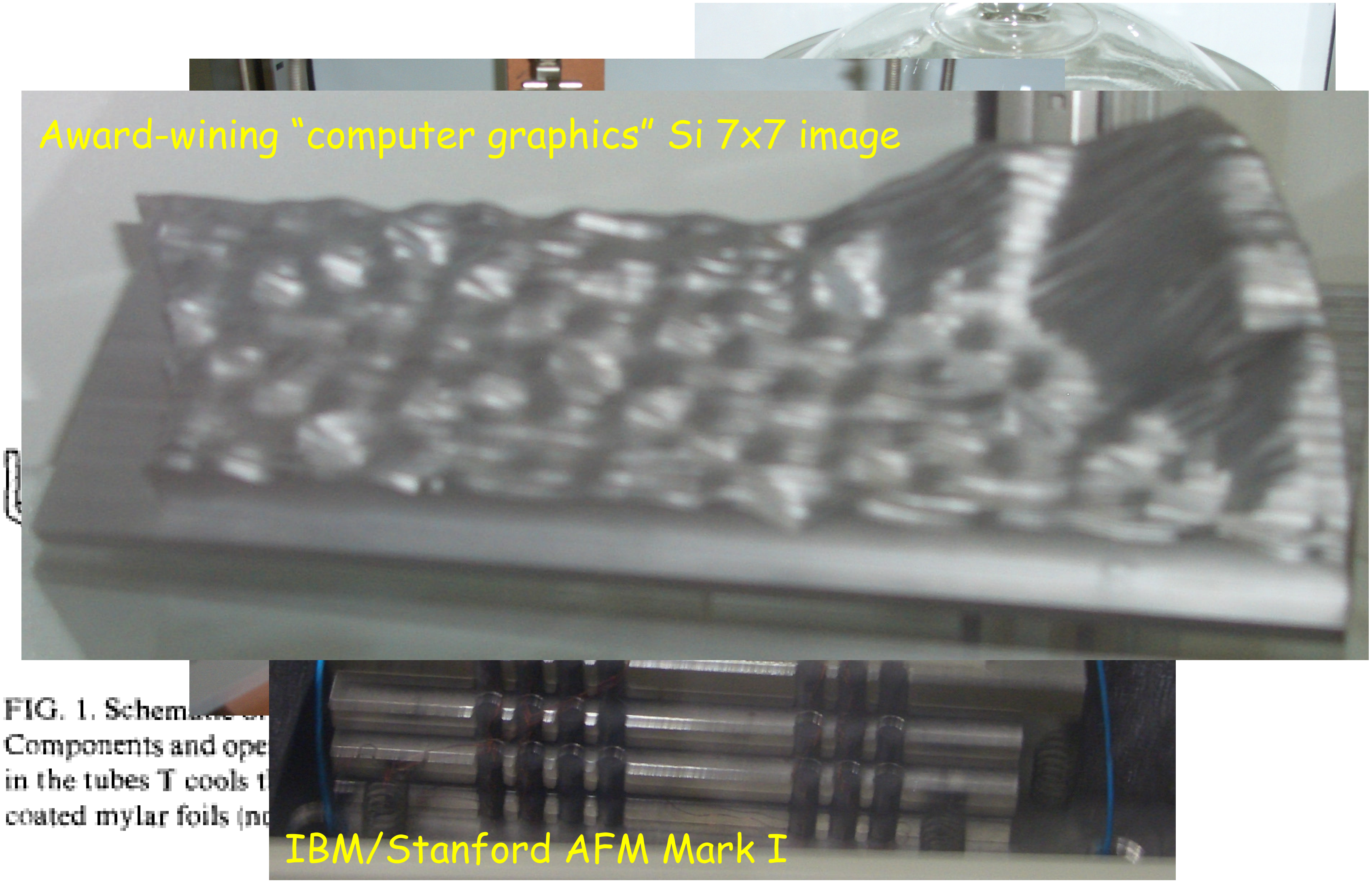

Vacuum tunneling between W tip and Pt foil, First APL, Binnig & Rohrer Jan 1982 (results from March 81)




Atomic Steps on Au(110) in UHV
First PRL, July 1982

# Hardware



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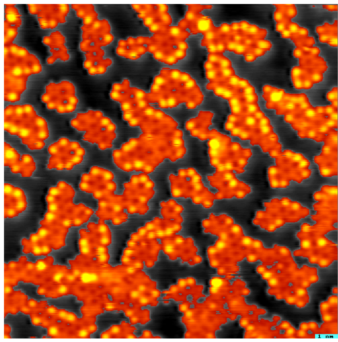
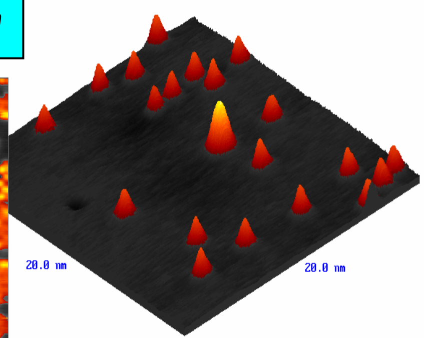
# SPM Timeline

- 1981 First STM results in the lab
- 1982 First PRL, Atomic steps on Au(110), Si(111)7x7 in '83
- 1984 Near field optical microscope
- 1985 First atomic resolution results by others
- 1985 Invention of AFM at Stanford
- 1986 Nobel Prize for Ruska, Binnig & Rohrer
  - first STM built at LBL (Miquel Salmeron, Joe Katz, Dan Coulomb Greg Blackman)
- 1987 First commercial instruments
  - Spin-offs from Quate group in Stanford (Park), Hansma group in UCSB (DI)
  - first computerized STM at LBL, maybe anywhere… (RHK/McAllister)
- 1989 First AFM and first UHV STM at LBL
  - Bill Kolbe
- 1991 first year > 1000 STM papers published
  - commercial instruments that work…
- ~ 1995 AFM widely used in industry, SPM widely used by non-specialist groups
- Over 2,000 STM and 6,500 AFM papers published last year

# Scanning Probe Microscopy at LBL

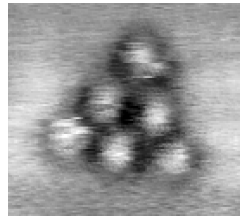
## Imaging

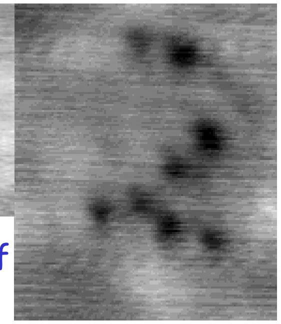





$H_2O$ Pd(111) 40 k

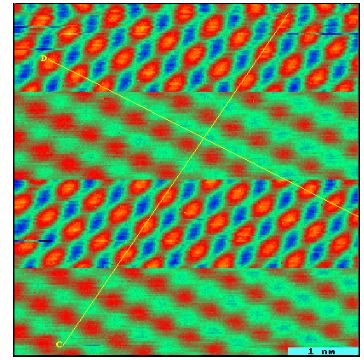
## Reactions





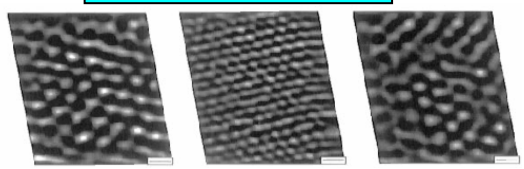
Dissociation of $O_2$ on Pd(111)

## Spectroscopy



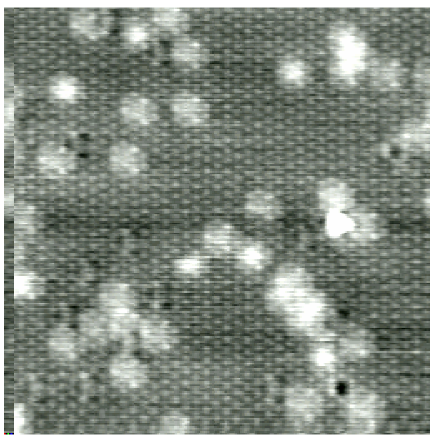
GaAs (110) bias contrast

## Local Order



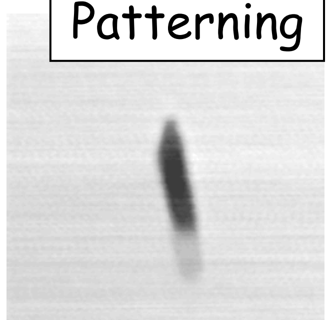
thiol displaced from Au(111)

## Dynamics

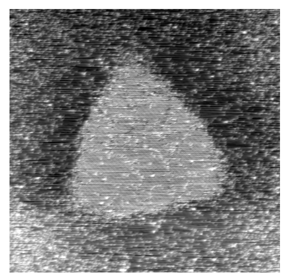


Pd(111) 215 K subsurface C

## Patterning

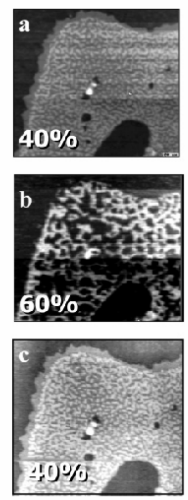


Monolayer groove machined in mica



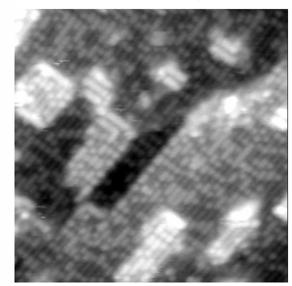
Electrostatic manipulation of H on Pd(111) at 40 K

## in-situ observation

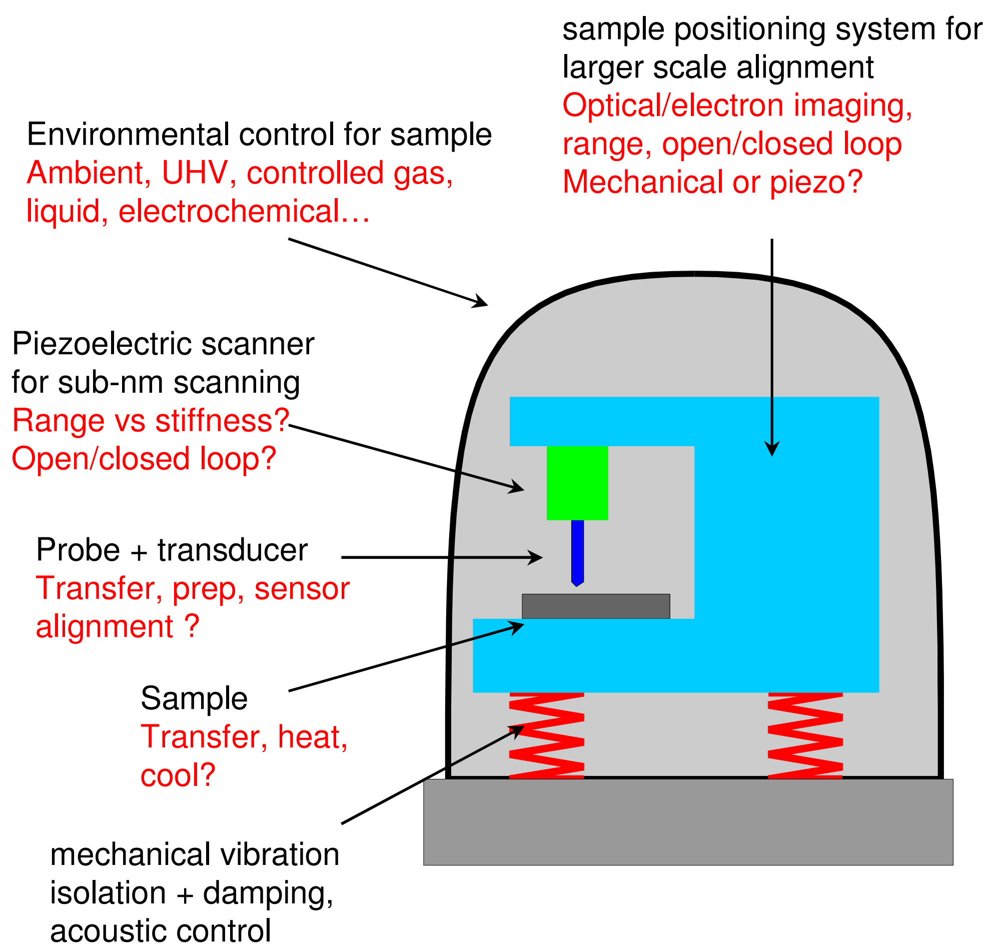



Humidity and SAM morphology

Co on CuO growth



# The SPM Instrument




- ♦ **Typical Design Trade-offs**
  - Large-scale sample translation vs stability
    - » Thermal drift
    - » Stiffness/mechanical resonance
  - Flexibility vs reliability
    - » Tip exchange
    - » In-situ sample control
    - » Open/closed loop
  - Dynamic range and resolution
  - Weak/strong thermal coupling



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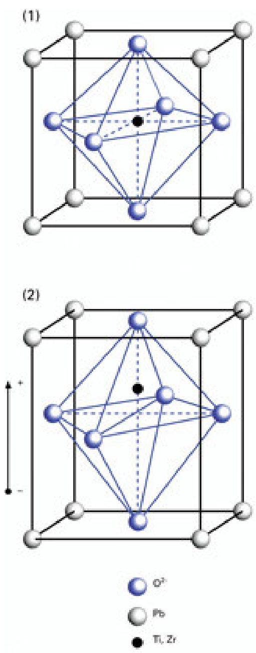
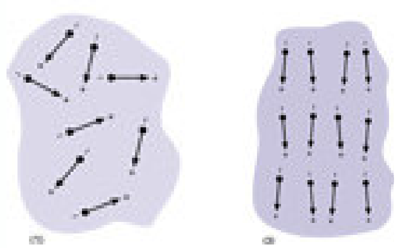
# SPM Technical Challenges

- Piezo translators
  - sub-pm resolution, but hysteresis, creep, etc
- Coarse approach
  - Sample transfer, mm motions with sub-micron precision
- Environmental noise
  - Mechanical building vibrations
  - Acoustic Noise, Air currents
  - Thermal drift (~ 10 ppm/K, so for 1 cm, 100 nm/K !)
  - 60 Hz induced by B-fields (flat screens are great!), ground loops
- Tip+Sample control
  - sharp, stable, reproducible, clean, etc
  - controlled environment: UHV, electrochemical, etc
  - feedback details…

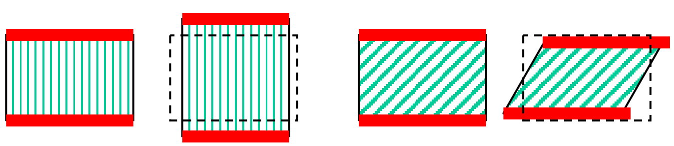
# Piezo Electric Translators




Lead-Zirconate-titanate Perovskite unit cell
3 axis, 6 possible J-T distortions to PZ



Practical Piezo Actuators are sintered polycrystalline ceramics with random domain orientations, polarized by the application of E or E+T

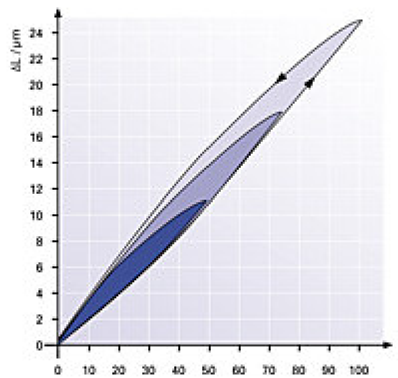


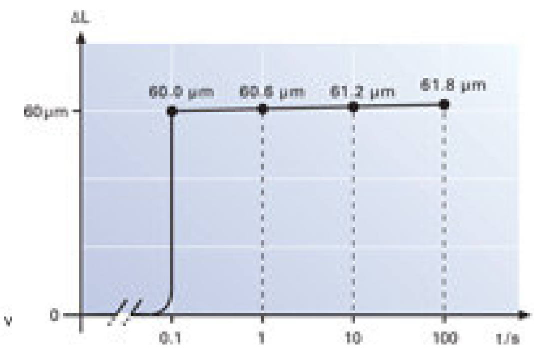
standard shear

$\Delta L/L = d_{ij}E$, $d_{ij}$~1-300 pm/V

$E_{max}$~1 kV/mm, $\Delta L/L_{max}$~$10^{-4}$

SPM actuators ~ 1 to 20 nm/V



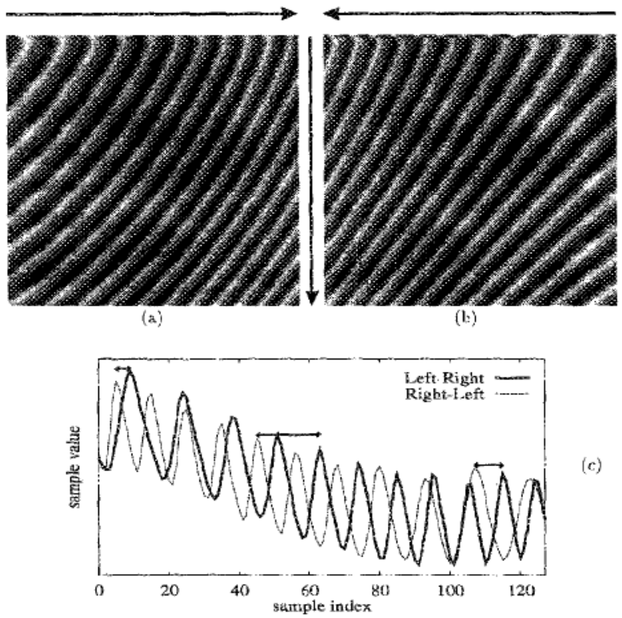




Hysteresis and Creep
Caused by changes in domain structure
Thermally activated, much better at 4 K



Piezo University at www.physikinstruemente.com

# Piezo Creep & Hysteresis



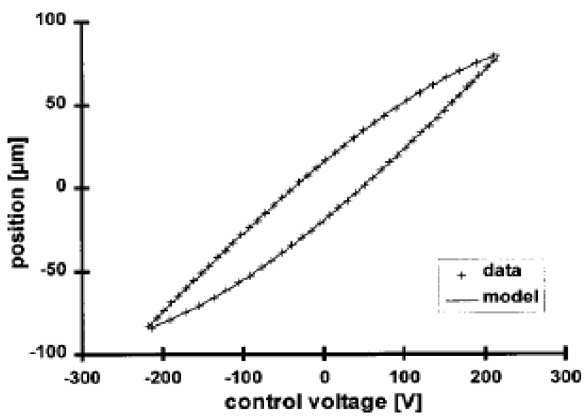




FIG. 1. Typical hysteresis loop as sampled by a SPM with disabled on-line correction. The measured position $x$ of the piezo is marked with crosses vs the value of the applied control voltage $V$ for the scan range of 440 V. This corresponds to 160 $\mu$m. The plot of the model is shown by the solid line.

PbZrTiO, sintered polycrystalline materials

max $\Delta L/L$ ~ $10^{-4}$, much worse for quartz, etc

solutions:

Live with it, Better at 4 K

Non-linear voltage drive, corrections

Use closed-loop sensors

(0.5 nm resolution, capacitive, optical, etc, but alignment required)

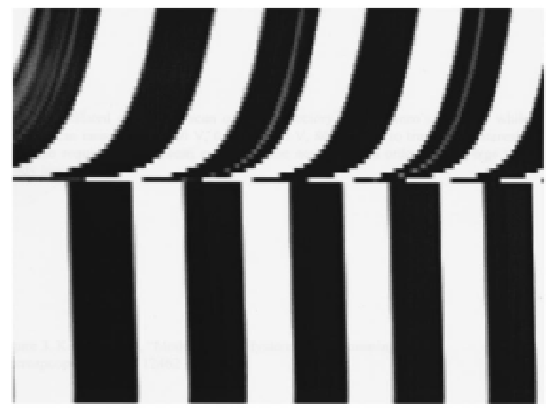


FIG. 4. Experimental image. A line-pattern; with 3.0 $\mu$m period is scanned upwards. At the center of the image the scan offset was changed from −80 to 0 V while the SPM continued scanning. The curvature is typically related to ''creep'' but also contains time-independent transition.

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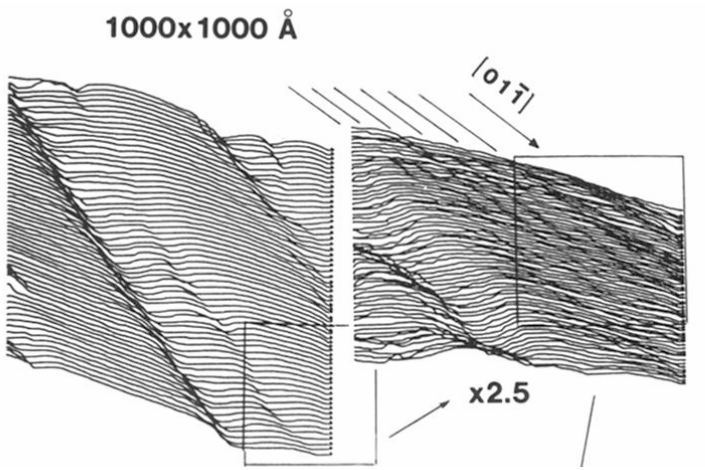
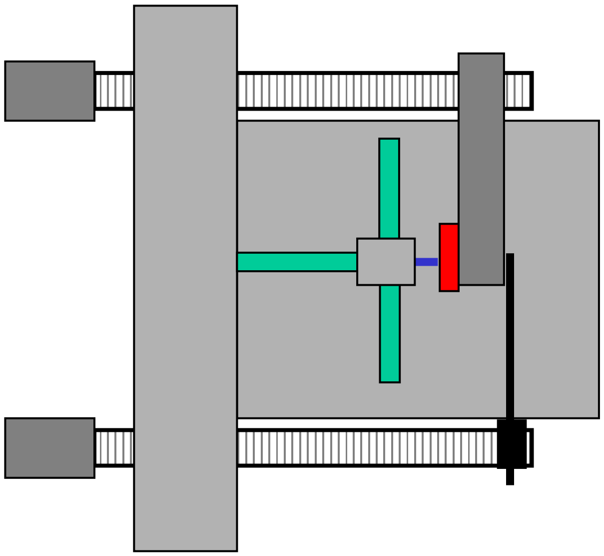
# Early STM developments at LBL




STM images of stepped Au(334) in air
first LBL STM paper
chart recorder data

STM study of Au(334) in air, Salmeron, Marchon, Ferrer, Kaufman, Phys Rev B 1987.



STM with tripod XYZ scanner
and mechanical screw approach
with differential spring
used in air and low vacuum

**Instrument development**

2ed generation control electronics
(with Joe Katz)
UHV STM and Chamber
Software for data acquisition

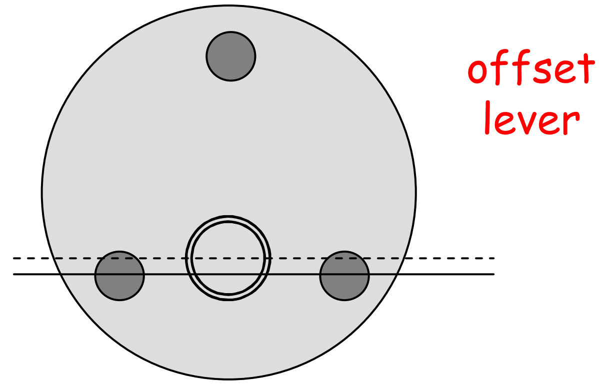
# Coarse Approach - Screws

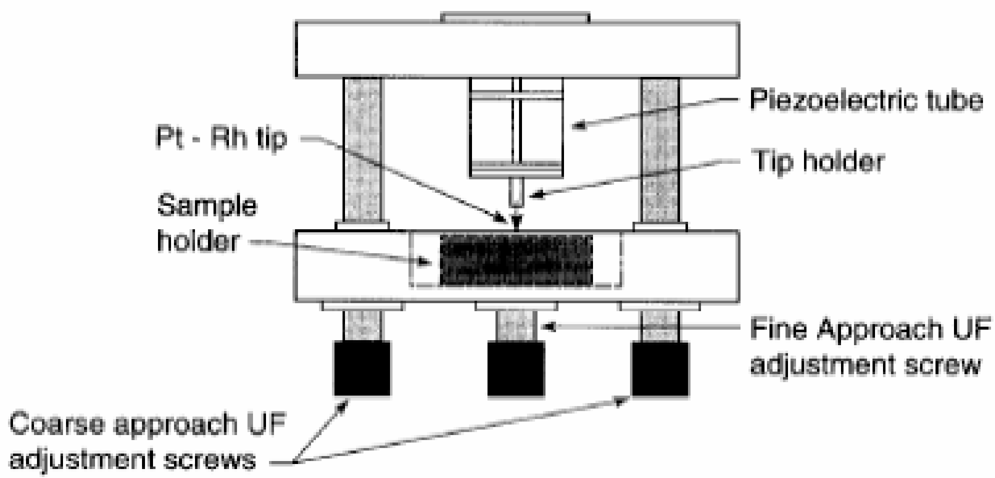
**Drive Screws**

80 TPI = 3 um/turn

1% rotation 300 nm

10:1 reduction 30 nm




(a) Front view of Tripod ESTM

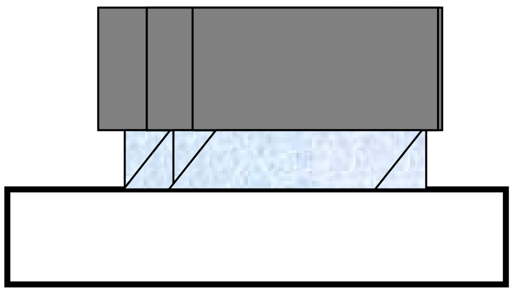
**Limitations**

Backlash, stiction, wobble, runout…

Manual, stepper motor, DC servo, piezo motor

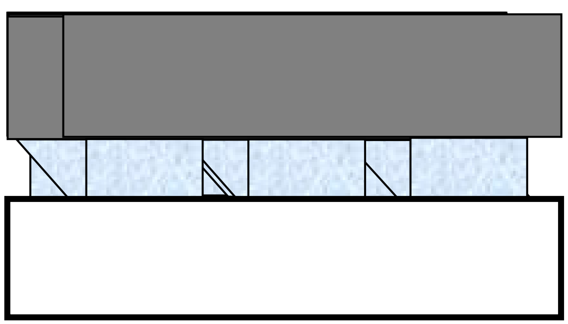
# Coarse Approach – Piezo motors

## Kinetic or Stick-Slip motor



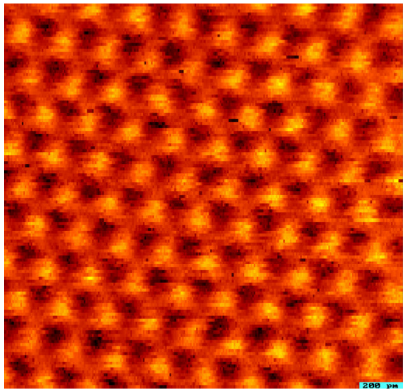
Friction can be overcome by
piezo acceleration
Friction sufficient for stability
(mass or spring load)
Friction **uniform** along track
(no scratches, contamination)

## "Pan" motor



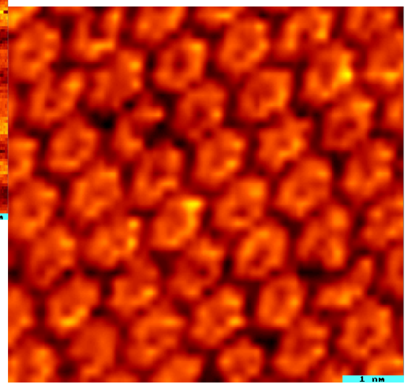
Friction against Friction N:1
Friction sufficient for stability
(mass or spring load)
Friction **uniform** along track
(no scratches, contamination)
Motions can be slow
Low compliance required

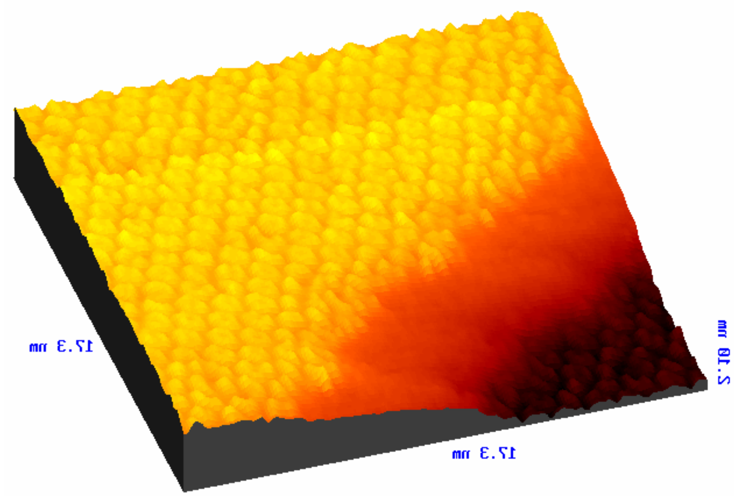
# $2^{rd}$ Generation, UHV

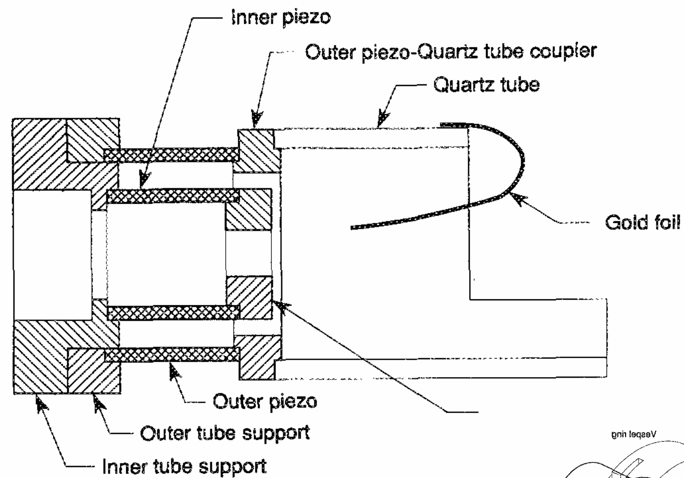


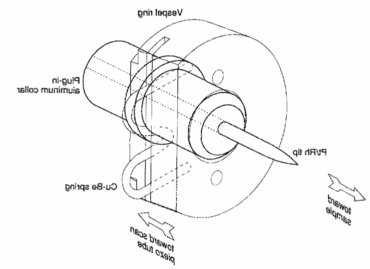
HOPG in UHV

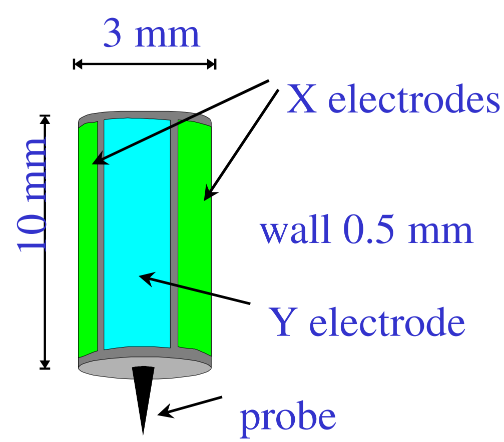
S on Re(0001)

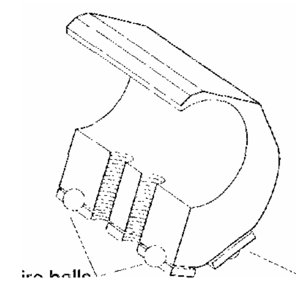




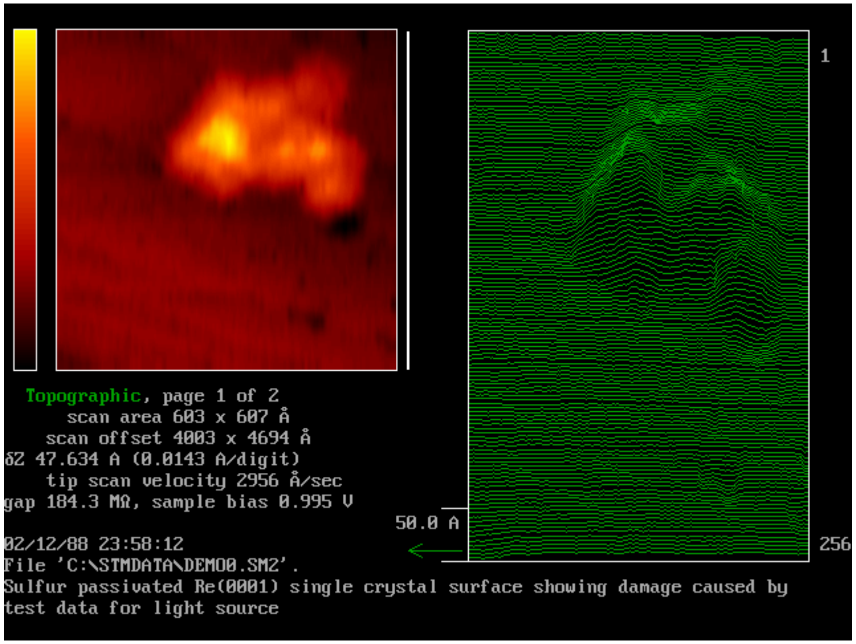




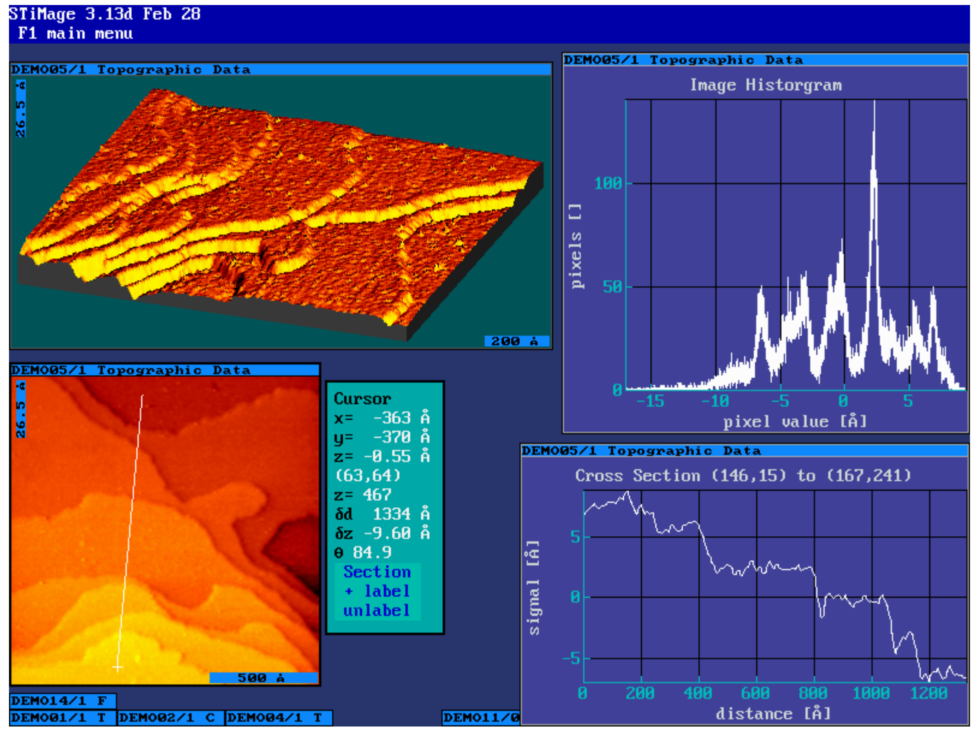



# STM Software



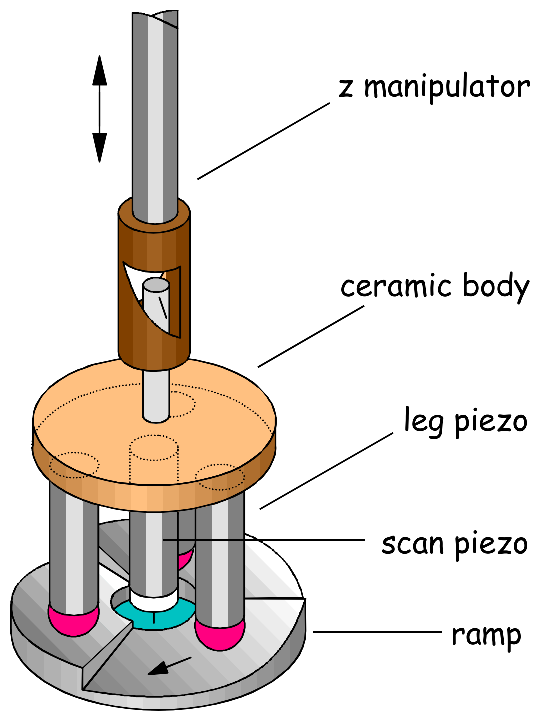

Screen capture of first STM program
Fortran on DEC LSI-11 minicomputer,
5 MB disk 64 kB RAM
$6,000 display system, 640x480 pixels

STM program in 1993, C on
Compaq 80386 ($19 k), 0.02 GHZ 1 MB RAM
32 bit CPU, SVGA display, extended DOS

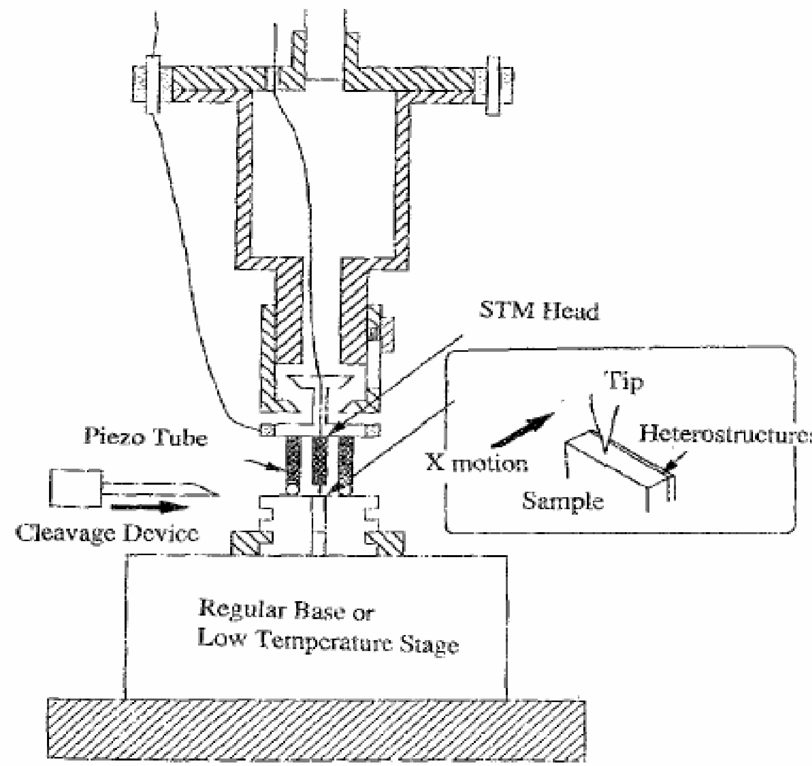


# 3rd Generation "Beetle"

STM and Sample Holder

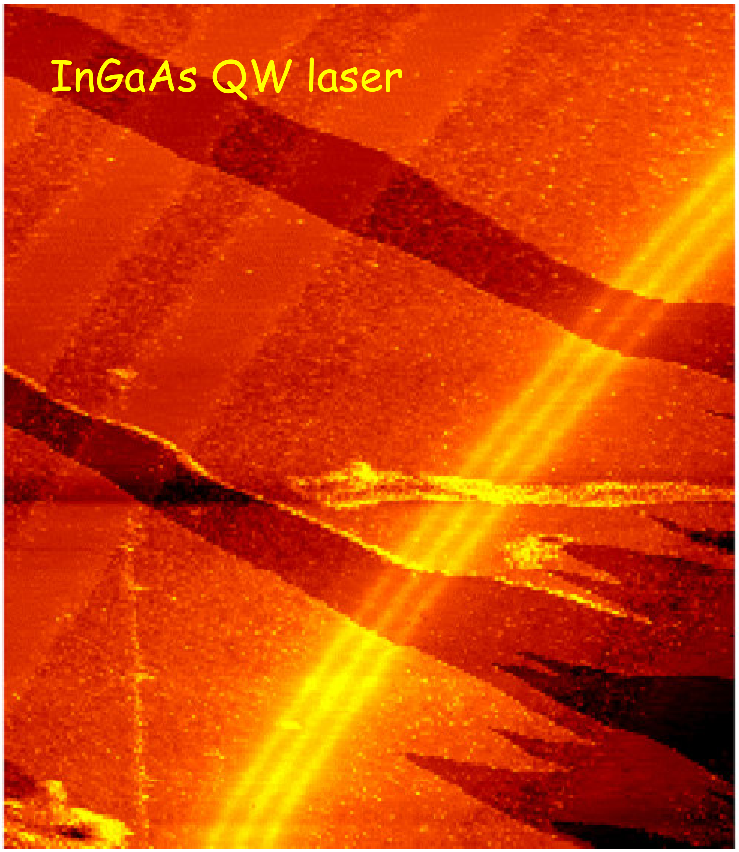


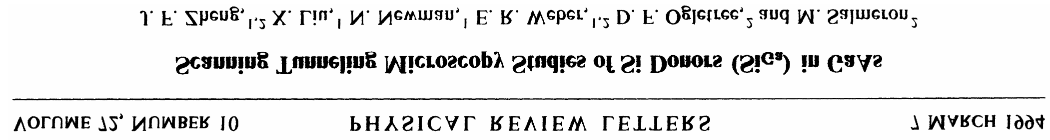

"Walker" style STM




Cross-Section STM for cleaved semiconductor heterostructures, with J.-F. Zheng in Eicke Weber's group

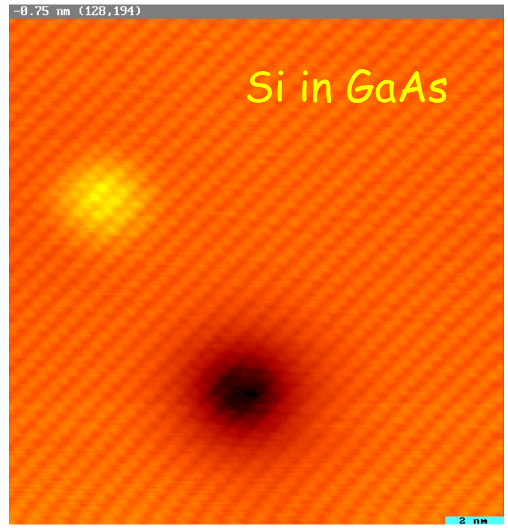
# Results on Semiconductors

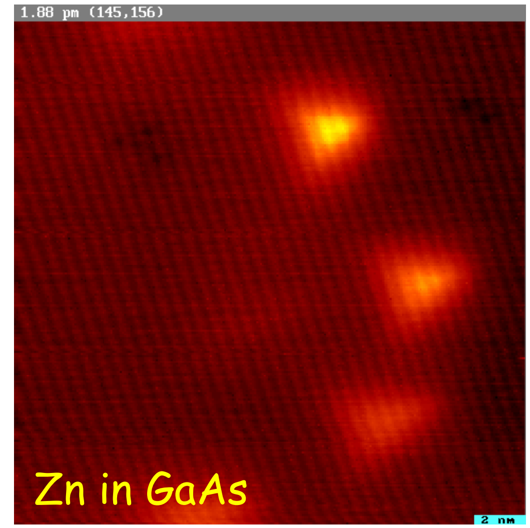


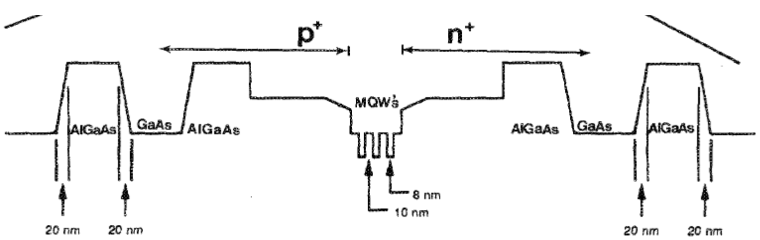


VOLUME 72, NUMBER 10 PHYSICAL REVIEW LETTERS 7 MARCH 1994

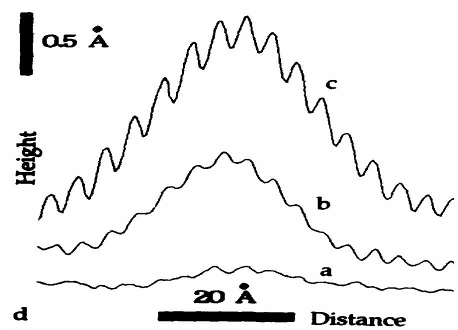
Scanning Tunneling Microscopy Studies of Si Donors ($Si_{Ga}$) in GaAs

J. F. Zheng,[1,2] X. Liu,[1] N. Newman,[1] E. R. Weber,[1,2] D. F. Ogletree,[2] and M. Salmeron[2]



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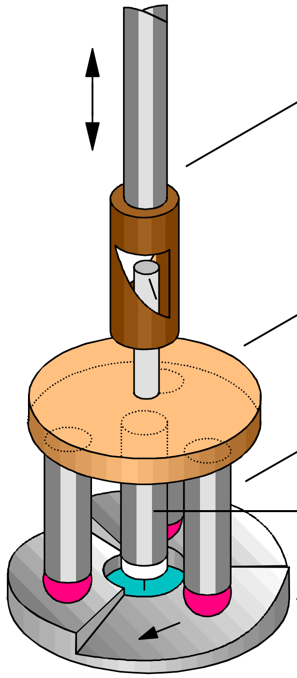
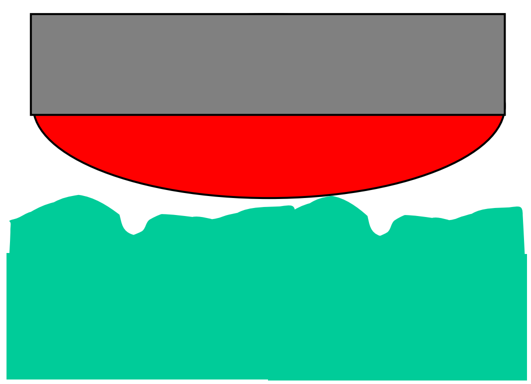
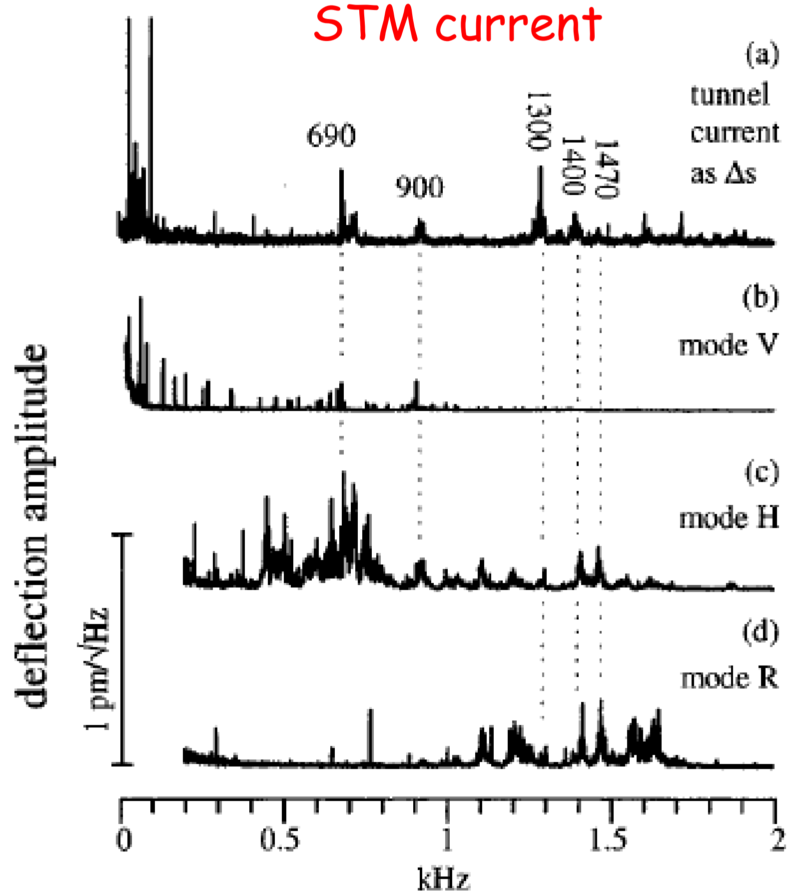
# Mechanical Response



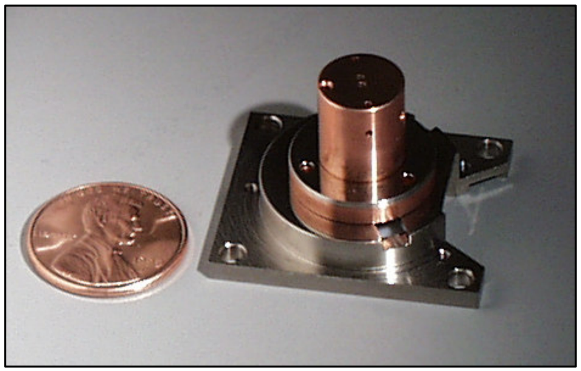
STM current

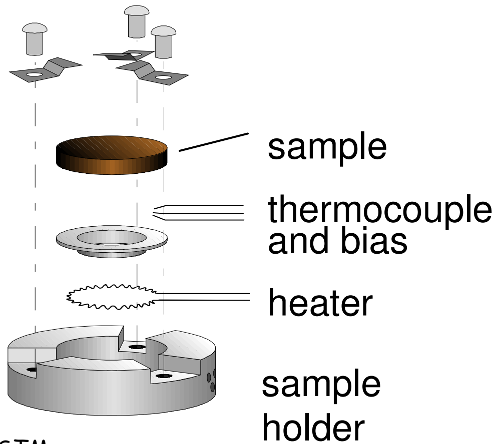


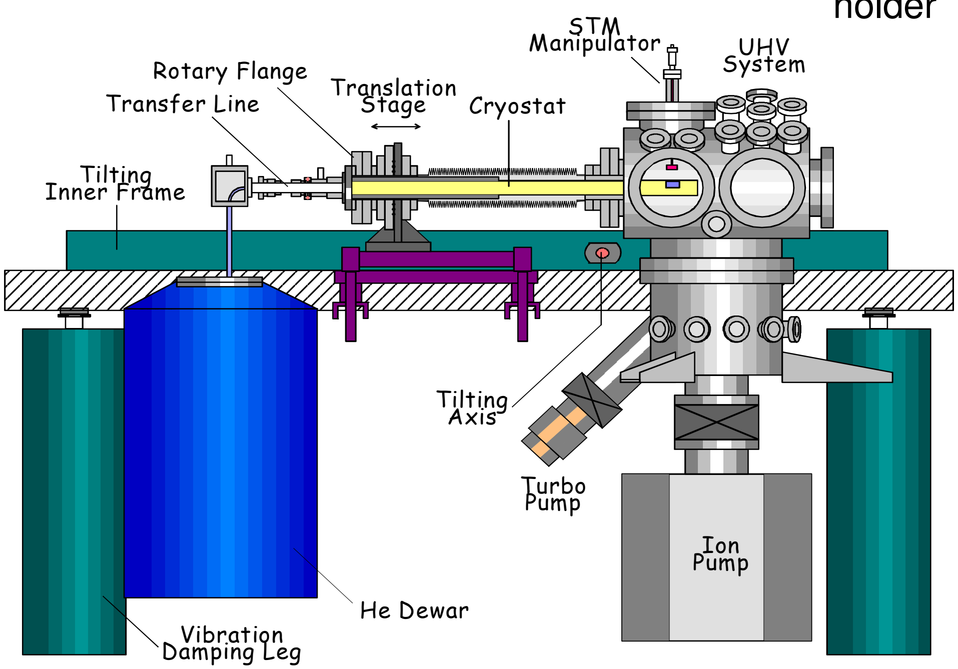

Piezo excitation response tests

# Cryo-STM developments

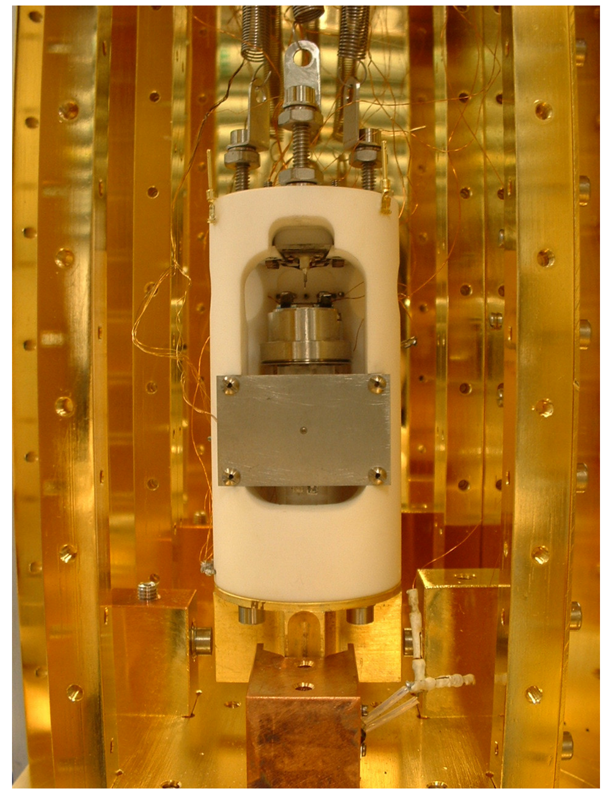
Variable Temperature UHV STM
25 – 300 K, operating ~ 1998



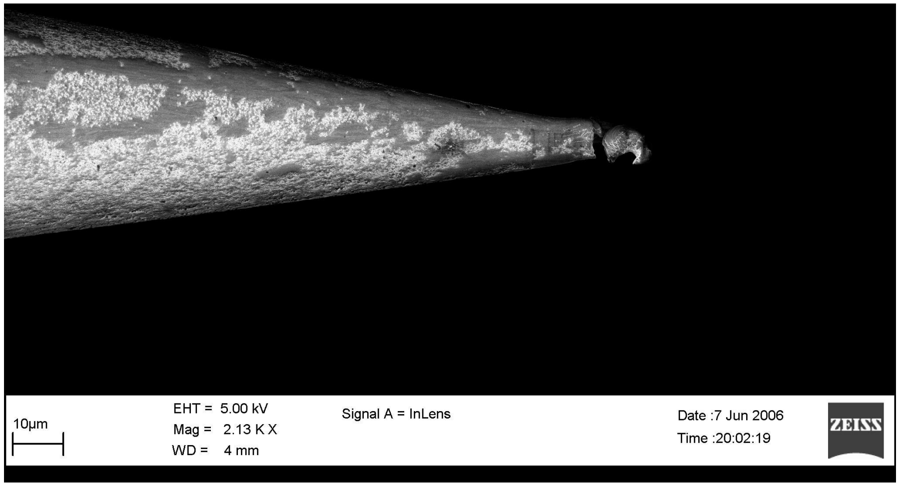


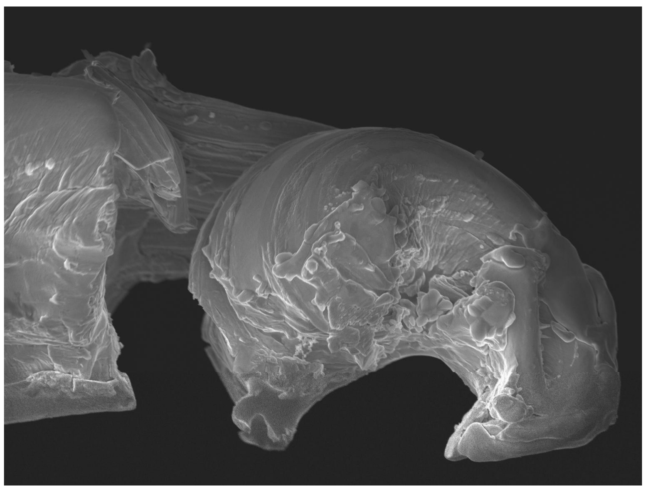

Helium Temperature UHV STM for spectroscopy, operating ~ 2005
weakly coupled

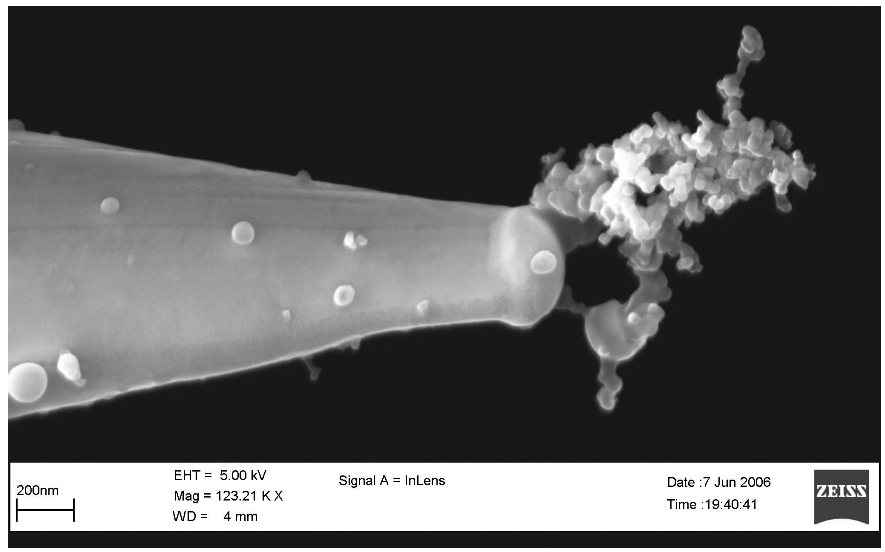


# Tip Problems




Electrochemically etched Tungsten STM Tips





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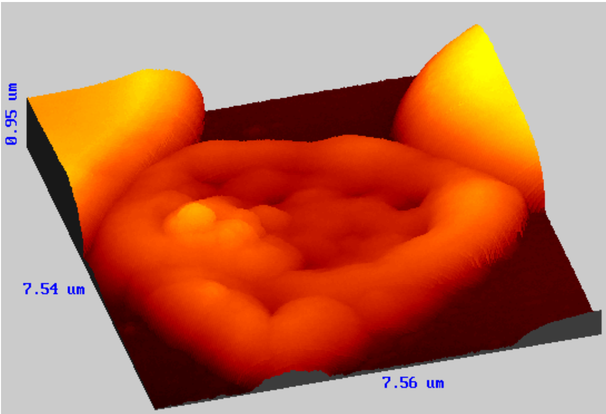
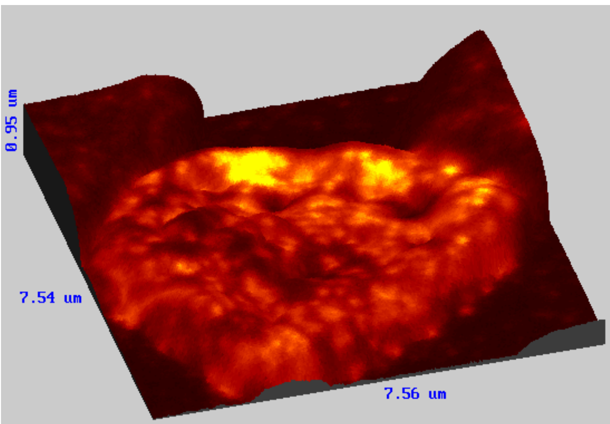
# Near Field Optical Microscopy

## with Shimon Weiss, in Daniel Chemla's group

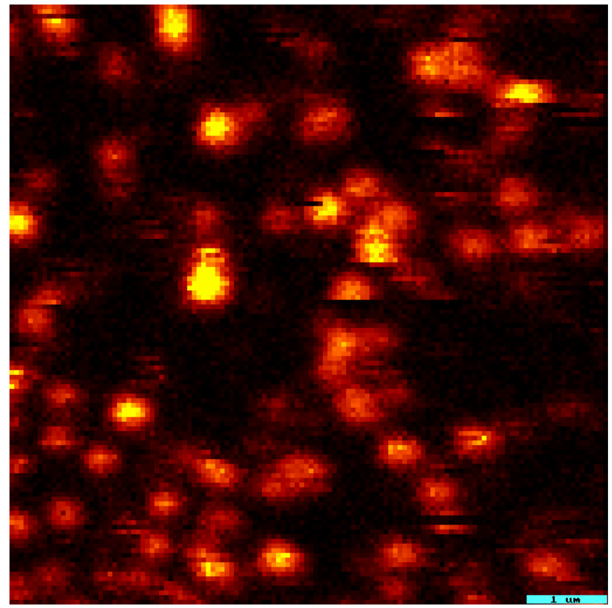



AFM image of red blood cells




NSOM of labeled malaria membrane proteins

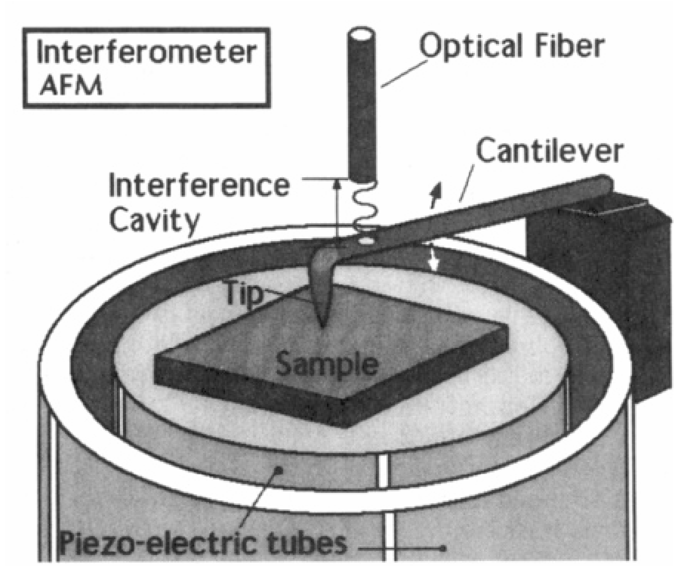
Optical spectroscopy of individual molecules is possible if they are dispersed and bright



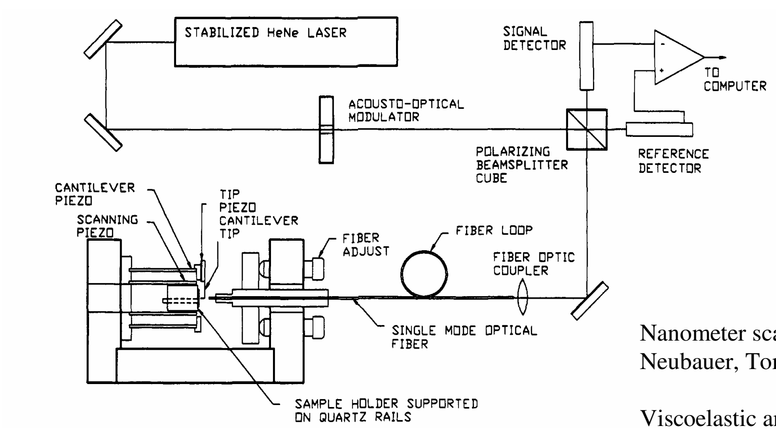
confocal image of individual dye molecules ~ 1995

Membrane specific mapping and colocalization of malarial and host skeletal proteins in the Plasmodium falciparum infected erythrocyte by dual-color near-field scanning optical microscopy.
T. Enderle, T. Ha, D. F. Ogletree, D. S. Chemla, C. Magowan and S. Weiss, *Proceedings of the National Academy of Sciences* (1997.

# First LBL AFM-STM ~ 1990




W wire for tip-cantilever




Combined STM and AFM

control tip position and bias
record forces and currents

dielectric and partly conducting samples

investigate fixed charges, surface potential variations, local polarizability and conductivity

Nanometer scale mechanical properties of Au(111), Salmeron, Folch, Neubauer, Tomitori, Ogletree, *Langmuir* 1992.

Viscoelastic and Electrical Properties of Alkylthiol Monolayers on Au(111) Films, Salmeron, Neubauer, Folch, Tomitori, Ogletree, Sautet, *Langmuir* 9 3600 (1993).



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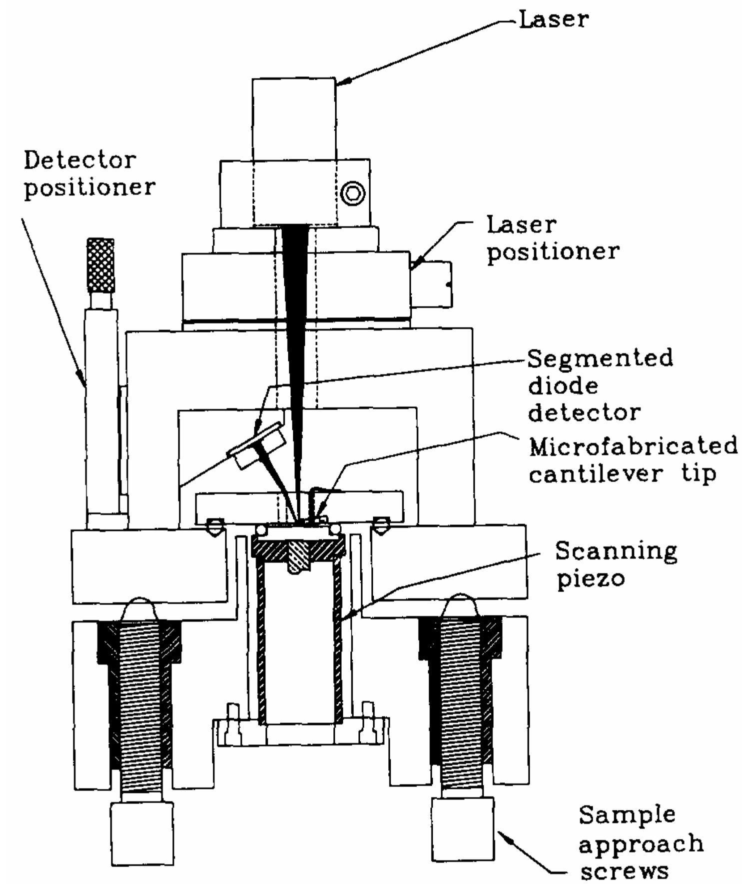
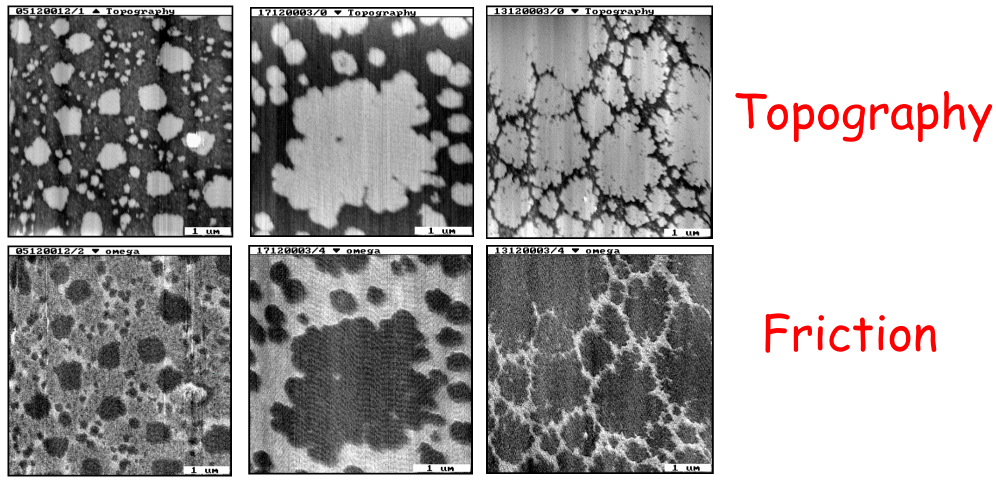
# Air AFM for SAMs ~ 1992

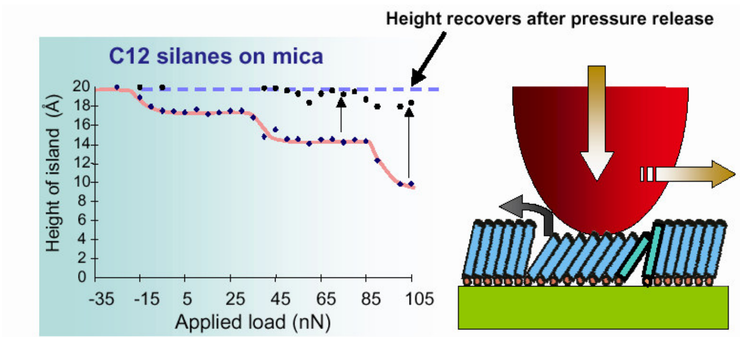



Atomic Force Microscopy Imaging of $T_4$ Bacteriophages on Silicon Substrates, Kolbe, Ogletree, Salmeron, *Ultramicroscopy* 1992.

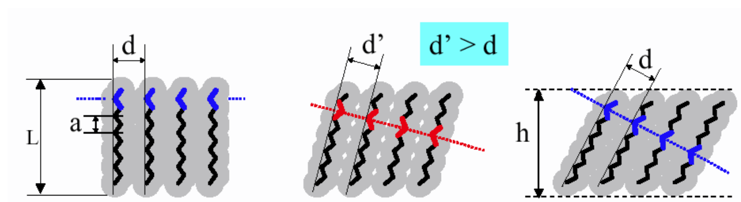
The relationship between friction and molecular structure: Alkylsilane lubricant films under pressure, Barrena, Kopta, Ogletree, Charych and Salmeron, *Physical Review Letters* 1999.

## Silane islands on mica




## Transformation under pressure




Intermediate Instrumentation Colloquium
Frank Ogletree, September 2006

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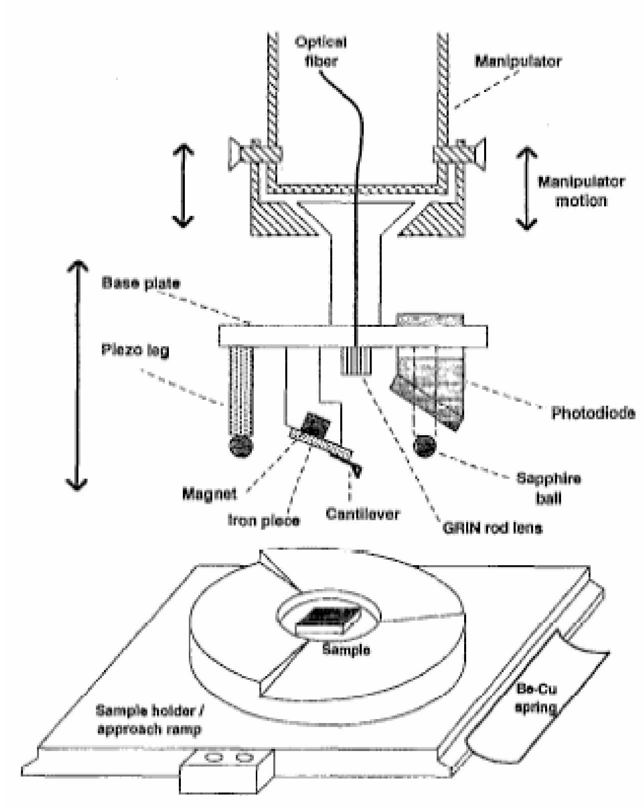
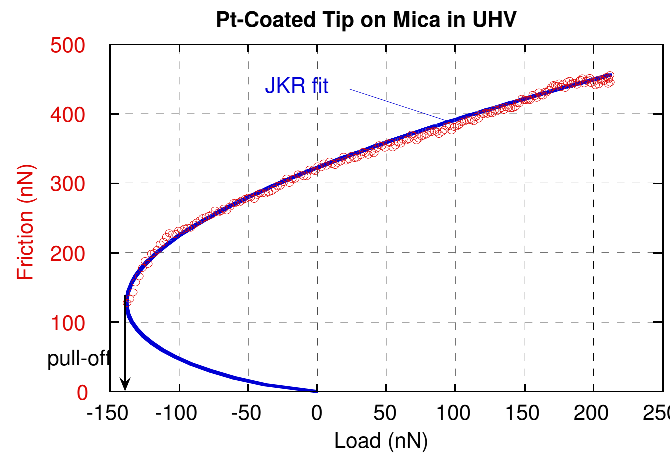
# UHV AFM for Tribology, 1995



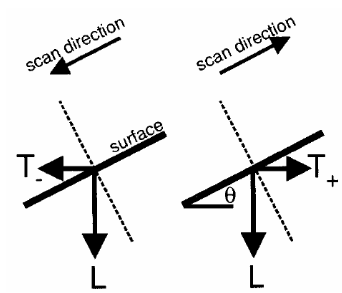

A Variable Temperature Ultra-high Vacuum Atomic Force Microscope, Dai, Vollmer, Carpick, Ogletree, Salmeron, *Review of Scientific Instruments* 1995.

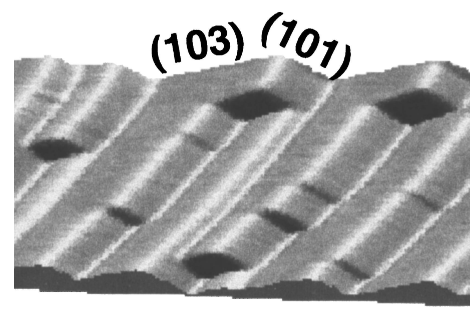
Variation of the Interfacial Shear Strength and Adhesion of a Nanometer-sized Contact. Carpick, Agraït, Ogletree, Salmeron, *Langmuir* 1996.

Calibration of frictional forces in atomic force microscopy
Ogletree, Carpick, Salmeron, *Review of Scientific Instruments* 1996.




Friction is proportional to tip-surface contact area

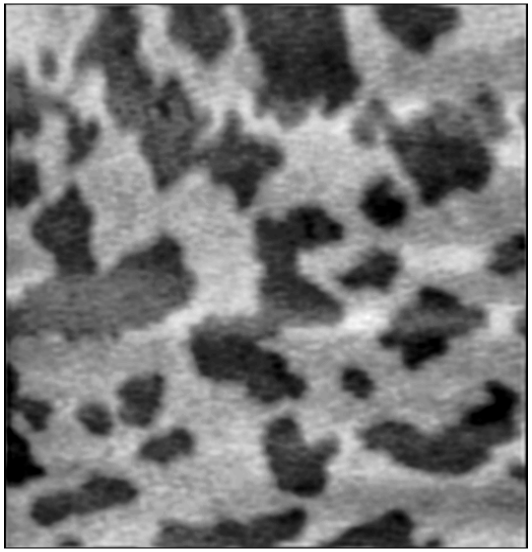


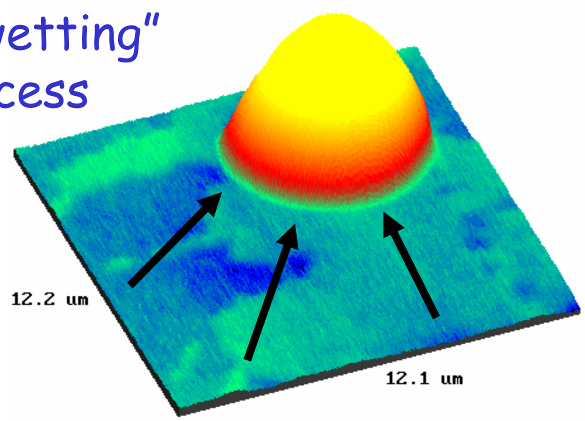

Friction "wedge" calibration

# Nanoscale Liquid Films and Droplets

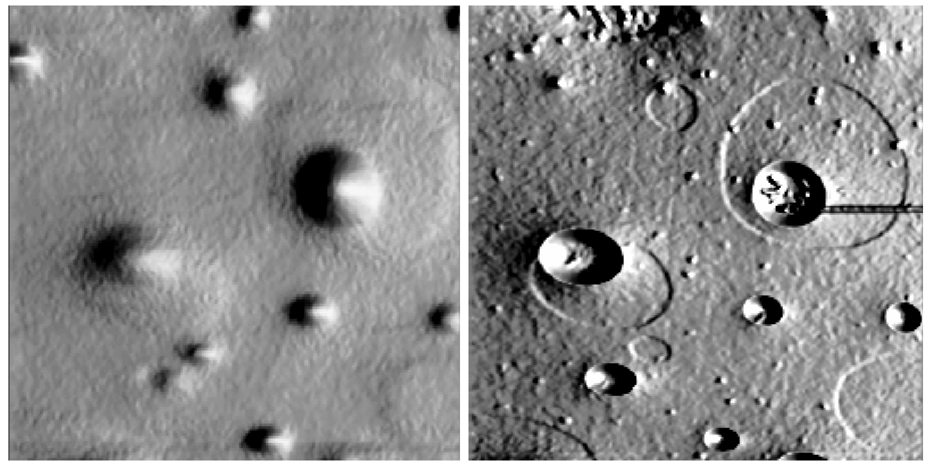
PFPE Lubricant Film
on Disk Substrate



"De-wetting"
of excess
lube




Corrosion of oxidized Al by $H_2SO_4$:$H_2O$



Non-contact electrostatic image of droplets

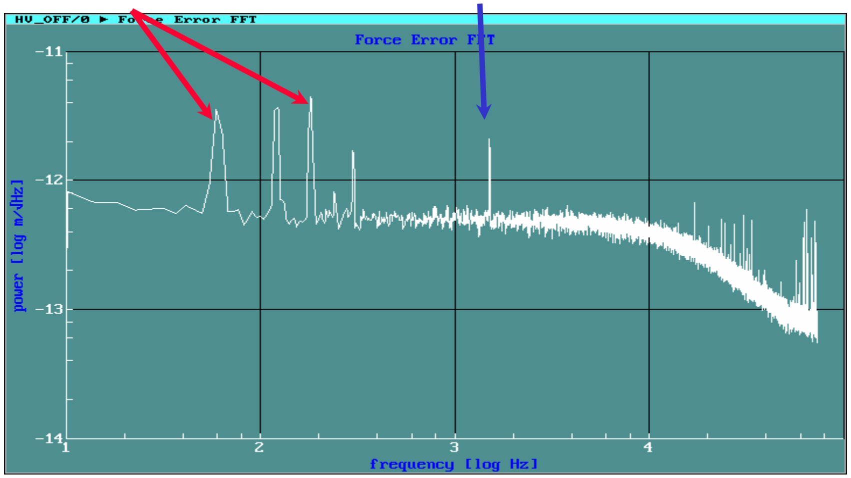
Contact image show corrosion correlated with droplet locations

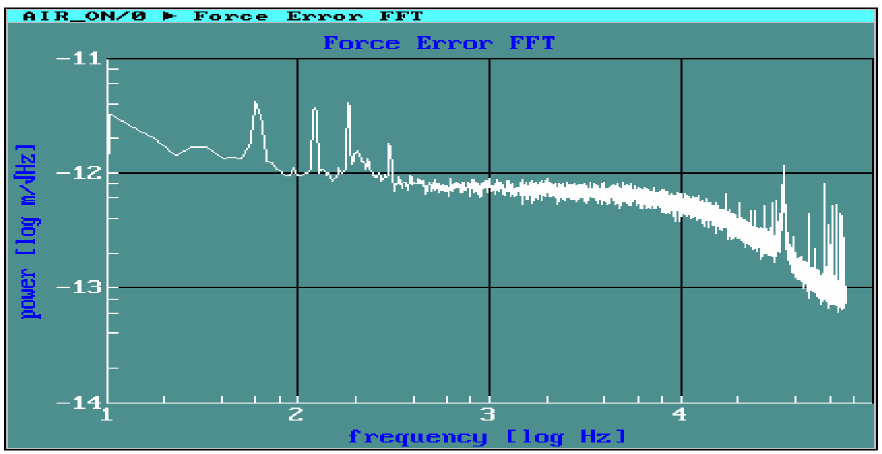
Q. Dai, J. Hu, A. Freedman, G.N. Robinson and M. Salmeron, J. Phys. Chem. 1996

De-wetting of lubricants on hard disks, Xu, Ogletree, Salmeron, Tang, Gui, Marchon. *Journal of Chemical Physics* 2000.

# AFM Transducer Noise

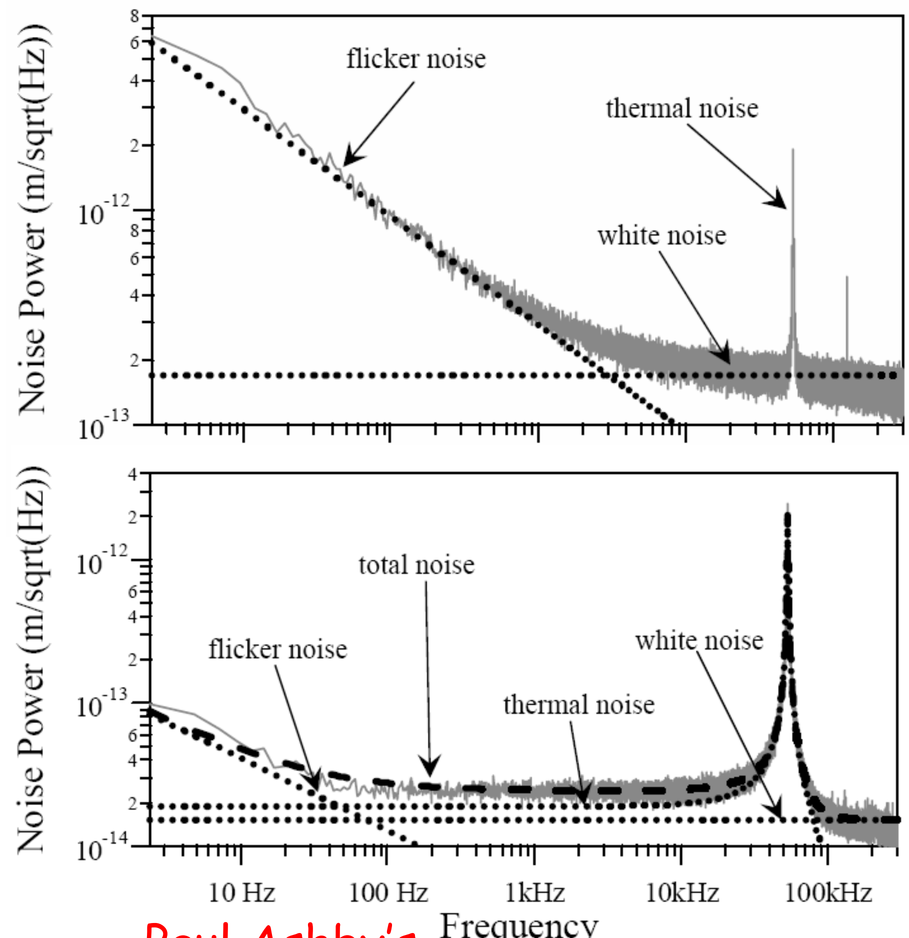
60 Hz Noise turbo, 1.51 kHz




LBL AFM 1990's
Integrated noise 0.5 Å rms, 2.5 p-p
0-500 Hz noise 0.15 Å rms, .75 p-p

Modern Commercial System




Paul Ashby's optimized system

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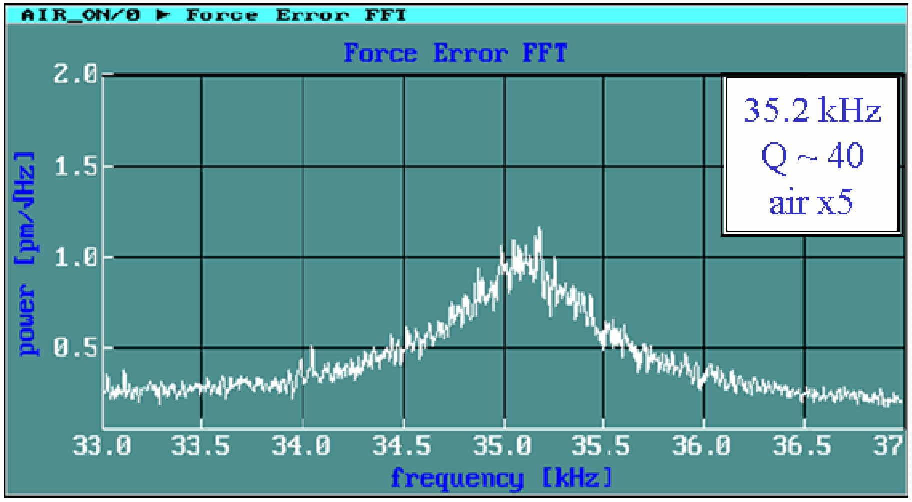
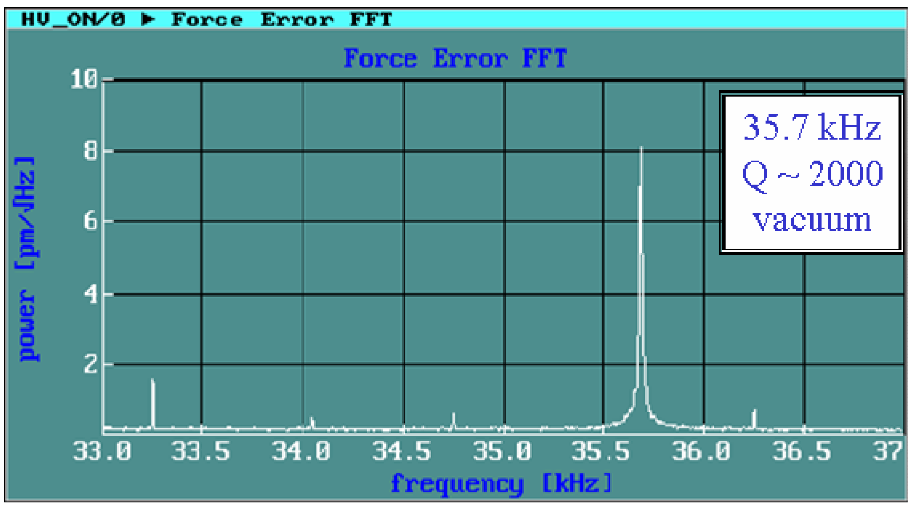
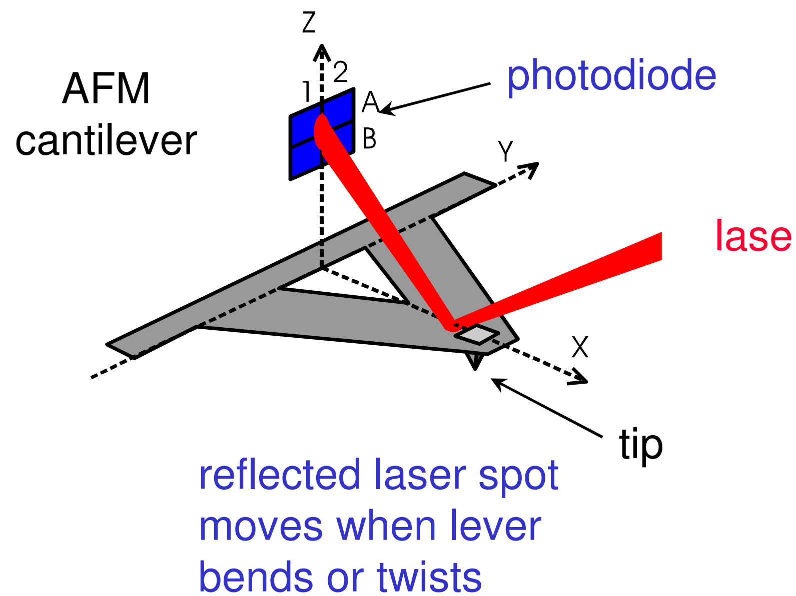
# Coupling to Environment



# Acknowledgements

Miquel Salmeron and many students, postdocs and visitors from his group

Joe Katz, Bill Kolbe, LBL Engineering Division
Mechanical shops in Bldg. 62, UCB Physics and Chemistry

Gabor Somorjai's group
Jun-Fei Zheng and Eicke Weber's group
Shimon Weiss and Daniel Chemla's group

Supported by the Office of Science
Office of Basic Energy Sciences
U.S. Department of Energy



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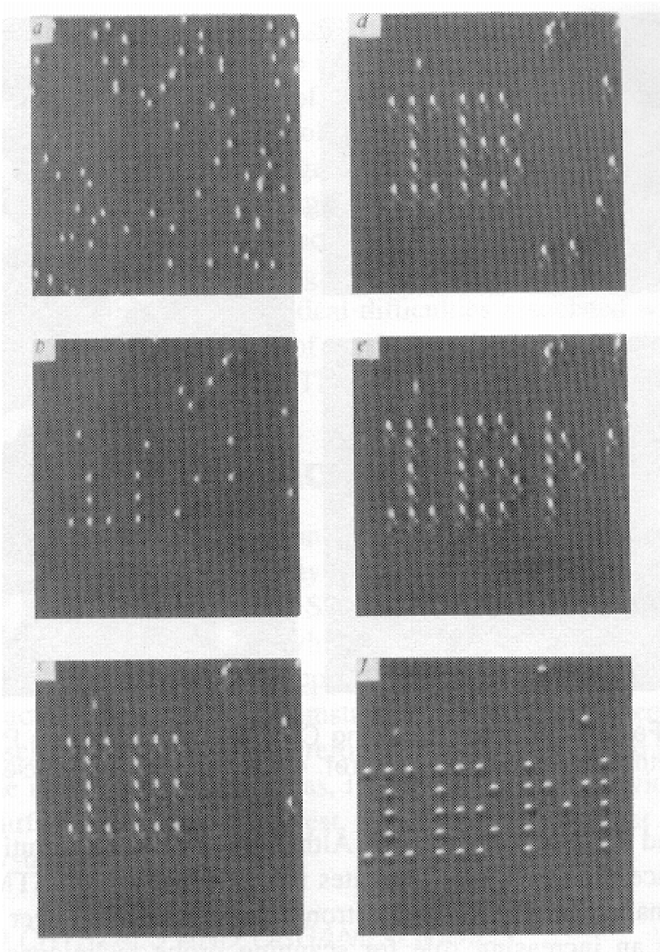
# Atom Manipulation - Don Eigler IBM



Xe atoms on Ni(100) at 8 K assembled by tip manipulation to spell “IBM”. 1989

Quantum mechanical electron “standing waves” change the STM Tunnel Current

Fe atoms arranged by STM manipulation

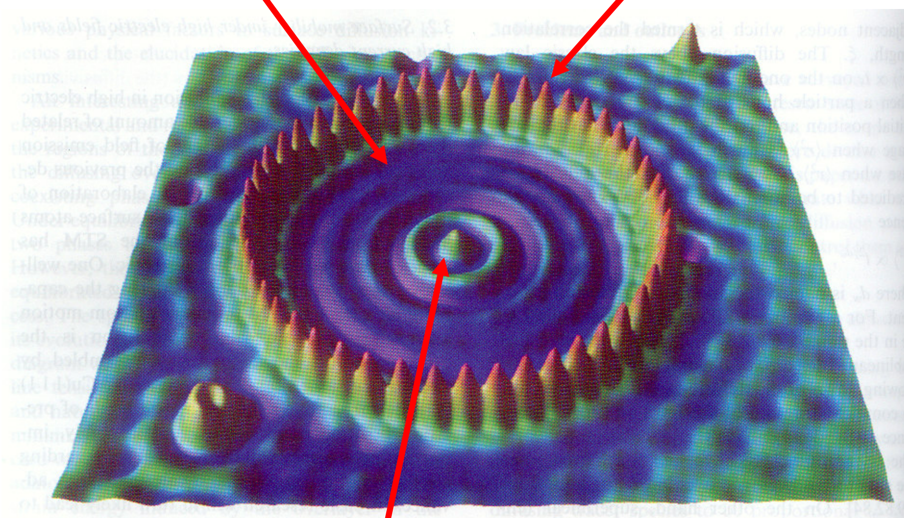
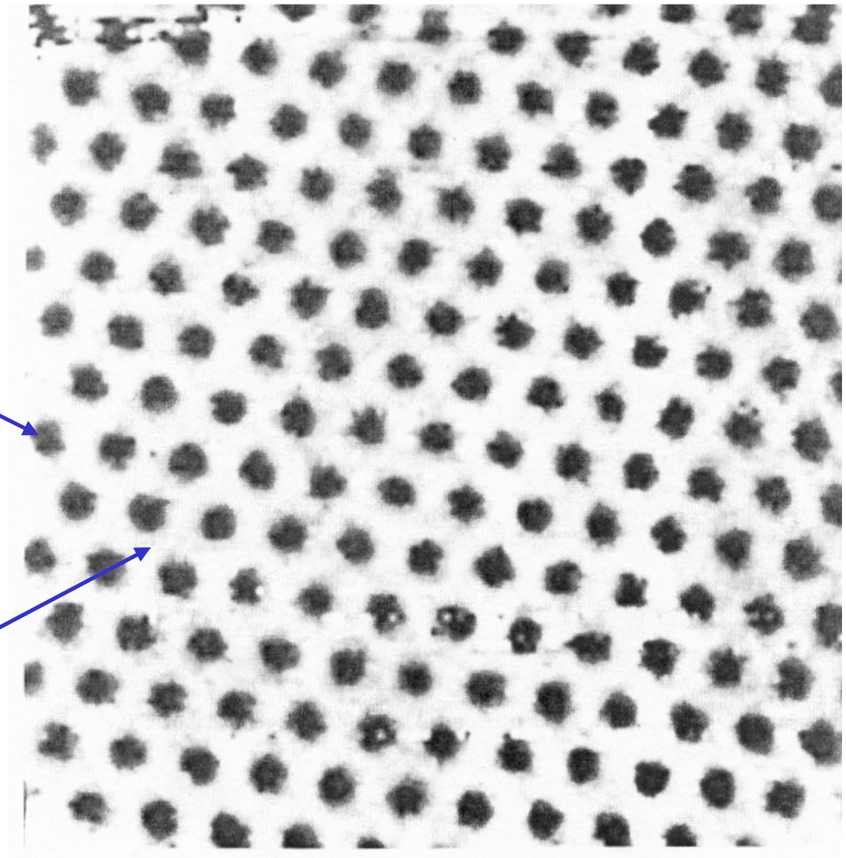


Fig. 9. An STM image of the quantum corral, consisting of 48 iron atoms on Cu(1 1 1). The image size is 200 × 200 nm² [89] (courtesy of IBM Almaden Research Center).

A node in the electron standing wave pattern (not an atom)

# Vortex Lattice in a Type-II Superconductor

The dark spots are the non-superconducting vortex cores



The light areas have a superconducting band-gap in the electronic density of states

600 nm

$NbSe_2$ at 1.8 K in a 1 T (10 kGauss) magnetic field

This image took many hours to record

Harald Hess, Bell Labs



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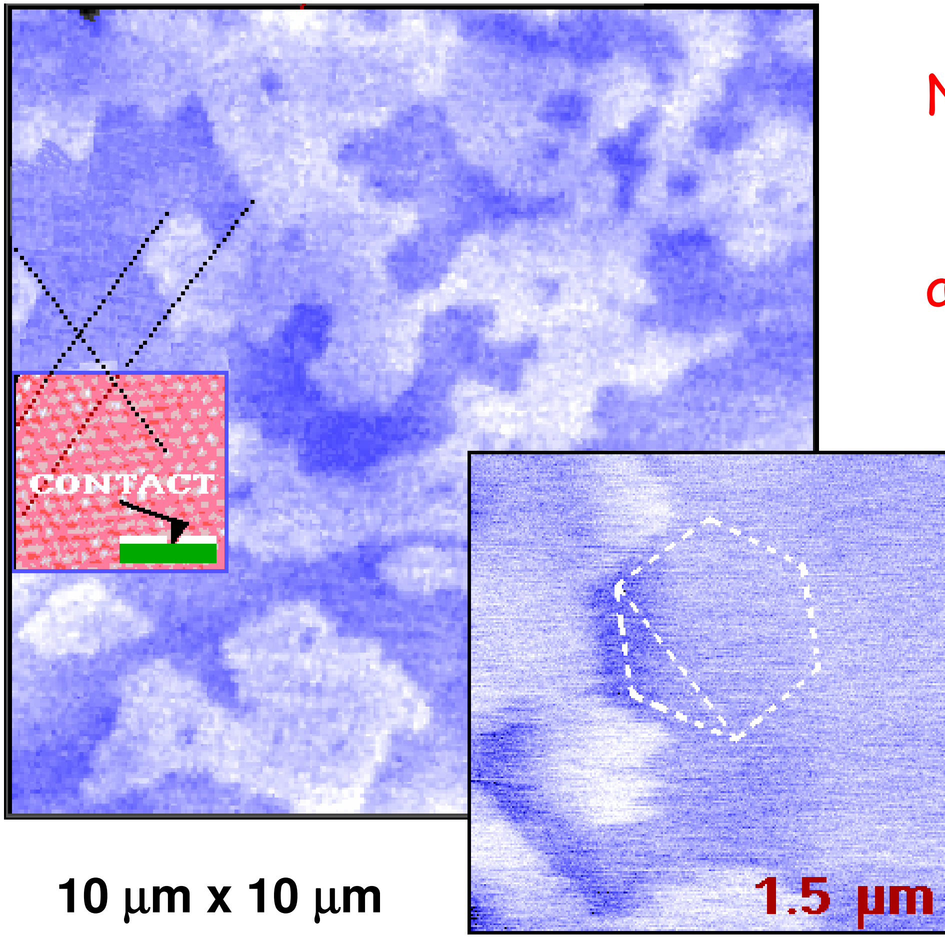
# Water on Mica




**10 µm x 10 µm**

Non-contact electrostatic images reveal humidity-dependent epitaxial water films on mica attractive DC electrostatic force

AFM tip in contact or tapping modes disrupts the water film

Apparatus for imaging liquid and dielectric materials with scanning polarization force microscopy, Jun Hu, D. Frank Ogletree, Miquel Salmeron and Xu-dong Xiao, *United States Patent 5,704,744* filed June 7, 1995, issued April 28, 1998.

Imaging the Condensation and Evaporation of Molecularly Thin Films of Water with Nanometer Resolution, Hu, Xiao, Ogletree, Salmeron, *Science* 1995.

The structure of molecularly thin films of water on mica in humid environments, Hu, Xiao, Ogletree, Salmeron, *Surface Science* 1995.

Wetting and capillary phenomena of water on mica, Xu, Lio, Hu, Ogletree, Salmeron, *Journal of Physical Chemistry* 1998.

# Technology Transfer

Commercial UHV STM Developed by McAllister Technical Services based on LBL UHV STM

(before starting his own company, Bob McAllister was an LBNL mechanical technician)

Commercial SPM Controller Developed by RHK Technology, Inc., based on LBL STM control system

Most of our LBL SPM systems now use RHK controllers, although we did develop a 3rd generation DSP system used for the variable temperature STM