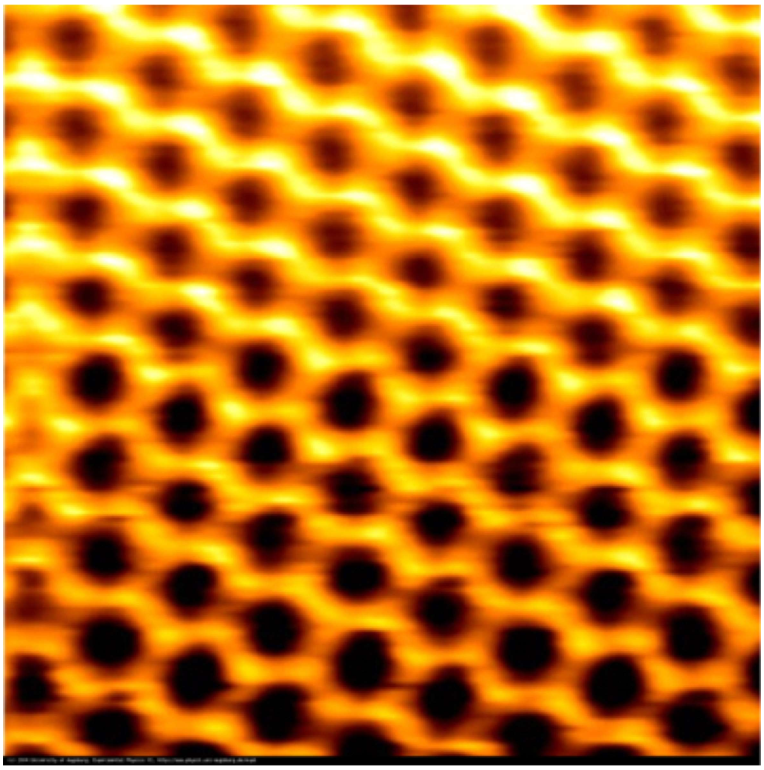
M5052-Characterization of Materials and Nanomaterials

Graduate Program in Nanotechnology

Scanning Probe Microscopy 2

Atomic Force Microscopy



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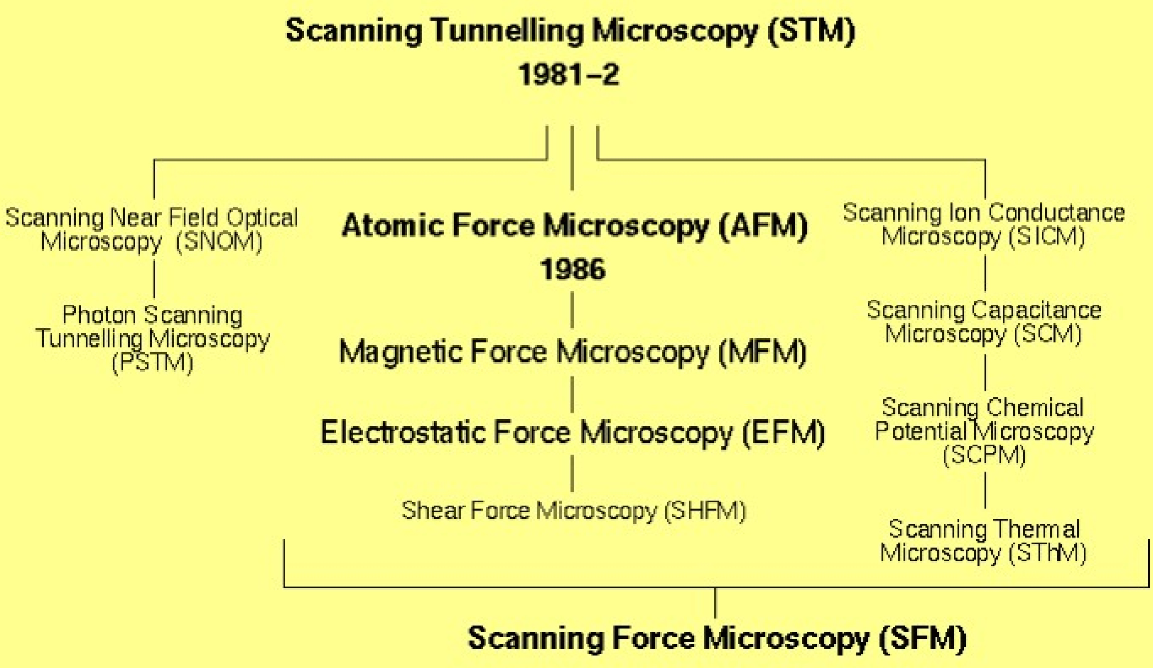
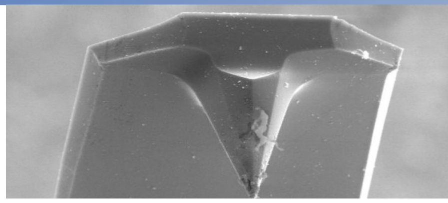
Scanning Probe Microscopy "Family Tree" (SPM)



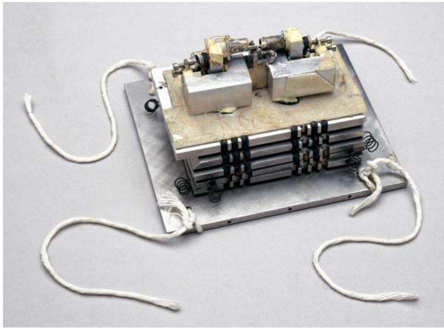
Atomic Force Microscopy

- Scanning Force Microscopy: measures superficial forces between a surface and a fine tip scanned over the surface
- Developed by Gerd Binnig, Christoph Gerber, and Calvin Quate
  - They used an STM to detect movement of a cantilever mounted tip
  - Kavli Prize in Nanoscience of 2016: "for the invention and realization of atomic force microscopy, a breakthrough in measurement technology and nanosculpting that continues to have a transformative impact on nanoscience and technology."
- Cantilever: Projecting beam structure, supported at one end
- Studies based on various attractive and repulsive surface forces:
  - van der Waals forces, ion-ion repulsion, electrostatic, magnetic forces, adhesion, friction



SEM image of an AFM probe

Binnig Gerber Quate

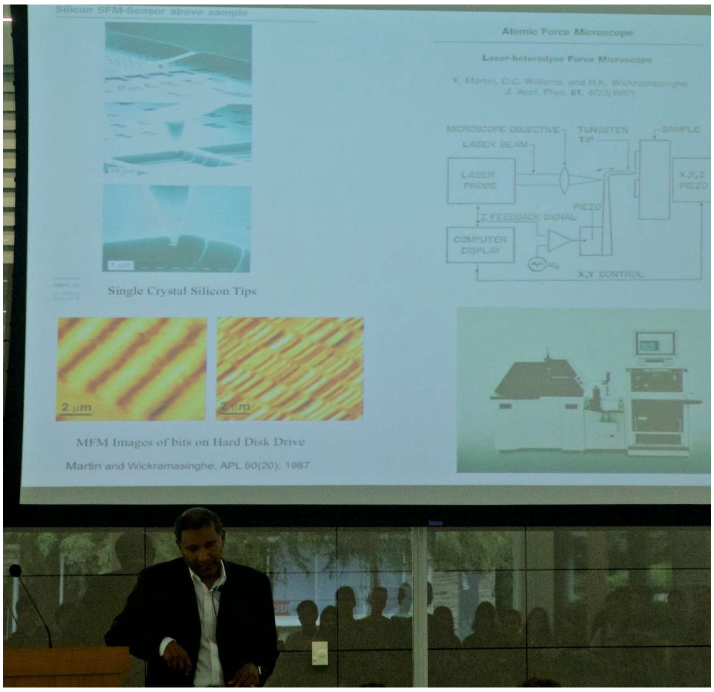


The first Atomic Force Microscope

Photos (slightly modified) taken from http://kavliprize.org/prizes-and-laureates/prizes/2016-kavli-prize-nanoscience

AFM: Vibrating Cantilever

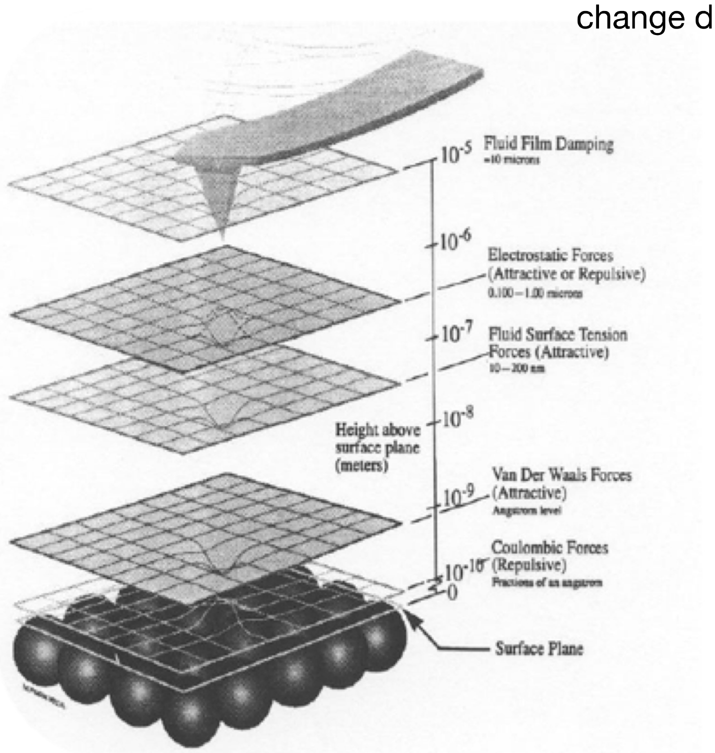
- Wickramasinghe et al. demonstrated the vibrating cantilever technique in 1987
  - Binnig, Quate and Gerber had suggested in 1986 that a vibrating cantilever could increase resolution
- Vibrating cantilever technique enabled several further developments
- "Tapping Mode" AFM allows imaging of soft materials and biological samples without damage
- Prof. Kumar Wickramasinghe is now a collaborator in Tecnologico de Monterrey
  - Federico Baur Endowed Research Chair in Nanotechnology

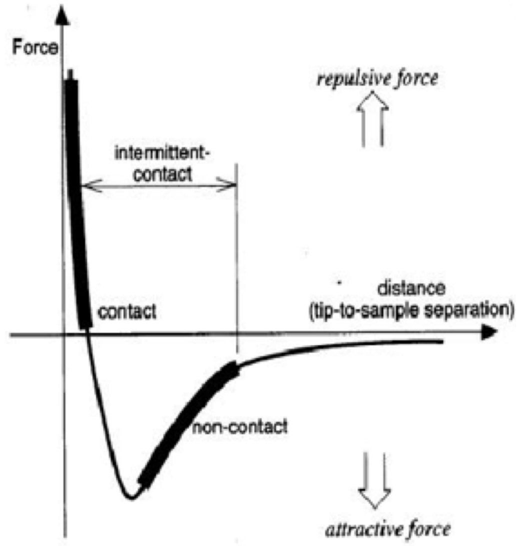


Prof. Kumar Wickramasinghe speaking at Tecnologico de Monterrey, Campus Monterrey, 11th of September, 2018

Forces Involved in AFM

The atomic level forces that make this microscopy possible change depending on the distance between tip and sample





AFM Equipment

- Basic instrumentation very similar to STM
  - Piezoelectric Positioners
  - Vibrational Isolation
  - Electronic Control Systems
  - Computer Control
- Types of tips and detection of their motion are different
  - Cantilever deflection is feedback signal for Z-control
  - The Cantilever is the critical component

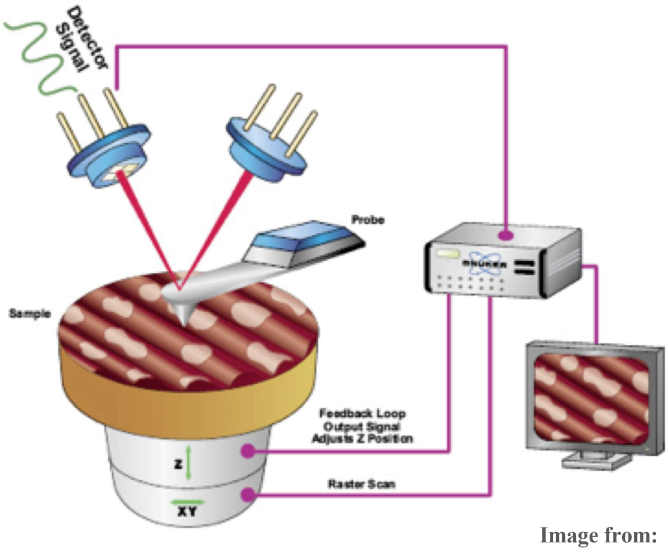
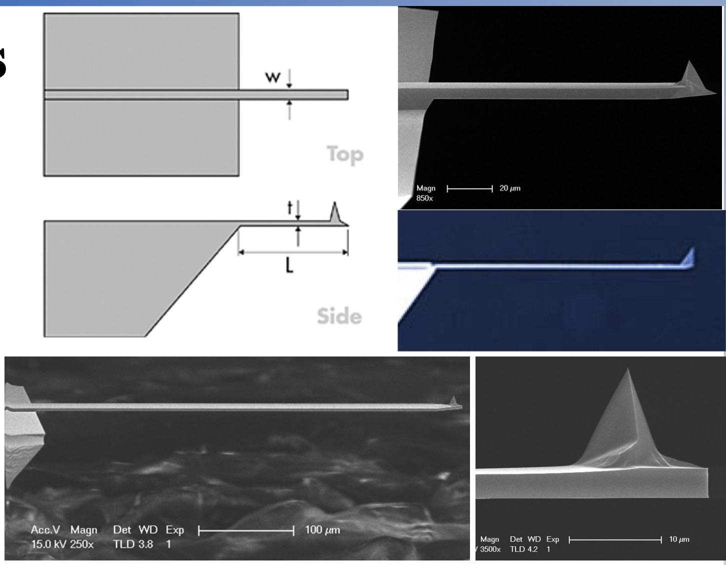


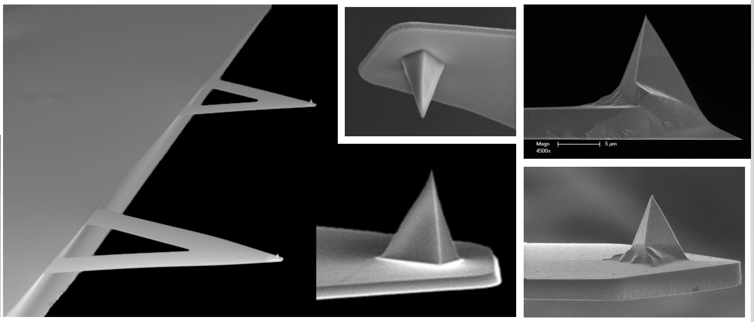
Image from:
http://blog.brukerafmprobes.com/2011/06/spm-operation-2/

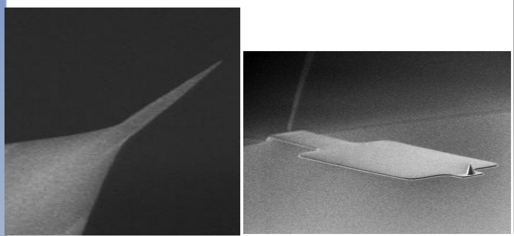
- For high sensitivity, small force must produced large deflection
  - Cantilever must be made with a soft material
- To reduce sensibility to vibrations a large resonant frequency (ω_0) is necessary
  - Resonant frequency of a spring is $\omega_0 = (c/m)^{1/2}$
    - c = spring constant (small for a soft material), m = effective mass of spring
- To maximize ω_0 mass must be minimized: cantilevers must be small

AFM Cantilevers

- Si_3N_4, SiO_2 or mono-crystalline Si formed with micro-fabrication techniques
  - Doped Si can be used
- Many variations possible
  - V shape: less sensitive to lateral forces
    - Typically single beam is used
  - Finer tips can increase resolution







Images ©2019 Bruker Nano Inc., taken from www.brukerafmprobes.com

Cantilever tips and resolution

- Resolution of AFM is determined by scanning probe
  - Sharp tip gives better resolution
  - Tips can be sharpened with a Focused Ion Beam
  - Attaching a carbon nanotube to the cantilever tip can provide a high aspect ratio tip

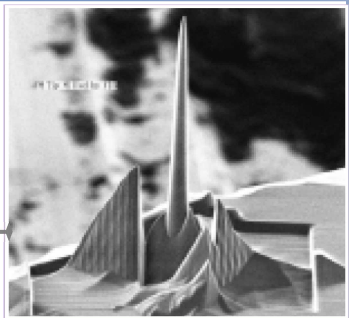
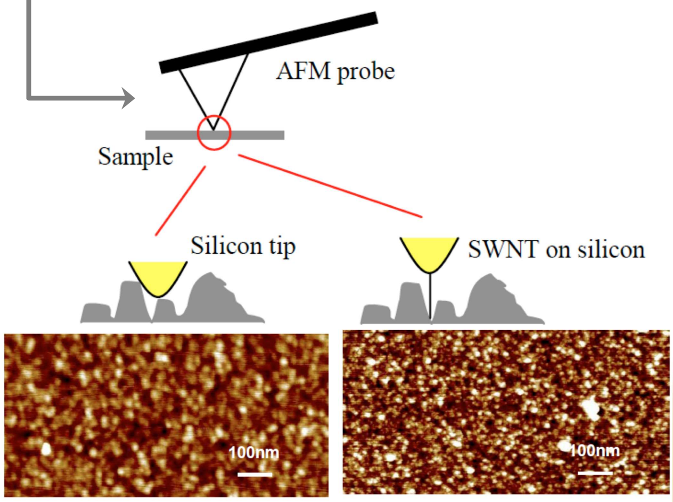


Figure 44: SE image made with FIB showing a silicon AFM tip machined to be a super-tip, with very small radius for high resolution AFM imaging.

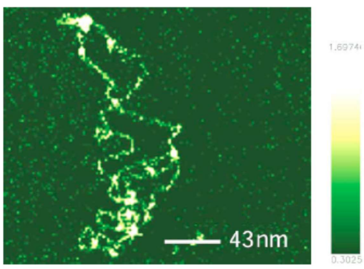


(a) Imaged with a silicon probe. *(b) Imaged with an SWNT probe.*

Poly-crystalline-silicon surface

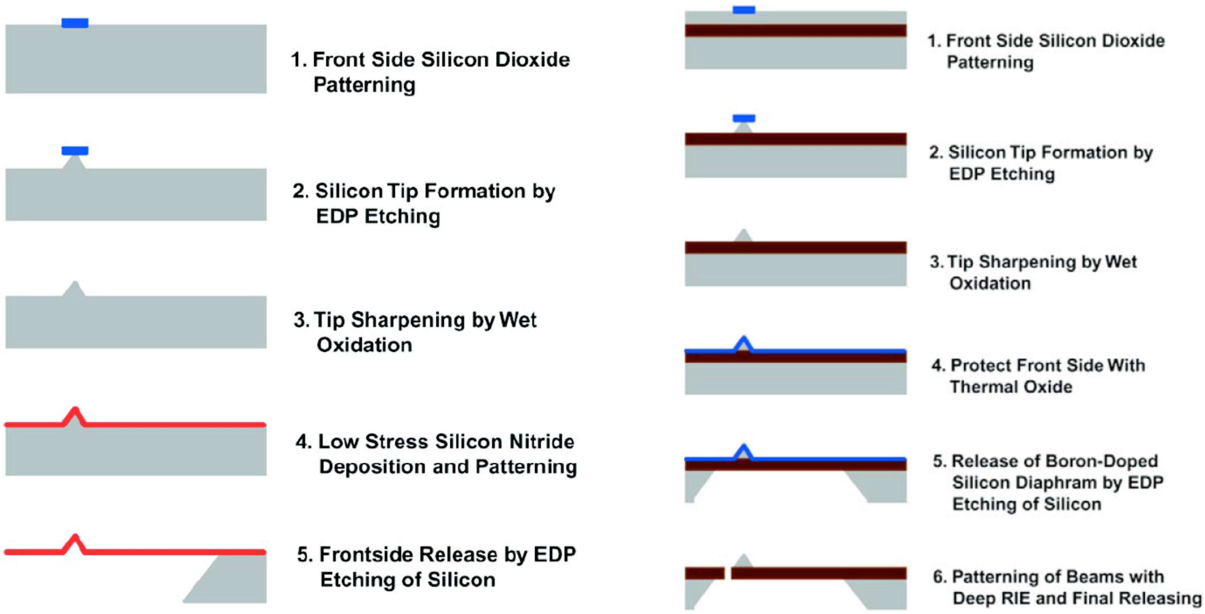
1 µ m scan length, 256 lines, 512 samples, 0.5 Hz scan rate

Single Strand DNA AFM imaging under liquid with SWNT providing lateral resolution < 2nm



Images from: L. Zhang, E. Ata, S.C. Minne, P. Hough "Single-Walled Carbon Nanotube Probes For AFM Imaging", < http://nanoscaleworld.bruker-axs.com/nanoscaleworld/media/p/1492.aspx > (accessed and downloaded march 2013). And from: "Focused ion beam technology, capabilities and applications" electronic brochure (PDF), © FEI Company 2005 (downloaded in march 2010)

Some Examples of Cantilever Fabrication Processes



- EDP: **E**thylene-**D**iamine **P**yrocatechol, a solution for anisotropic etching of silicon (also containing water and pyrazine)
- EDP etches Si(100) planes with a 35 times greater rate than etching of (111) plane
- RIE: Reactive Ion etching

Images from: M. Zhang, D. Bullen, S.-W. Chung, S. Hong, K.S. Ryu, Z. Fan, C.A. Mirkin, C. Liu *"A MEMS nanoplotter with high-density parallel dip-pen nanolithography probe arrays"* Nanotechnology 13 (2002) 212–217

Cantilever Deflection Detection

- "Light lever": laser reflected from the back of cantilever to a photodetector
  - Typically 670 nm laser with ~1 mW power
  - Position Sensitive Detector: photoactive sections (e.g. Si) with a few μm separation
  - The most common method
  - Method developed in the early 1990s
- Exit signal from photodiode is directly proportional to cantilever movement
  - Angular deviations of seconds correspond to sub-Angstrom deflections of the cantilever
    - Accurate detection
  - Aluminium or gold coating can be applied to back of cantilever to increase laser signal
    - Typically by a factor of 2-3

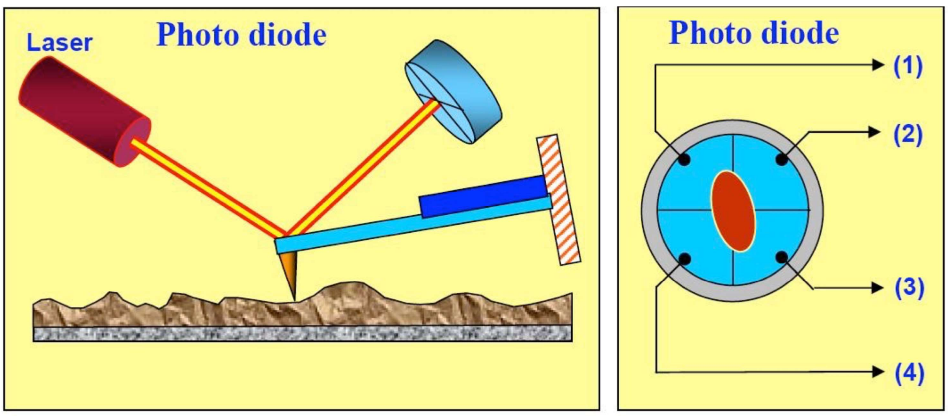


Fig. 62. Schematic description of the optical system to detect the cantilever bending

Figure from: V. L. Mironov, Fundamentals of Scanning Probe Microscopy, Institute of Physics of Microstructures of RAS, Nishny Novgorod, ©NT-MDT 2004 (downloaded from http://ipmras.ru/en/structure/people/mironov)

Cantilever Deflection and Motion Detection

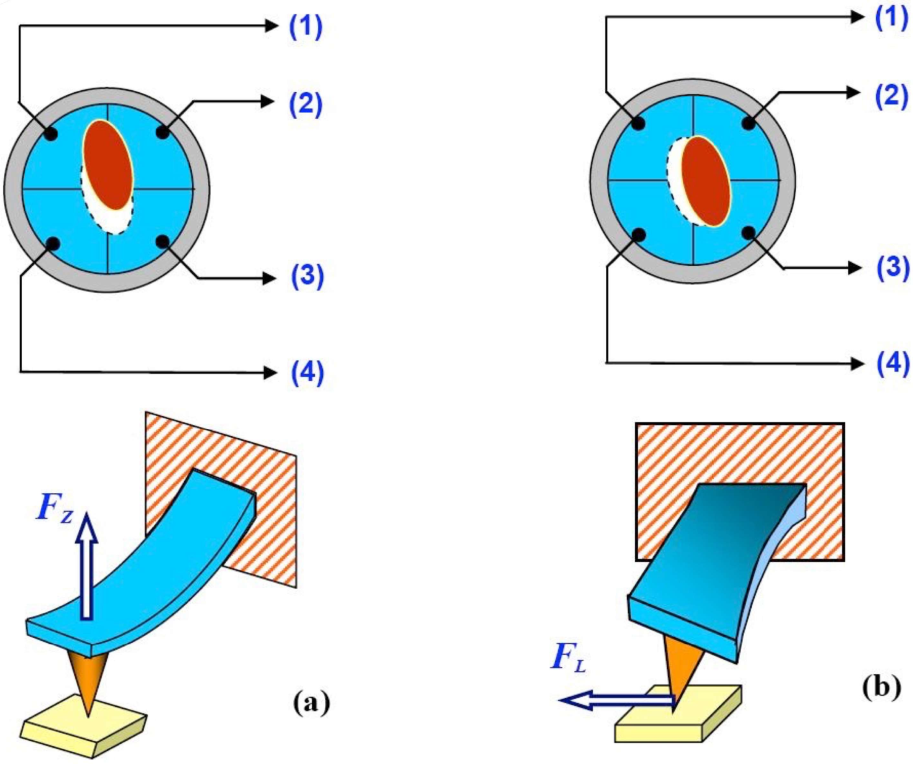
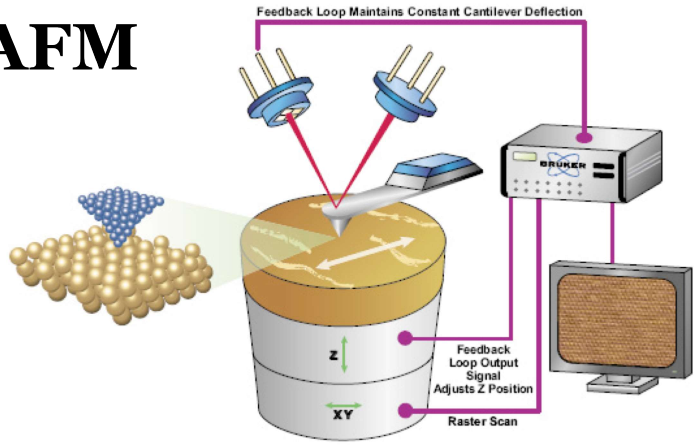


Fig. 63. Relation between the types of the cantilever bending deformations (bottom) and the change of the spot position on the split photodiode (top)

Figure from: V. L. Mironov, Fundamentals of Scanning Probe Microscopy, Institute of Physics of Microstructures of RAS, Nishny Novgorod, ©NT-MDT 2004 (downloaded from http://ipmras.ru/en/structure/people/mironov)

Contact Mode AFM

- Tip in contact with surface
- Scanned in the X-Y plane, parallel to surface
  - Used mostly for harder samples for which lateral forces are not expected to deform sample
- Constant Force Mode
  - Vertical deflection of cantilever measured
  - Feedback control used to keep constant deflection
  - 10^{-6}-10^{-10} N forces
  - Can achieve atomic resolution
- Limitations:
  - Damage to soft samples
    - Polymers, biomolecules, some semiconductors, etc.
  - Effects of fluid layer over surface



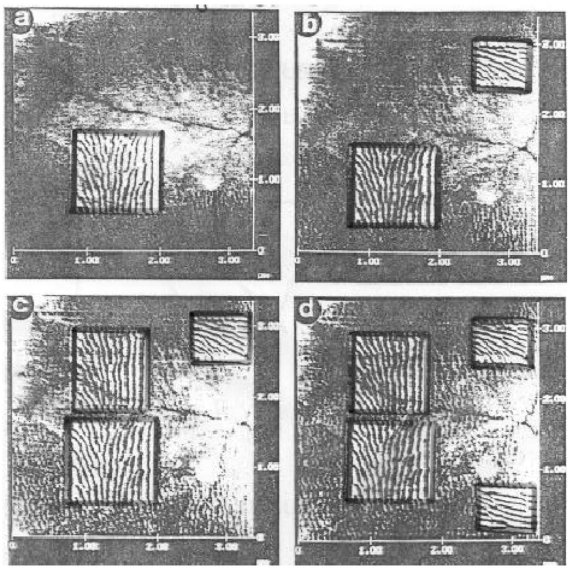
CdF_2 films grown on a CaF_2 (111) substrate. Scan in contact mode, (2 x 2 µm, height 2 nm)

Illustration of contact mode AFM from: http://blog.brukerafmprobes.com/2011/06/contact-mode-afm/
Image of film taken from: http://www.spmtips.com/how-to-choose-by-AFM-technique-contact-mode.html

Drawbacks of contact-mode AFM

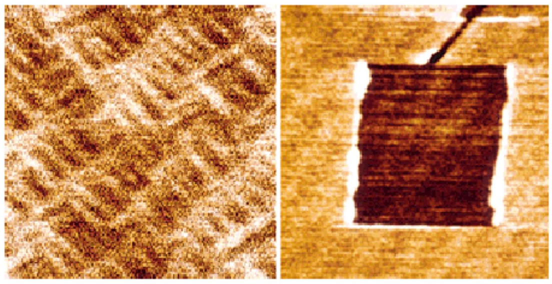
- Damage to soft samples: Elastomers, Biomolecules, Liquids, Biological samples, solid materials softer than the tip

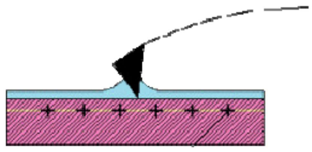
Polymer surface



Semiconductor surface

1 μm scan — 2μm scan





Fluid layer drags the tip down

Non-Contact Mode AFM

- Developed in 1987
- Advantages of Non-Contact Mode
  - More suitable to soft samples or elastic samples
  - Avoids contamination from tip contact
  - No damage to surface
- Cantilever vibrating with a small amplitude, near the surface
  - Separation in the order of 10-100 nm
  - Very low interaction forces (van der Waals forces, ~10^{-12} N)
    - More difficult to measure forces
  - Rigid cantilever used so that is not dragged down by attractive forces
  - Changes in resonant frequency of cantilever reflect topography
    - Resonant frequency depends on spring constant
    - Spring constant changes depending on forces experienced by cantilever
    - Force gradient changes due to sample-tip separation
  - Detected signal is small and hard to measure
- Non contact mode is more useful when there are additional forces
  - Stronger interaction with those forces can be measured more easily
  - ❋ Electrical Force: EFM
  - ❋ Magnetic Force: MFM

Magnetic Force Microscopy

- Images of the spatial variation of magnetic forces in the sample surface
- Tip coated by a thin layer of ferromagnetic material
- Image combines magnetic and topographic information
  - On short distances image is mostly topography
  - At larger distances (~100 nm) magnetic forces dominate
  - With an oscillating cantilever phase image depends on magnetic domains
- Resolution of 10-100 nm with commercial instruments
- Limitations related to the probe (magnetized tip) size
  - The smaller the magnetic area on the tip the higher the resolution
    - Less interaction with adjacent areas
  - The smaller the volume of the magnetic probe the less the magnetic moment
    - Less interaction with the sample

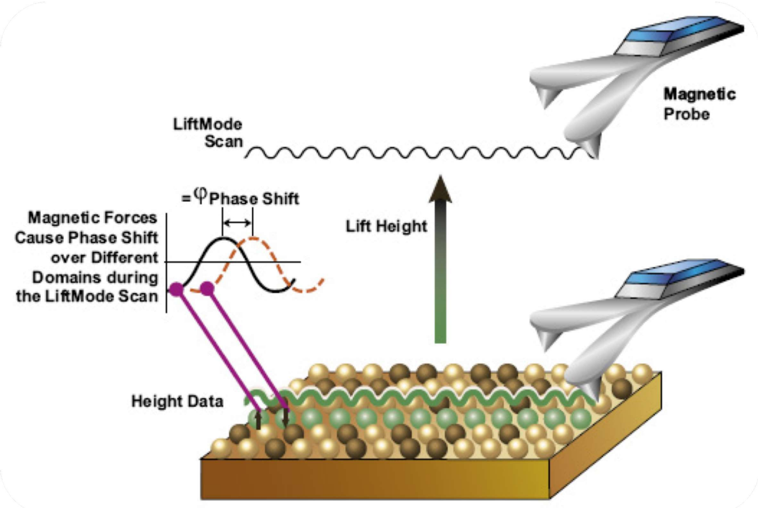
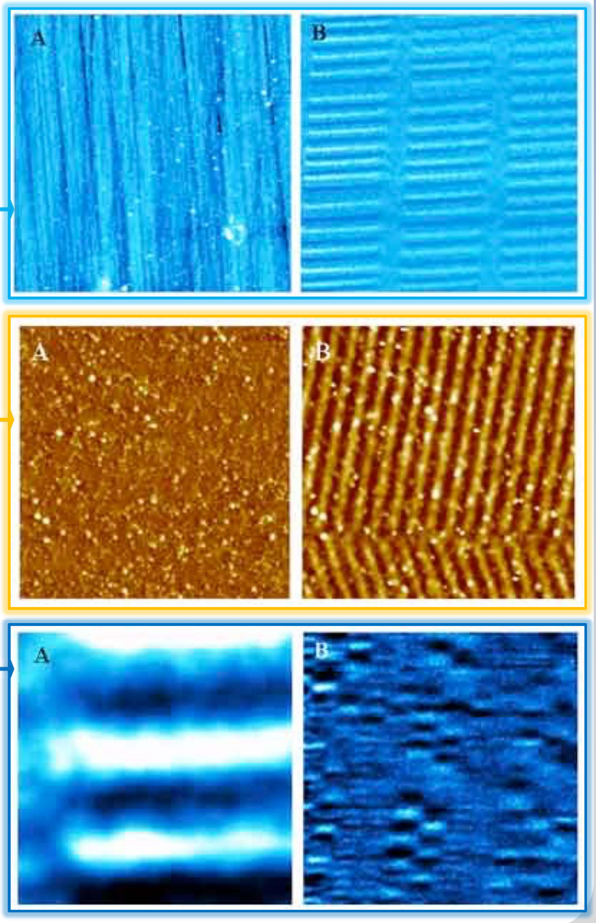


Image from: http://blog.brukerafmprobes.com/wp-content/uploads/2011/06p29-Magnetic-Force-Microscopy-MFM-main.jpg (downloaded march 2013)

Magnetic Force Microscopy

- Example: 5 GB Hard Drive
  - 40x40 μm images
    A. Topography Image
    B. Phase Image (magnetic signal)
- Example: Magnetic Tape
  - 10x10 μm Images
    A. Topography Image
    B. Phase Image: domains ~650 nm wide
- Example: Hard Drives
  - 5x5 μm images
    A. 5 GB Hard Drive, magnetic domains ~12 μm
    B. 70 GB Hard Drive, magnetic domains ~250 nm



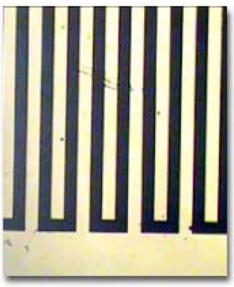
▪ Prof. Fernando J. Rodríguez Macías ▪ ▪ Tecnologico de Monterrey ▪ ▪ © 2019

Electrostatic Force Microscopy

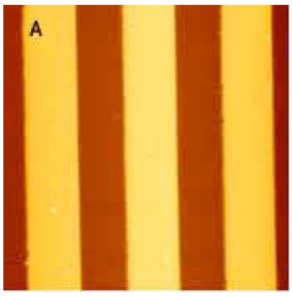
- Allows to distinguish between conducting and non-conducting regions
- Cantilever connected to power source providing a controllable difference in electric potential
- Images of Electric Field gradients
  - Tip kept at constant voltage and scanned at a certain height from surface
  - Deflections measure changes in the internal electric field of the sample
    - Tip over an attractive electric field gradient is pulled towards surface
    - Tip over a repulsive field gradient is pushed away from a surface
- Images of Surface Potential
  - Measures voltage at the surface
  - Voltage at the tip adjusted to keep a constant distance (or constant amplitude)
- As with MFM, topography image acquired with tip at a short distance from sample, tip raised (to ~800 nm) to remove the topographic component of the signal
  - Forces detected are usually larger, and can be modulated by varying the voltage

Electrostatic Force Microscopy

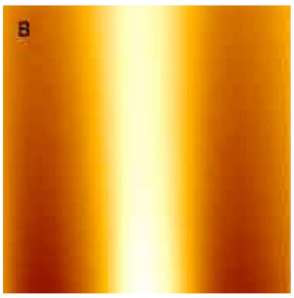
- Example: gold lines over glass



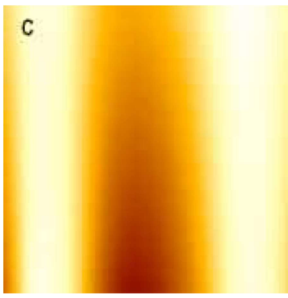
➢ Optical Image



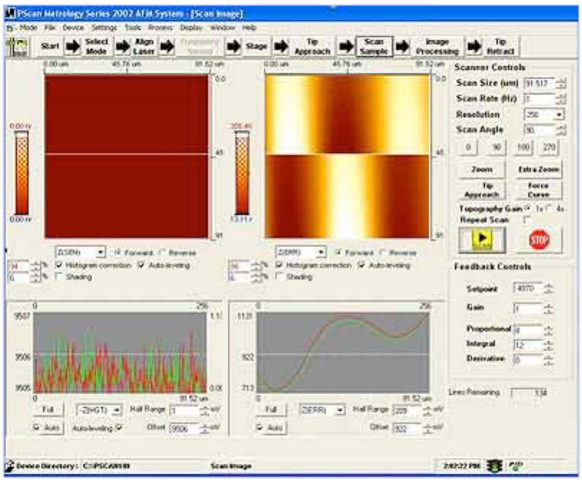
A. Topography



B. Tip at +17 V



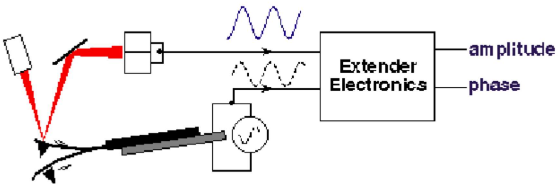
C. Tip at -17 V

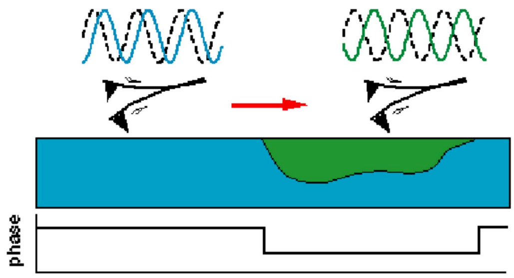


- Changing sign of voltage during the scan inverts image contrast

AFM: Intermittent Contact Mode

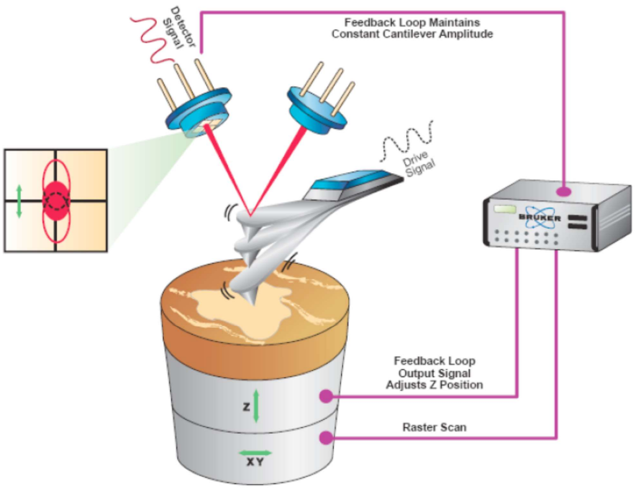
- Developed in 1993
- Intermittent contact mode is very useful for characterization of nanostructures
  - "Tapping Mode"™, Intermittent Contact, Semicontact, Dynamic Force Mode
- Oscillating cantilever tip makes short and frequent contact with sample
  - Effect of fluid layer is decreased
- An oscillation amplitude is selected (setpoint A_{set}) and kept constant by a feedback circuit
  - A_0: free oscillation amplitude
  - Soft tapping: $A_{set} / A_0 \sim 1$
  - Hard tapping: $A_{set} / A_0 << 1$
- Detection of the phase of the oscillation allows visualizing *phase contrast*
  - Measure shift of actual phase of cantilever oscillation with respect to phase of driving signal
  - Related to energy dissipation phenomena (viscoelasticity, friction, adhesion) which vary with composition

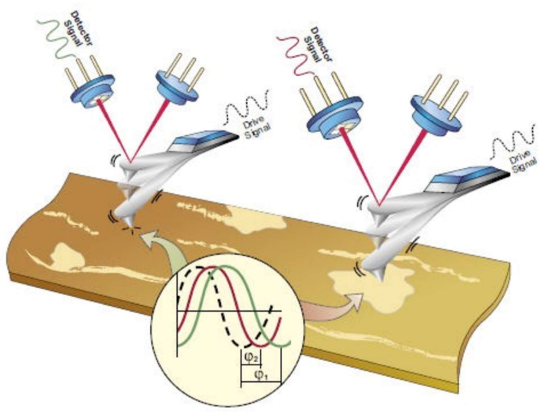




Phase Imaging in "Tapping Mode" AFM

- Phase delay depends on several factors
  - Frequency and amplitude of driving signal
  - Contact area between sample and tip
  - Ratio A_{set} / A_0
  - Surface topography
  - Material properties
- There is no direct, general and simple correlation between phase in TM-AFM and material properties
  - But relative differences between different materials within a sample provide a way to distinguish between two materials

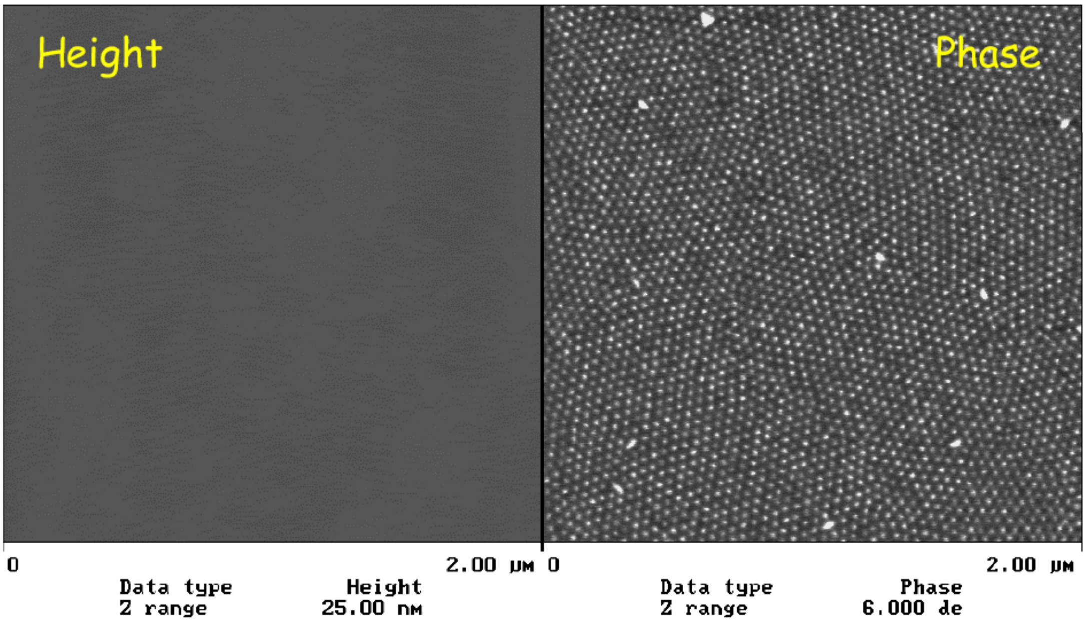




Images from:
http://blog.brukerafmprobes.com/2011/06/tappingmode-phaseimaging/
http://blog.brukerafmprobes.com/2011/06/tapping-mode-afm/

Tapping Mode AFM of Triblock Co-Polymer

Poly(cyclohexylmethacrylate-co-methylmethacrylate-b-isooctylacrylate-b-cyclohexylmethacrylate-co-methylmethacrylate)



10-170-10 kDa
(10.5% CM)

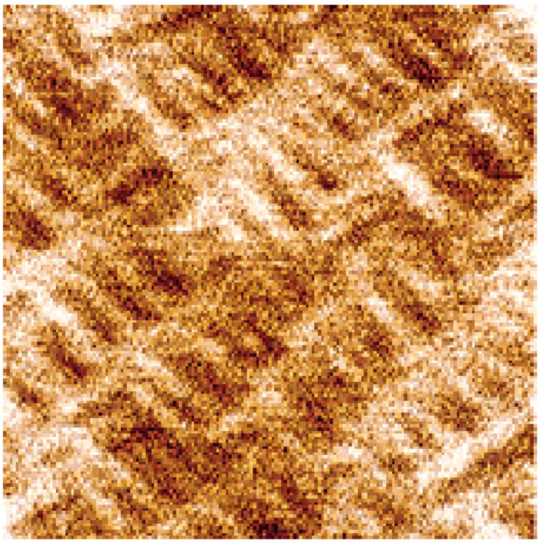
Spheres in a matrix (ϕ = 17±2nm, d = 38±2nm)

- Blocks on ends of polymer chains are not miscible with block on the center, phase separation occurs
- Due to regular size of polymer chains, domains of different compositions have well defined volumes
- Blocks forms monodisperse spheres with a regular separation between them

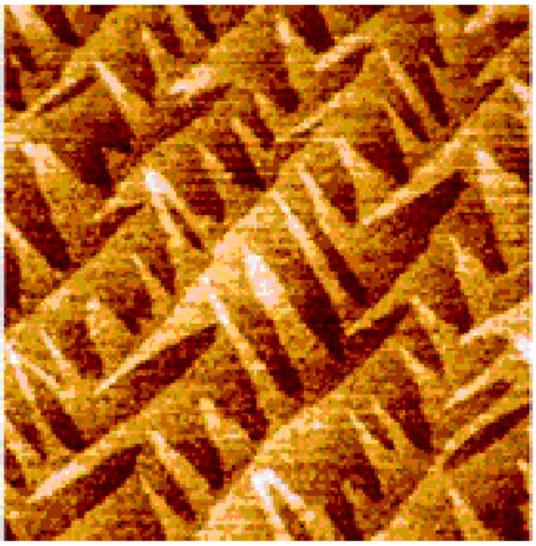
Resolution of TM-AFM can be better than with other modes

(though this may depend on the tip, and on the operating conditions)

Contact-mode

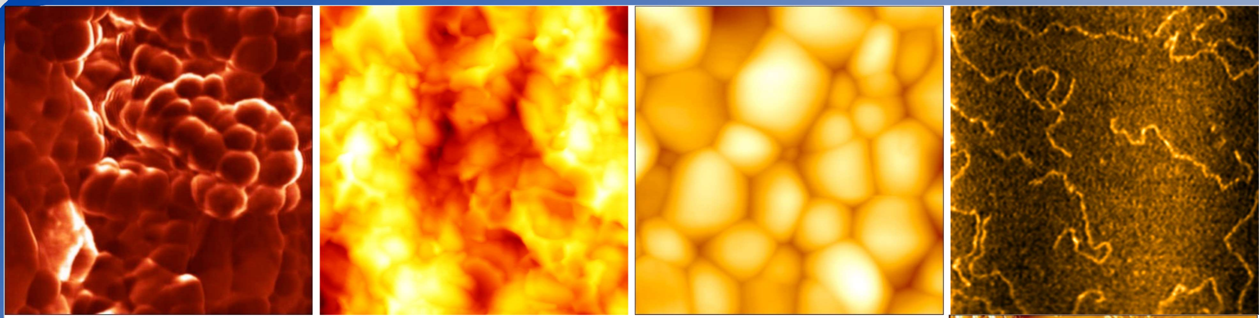


Tapping-mode



1 µm scans

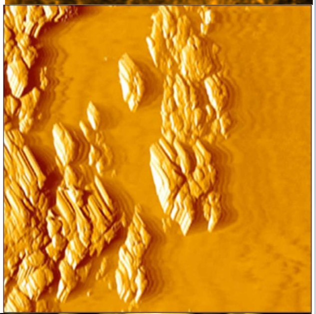
Epitaxial Si film

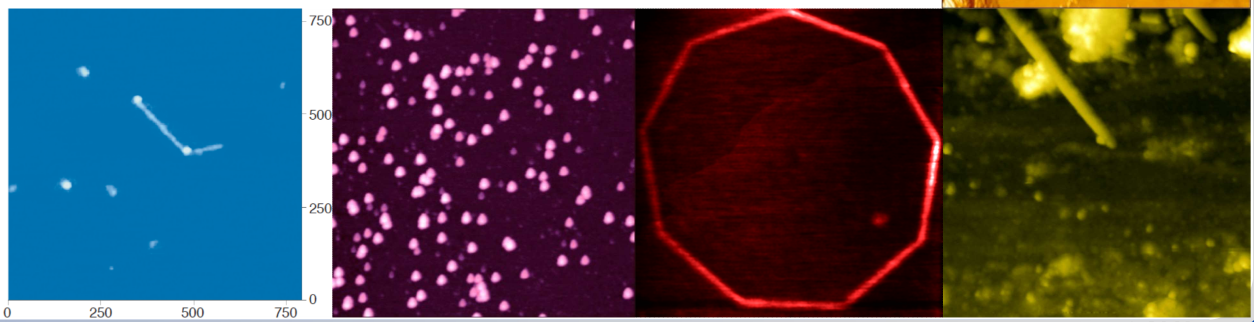


Examples of AFM applications

Image on lower left corner taken from: Science, (1998) v. 280, p. 1253

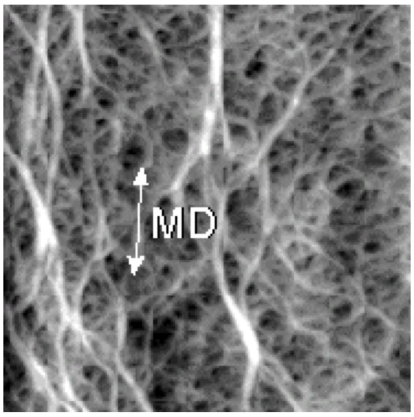
Other images: downloaded from www.veeco.com (2007) [no longer available online]





Example: PP treated with O_3 and UV

- Polypropylene surface presents low adherence for inks
- Oxidation treatments used to make surface (e.g. of bags) printable
- Ultraviolet radiation can make ozone oxidation more effective
- Isotactic polypropylene film, with biaxial orientation through thermal extrusion
  - Tapping mode AFM image, 2.5 μm wide. Grayscale (Z axis) 33 nm
  - MD - machine drawing direction
  - Biaxial orientation with transverse drawing perpendicular to MD. Fibrilar structure is due to drawing



- H.-Y. Nie, M.J. Walzak, N.S. McIntyre, *Atomic Force Microscopy Study of Biaxially-Oriented Polypropylene Films*, Proceedings of the 22nd Heat Treating Society Conference and the 2nd International Surface Engineering Congress, 15-17 September 2003, Indianapolis, Indiana, USA
- H-Y. Nie, M.J. Walzak, B. Berno, N.S. McIntyre, *Applied Surface Science*, 144-145, (1999), :627-632

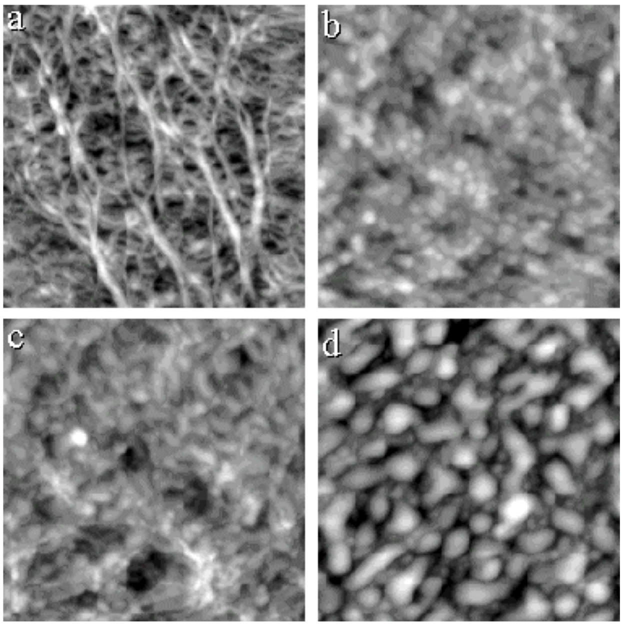
Example: PP treated with O_3 and UV

- Oxidative treatment to improve adhesion: Ozone under UV irradiation

  a) 1 min; b) 3 min, c) 5 min, d) 15 min

  - 2.5x2.5 μm areas, grayscale: 24 nm
  - Nodules formed on fibers may be due to low molecular weight oligomers
    - Oxidative treatment is aggressive enough to break polymer chains
    - Other studies have shown oligomers

1 min O_3+UV 3 min O_3+UV



5 min O_3+UV 15 min O_3+UV

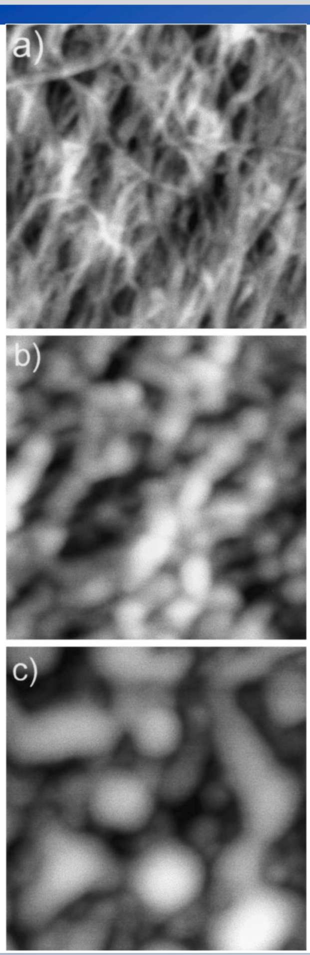
- H.-Y. Nie, et al., *Atomic Force Microscopy Study of Biaxially-Oriented Polypropylene Films*, Proceedings of the 22nd Heat Treating Society Conference and the 2nd International Surface Engineering Congress, 15-17 September 2003, Indianapolis, Indiana, USA
- H-Y. Nie, et al., *Applied Surface Science*, 144-145, (1999), :627-632

Example: PP treated with O_3 and UV

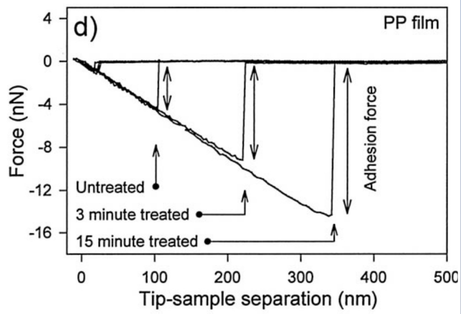
untreated

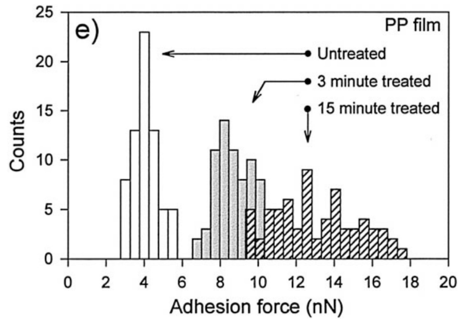
3 min O_3+UV

15 min O_3+UV



- Non-contact AFM topographic images for UV-ozone treated PP films in a 1000 nm sq. area.
  - a) untreated,
  - b) 3 min treatment
  - c) 15 min treatment
  - Gray-scale ranges for the three images are 21, 16, and 26 nm, respectively
- Oxidative treatment does increase adhesion forces on PP surface
  - Longer treatment increases adhesion further



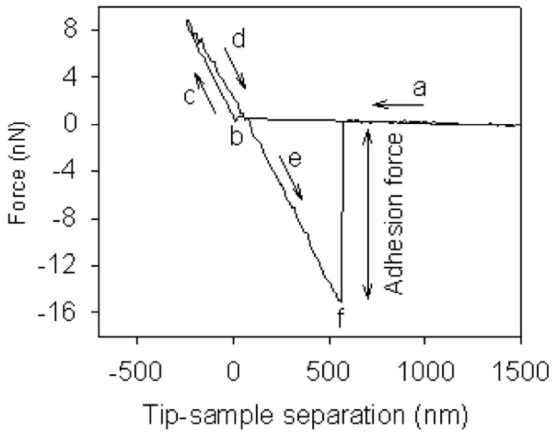


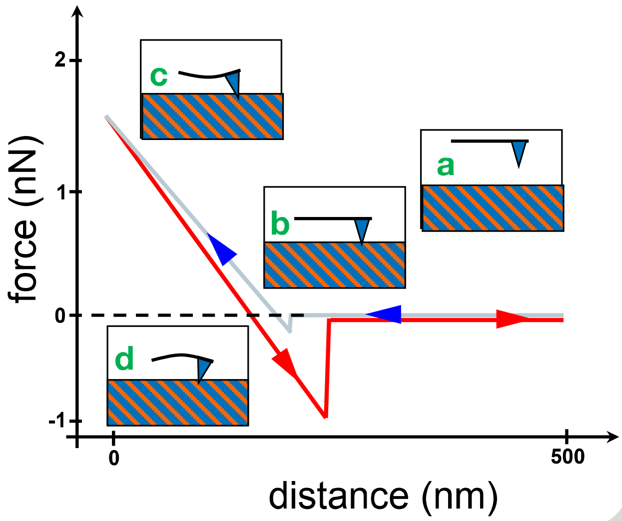
- H.-Y. Nie, et al., *Atomic Force Microscopy Study of Biaxially-Oriented Polypropylene Films*, Proceedings of the 22nd Heat Treating Society Conference and the 2nd International Surface Engineering Congress, 15-17 September 2003, Indianapolis, Indiana, USA
- H-Y. Nie, et al., *Applied Surface Science*, 144-145, (1999), :627-632

Measuring Adhesion Forces in AFM

- Adhesion force measured from the force vs. distance plot in contact mode

a) Tip approaches surface
b) Tip is dragged down towards the surface
c) Tip bends and touches surface
d), e) Tip is pulled away
f) Tip detaches and moves away from surface





Example: AFM Characterization of Contact Lenses

- AFM used under liquid to observe surface of contact lenses in “natural” conditions (saline solution)
  - Images showed fabrication defects
  - Pit like defects on surface can trap contaminants and/or proteins

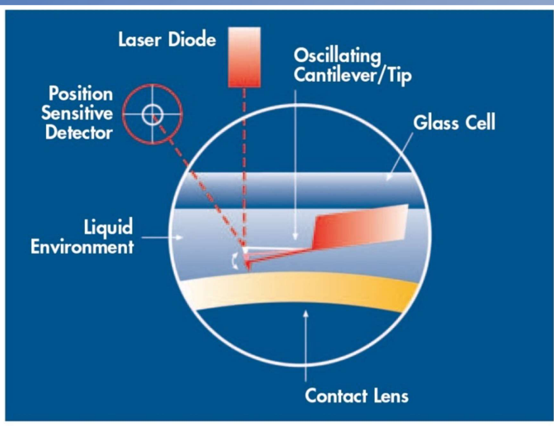
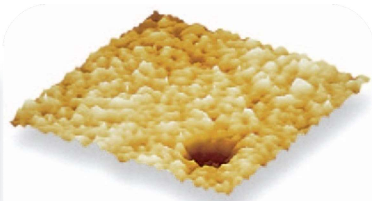


Figure 1. Schematic diagram of TappingMode AFM operation in liquid on a fully hydrated contact lens.



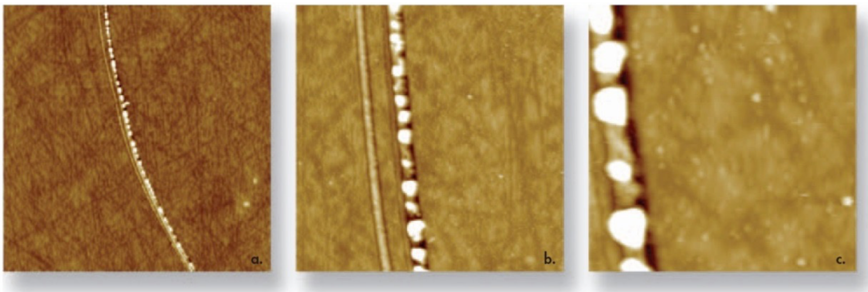
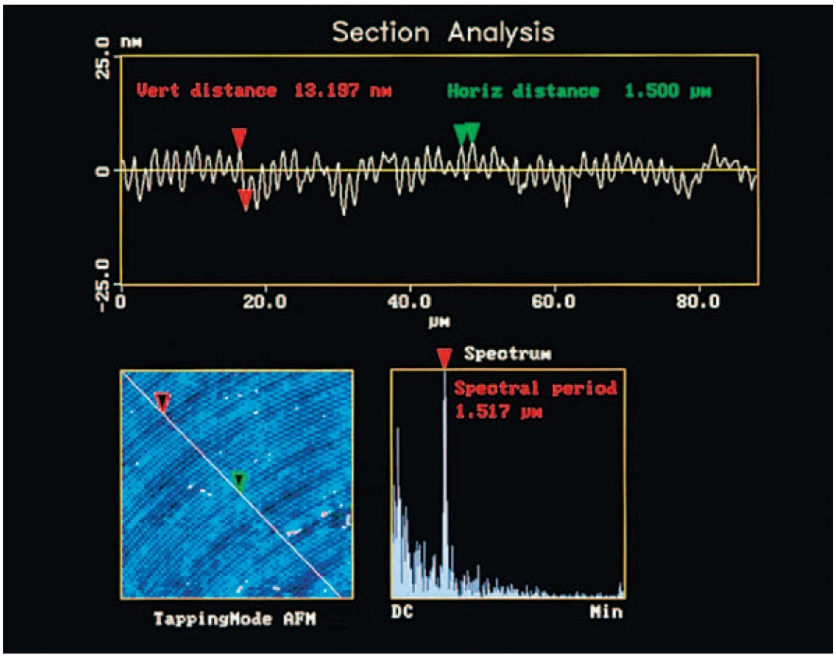


Figure 2. TappingMode in saline solution images of a fresh, out-of-the-box, commercially available contact lens. (a) 47μm, (b) 10μm, (c) 4μm scans.

Figure 3. TappingMode image of a 1μm x 1μm area of the same type of contact lens as in Figure 2, also immersed in saline. The RMS roughness is 3.5nm for the area shown. A surface defect or pit, clearly seen in the lower right of the image, measures 170nm in width and 150nm in depth and, therefore, is large enough to trap proteins or contaminants. However, it is too small to be resolved in liquid using conventional techniques.

Example taken from http://www.veeco.com/appnotes/AN22_ContactLens.pdf (accessed and downloaded 2007, no longer accesible online)

Example: AFM of Contact Lenses



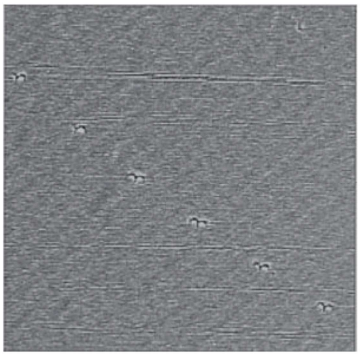


Figure 5. TappingMode AFM image of a hydrogel lens in saline. The grooves of the lens surface are faintly visible and run from lower left to upper right in the image. Periodic defects, running from top left to lower right in the image, are clearly detected. Such defects originate on the diamond-turned mold during the lathing process and are subsequently transferred to the lens surface. 20µm scan.

Figure 4. TappingMode AFM measurements on the grooves of a hydrogel lens in saline solution. The grooves originate from the diamond lathed mold. Section Analysis reveals a 1.5 µm periodicity (peak in spectrum) and nanometer-sized peak-to-valley heights of the grooves at various locations. The cross-section can be drawn and analyzed as often as desired, and in any direction, because the AFM image, unlike a SEM micrograph, is a digital object that includes 3-dimensional measurement information about the area scanned. 65µm scan.

AFM of Contact Lenses (3)

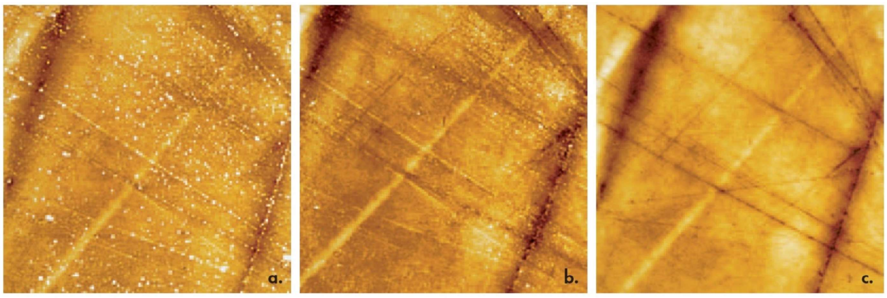
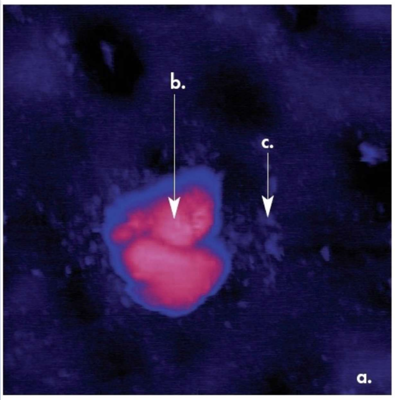


Figure 9. Series of AFM images of the same region on a used RGP lens in saline, (a) before cleaning, (b) after soaking in commercial cleanser, and (c) after soaking in cleanser and rubbing with latex glove. 30µm scans.



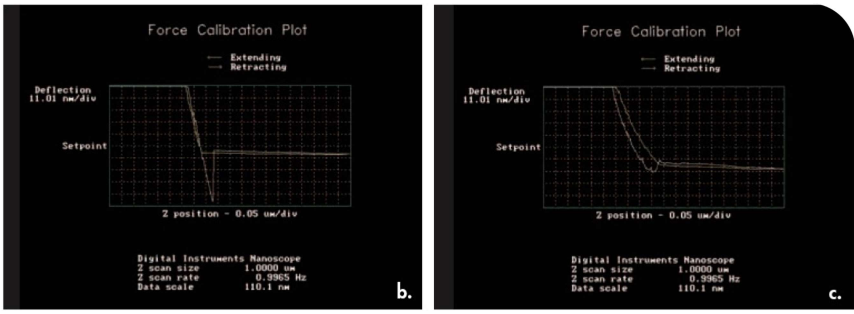


Figure 10. Force vs. distance curves allow characterization of stiffness and adhesion properties of lens surface. (a) TappingMode AFM image in saline of a surface feature (center of image) on a contact lens, 4µm scan. (b) Force vs. distance curve taken on the surface of the central feature. (c) Force vs. distance curve taken at a region adjacent to the central feature. The force vs. distance curves reveal that the central feature has a greater stiffness and is more adhesive to the AFM probe than the surrounding surface material. The surrounding region (c) compiles to the AFM probe as the probe pushes into the sample (yellow line), and very little adhesion is detected when pulling the probe away from the surface (white line).

- TM-AFM topography shows a defect
- Force measurement shows that impurity has different mechanical and adhesion properties

AFM of Contact Lenses (4)

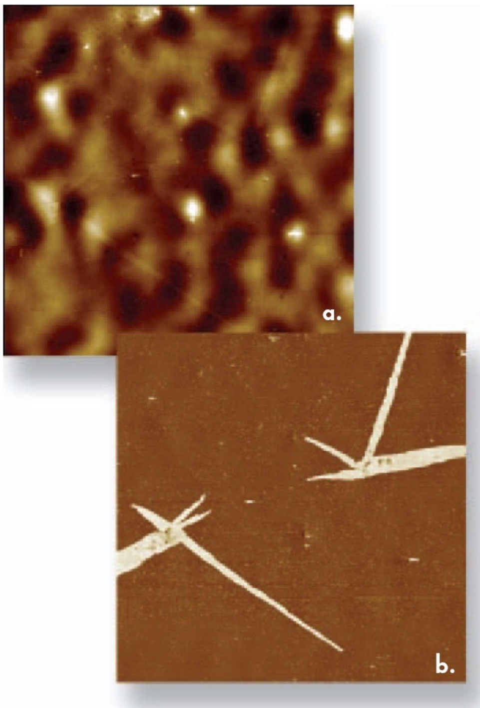


Figure 13. TappingMode topography (a) and phase images (b) of a contact lens in air. Crystalline-like structures in the phase image are possibly salt crystals left after water evaporated from the saline solution. 10μm scans.

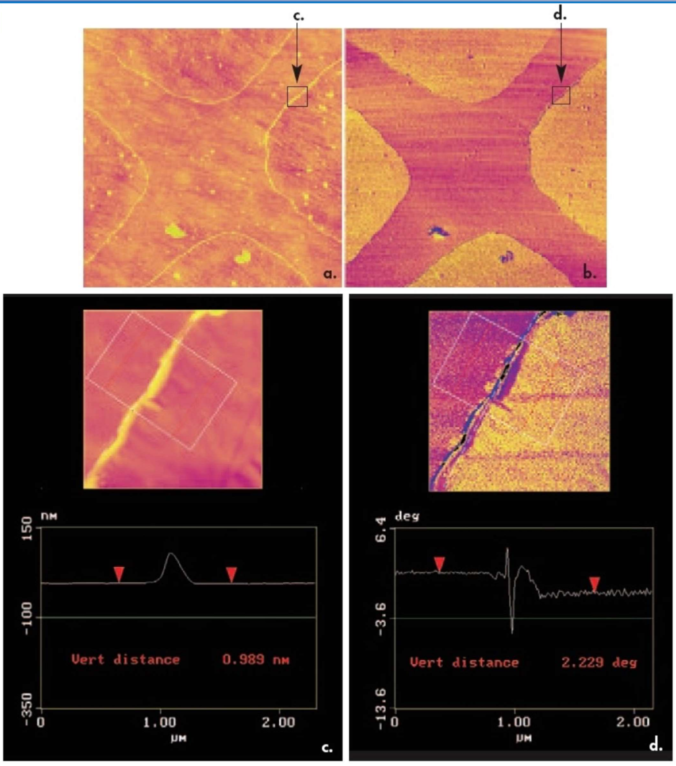
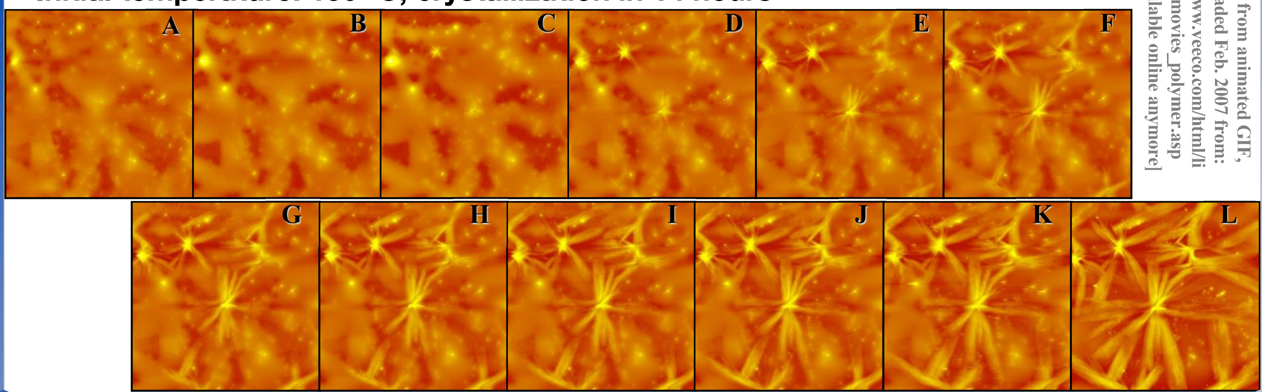


Figure 12. Simultaneously acquired (a) topography and (b) phase AFM images of silicone hydrogel in saline solution. The four outer areas were exposed to a sequence of chemical processing steps. The central cross-like region was masked and so protected from the processing steps and hence retained its hydrophobicity. The intention of the processing was to selectively alter the hydrophilicity of some parts, but not all of, the sample surface. In the phase images (b,d), a marked phase shift is clearly seen across the boundaries. However, the hydrophillic and hydrophobic region show no topographic contrast (a,c). The phase image is clearly providing material property contrast on this well-defined experimental hydrogel surface. 50μm scans.

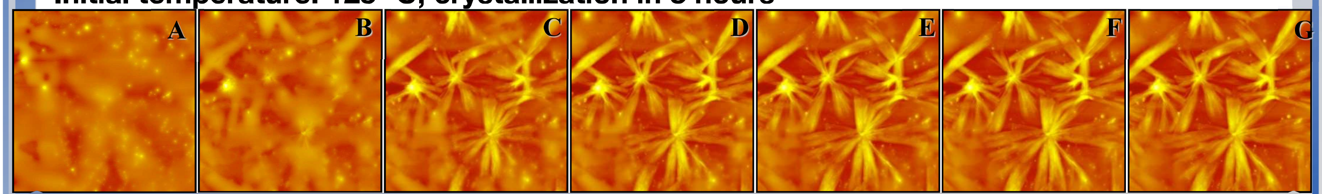
Observing Polymer Crystallization

Images from animated GIF, downloaded Feb. 2007 from: http://www.veeco.com/html/library_movies_polymer.asp [not available online anymore]

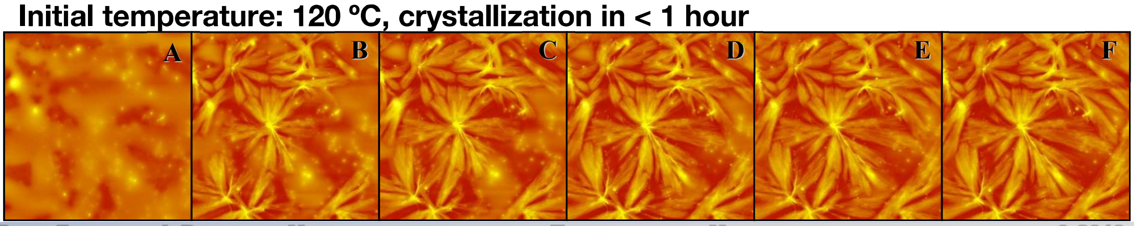
Initial temperature: 130 °C, crystallization in 14 hours



Initial temperature: 125 °C, crystallization in 3 hours

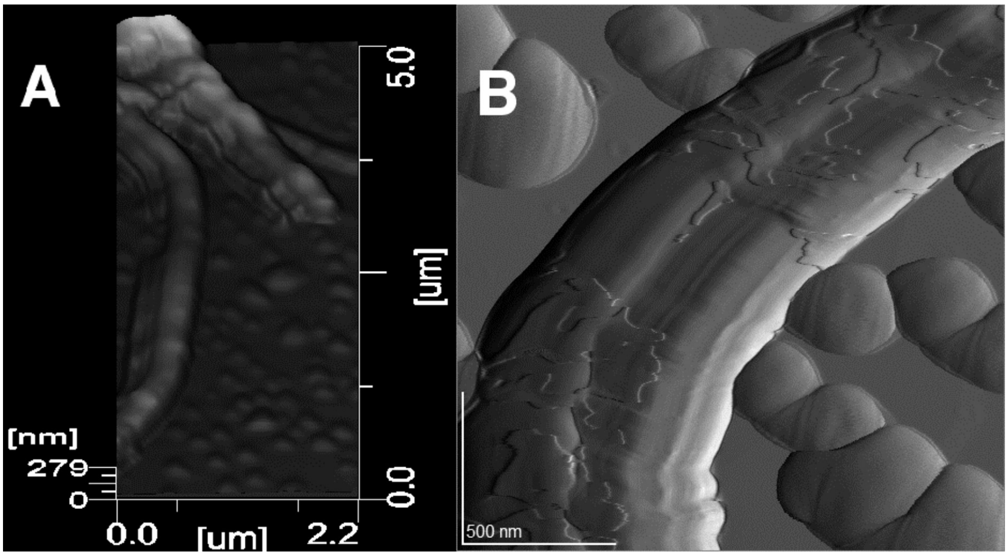


Initial temperature: 120 °C, crystallization in < 1 hour



AFM characterization of “Ex-MWNT” nanoribbons made from carbon nanotubes

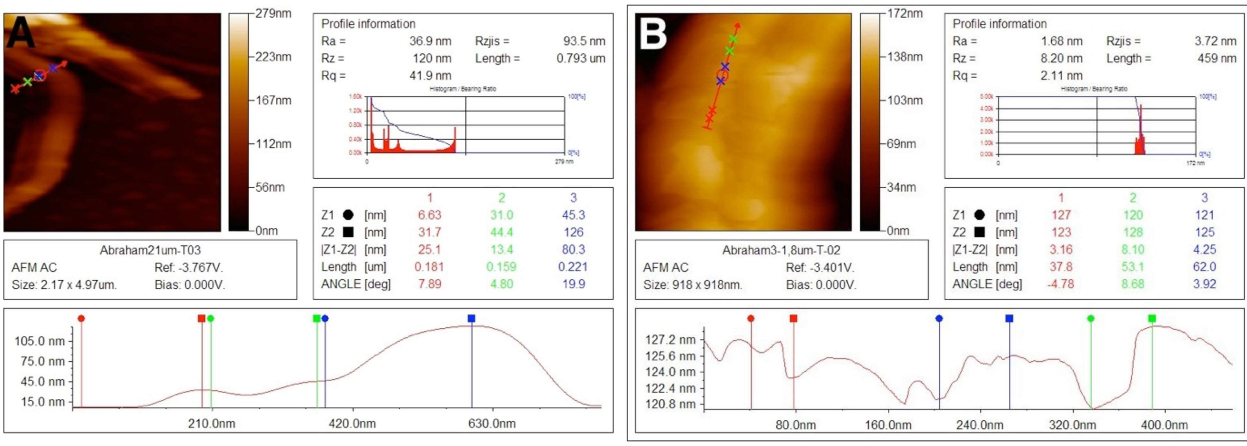
ACS Publications
High quality. High impact.



(A) AFM (topography image) showing steps due to the layered structure of ex-MWNTs. (B) Portions of graphene flakes are seen on the ex-MWNT surface (RMS image to show the features more clearly). In both images graphene pieces are seen coalesced as hemispheres over the HOPG substrate.

Published in: Abraham G. Cano-Márquez; Fernando J. Rodríguez-Macías; Jessica Campos-Delgado; Claudia G. Espinosa-González; Ferdinando Tristán-López; Daniel Ramírez-González; David A. Cullen; David J. Smith; Mauricio Terrones; Yadira I. Vega-Cantú; *“Ex-MWNTs: Graphene Sheets and Ribbons Produced by Lithium Intercalation and Exfoliation of Carbon Nanotubes“* ***Nano Letters****,* 2009 Vol. 9, No. 4 1527-1533
DOI: 10.1021/nl803585s

AFM in characterization of nanoribbons made from nanotubes (Ex-MWNT)



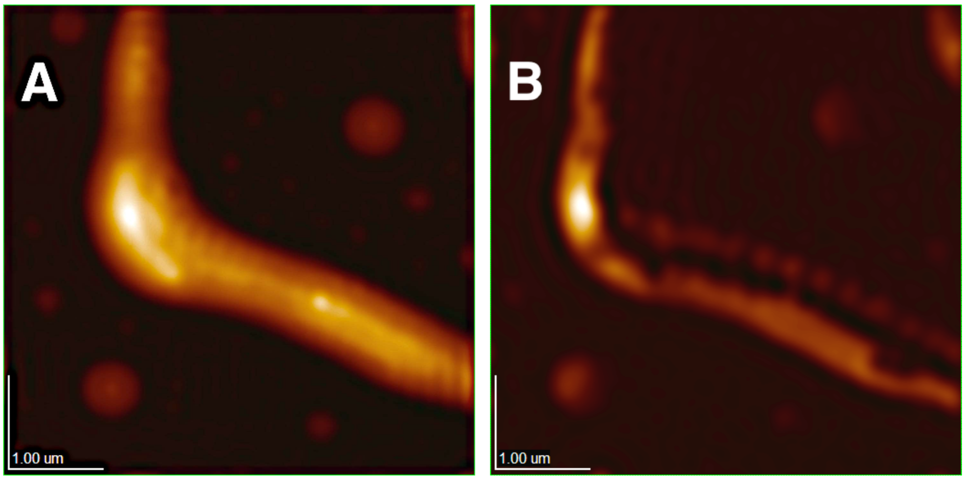
(A)		1	2	3
Z1 ●	[nm]	6.63	31.0	45.3
Z2 ■	[nm]	31.7	44.4	126
|Z1-Z2|	[nm]	25.1	13.4	80.3
Length	[um]	0.181	0.159	0.221
ANGLE	[deg]	7.89	4.80	19.9

(B)		1	2	3
Z1 ●	[nm]	127	120	121
Z2 ■	[nm]	123	128	125
|Z1-Z2|	[nm]	3.16	8.10	4.25
Length	[nm]	37.8	53.1	62.0
ANGLE	[deg]	-4.78	8.68	3.92

- **Figure S1. (A)** Height of steps for ex-MWNT of figure 7A (the correct aspect ratio is the one shown in Figure 7A), the steps marked as 1, 2 and 3 would be about 75, 40, and 239 layers respectively. The latter number corresponds to the maximum range of diameters for the MWNT used, suggesting that the layered material observed is formed by the superposition of more than one ex-MWNT. **(B)** Heights of some graphene flakes seen on the ex-MWNTs surface. The region measured corresponds to the lower left corner of Fig. 7B. The heights of the graphene layers are not completely uniform, 1 corresponds to ~9 graphene layers, 2 corresponds to ~24, and 3 to ~13 layers.

Abraham G. Cano-Márquez; Fernando J. Rodríguez-Macías; Jessica Campos-Delgado; Claudia G. Espinosa-González; Ferdinando Tristán-López; Daniel Ramírez-González; David A. Cullen; David J. Smith; Mauricio Terrones; Yadira I. Vega-Cantú; *“Ex-MWNTs: Graphene Sheets and Ribbons Produced by Lithium Intercalation and Exfoliation of Carbon Nanotubes“* ***Nano Letters****,* 2009 Vol. 9, No. 4 1527-1533
DOI: 10.1021/nl803585s

AFM in characterization of nanoribbons made from nanotubes (Ex-MWNT)



- **Figure S3. (A)** Topography image of an ex-MWNT and the graphene flakes generated in the process, **(B)** Phase Image, the contrast between regions is mostly a result of topography, indicating similar surface properties as would be expected for graphene pieces and open MWNTs over HOPG.

Published in: Abraham G. Cano-Márquez; Fernando J. Rodríguez-Macías; Jessica Campos-Delgado; Claudia G. Espinosa-González; Ferdinando Tristán-López; Daniel Ramírez-González; David A. Cullen; David J. Smith; Mauricio Terrones; Yadira I. Vega-Cantú; *"Ex-MWNTs: Graphene Sheets and Ribbons Produced by Lithium Intercalation and Exfoliation of Carbon Nanotubes"* ***Nano Letters**,* 2009 Vol. 9, No. 4 1527-1533
DOI: 10.1021/nl803585s

AFM for Nanoscale Mechanical Testing

- Nanoindentation
  - Use a hard tip (e.g. diamond) to indent surface
    - Tip mounted on a metal cantilever (stainless steel)
    - Cantilever typically thicker, wider, longer and with a smaller resonant frequency
  - Register a force vs. displacement curve while indenting
    - Record an image of indented area
  - Depth of indentation as function of applied force gives information about hardness of material
    - Can be used to compare different materials and coatings
- Scratching and Wear Tests
  - Can be made with the indentation tip
  - Evaluate adhesion of coatings by scratch tests
    - Set same parameters (applied force, depth, length of scratches) for comparisons
  - Wear tests to evaluate durability
    - Series of scans in contact mode with set parameters (force, scan area, number of scans)

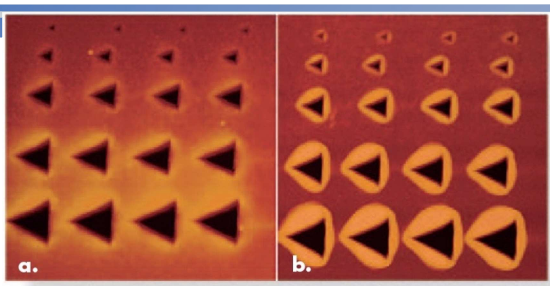


Figure 9. Indentations on two different polymers using the same forces to compare hardness. Each sample was indented four times using each of five forces. The first sample (a) is a PMDA-ODA polyimide, and the second sample (b) is a BPDA-PDA polyimide. The indentation depths vary from about 20-200nm and are deeper for the softer PMDA-ODA polyimide. 3μm scans.

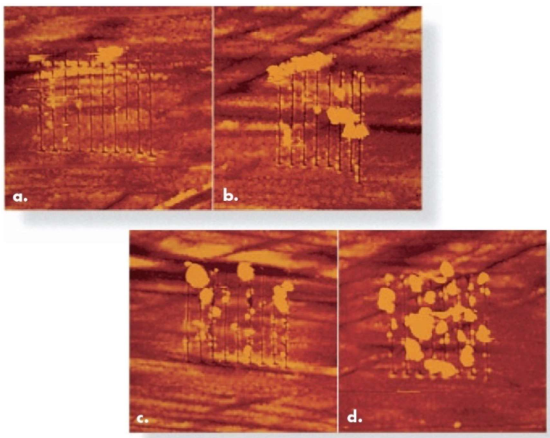
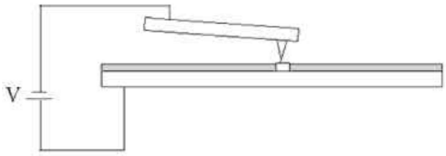


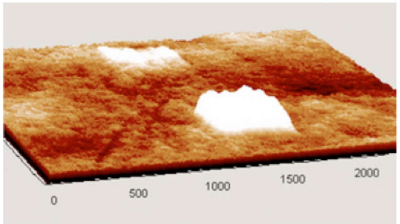
Figure 5. Array of scratches performed on four different 10nm thick diamond-like carbon thin films, all using the same force and cantilever in order to compare film adhesion and durability. The scratches are 1μm long and less than 10nm deep. 2μm scans.

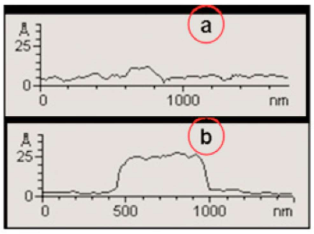
Example taken from http://www.veeco.com/appnotes/AN13_NanoIndent_081804_RevA1.pdf (accessed and downloaded 2007, no longer accesible online)

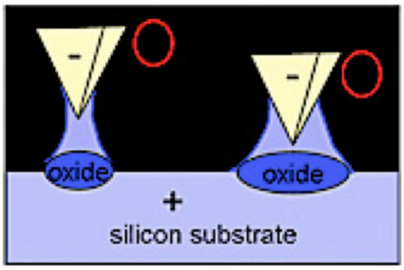
Surface Modifications with AFM (1)



- Electrical Modifications
  - Voltage bias between tip and sample can cause local oxidation and form patterns
    - Control dimensions of pattern with: applied voltage, probe diameter, tip-sample distance
  - Example: Anodic oxidation of surface
    - Left image: 50 nm width lines
    - Right image: change in bias changed width of line



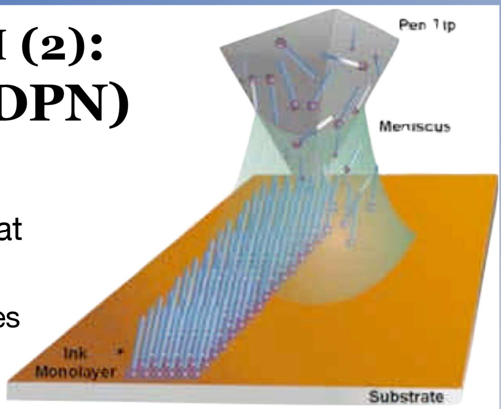




- Example: Anodic oxidation of silicon substrate.
  - Square patterns of SiO_2 made with a bias voltage of 2 V.
  - a) with a large tip-sample distance, b) with a small tip-sample distance

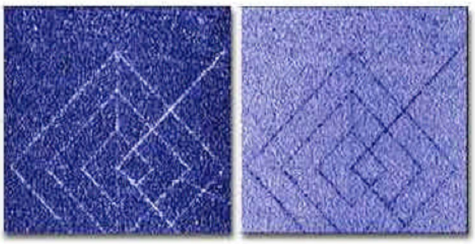
First example (top two images) from "Surface Modification", © 2003 Pacific Nanotechnology, Inc. < http://www.pacificnano.com/modifications-lithography_print.html > (Downloaded april 2005. Website no longer available online)
Lower set of 3 example images from < http://afmuniversity.org/index.php/2011-07-25-05-55-45/materials-science >

Surface Modifications with AFM (2): Dip Pen Nanolithography (DPN)



- DPN: Molecular Deposition:
  - Liquid on AFM tip used to deposit molecules that attach to surface
    - Inks with organic molecules, polymers, biomolecules
  - Calibration of piezo-scanner is essential for accurate patterning
  - Example: Alkane thiol over Au
    - Self Assembled Monolayers: R-SH groups react with Au surface, alkane chains aligned perpendicular to surface
    - Calibration problem results in defective square

Thiol 'ink' on Gold
(friction image)

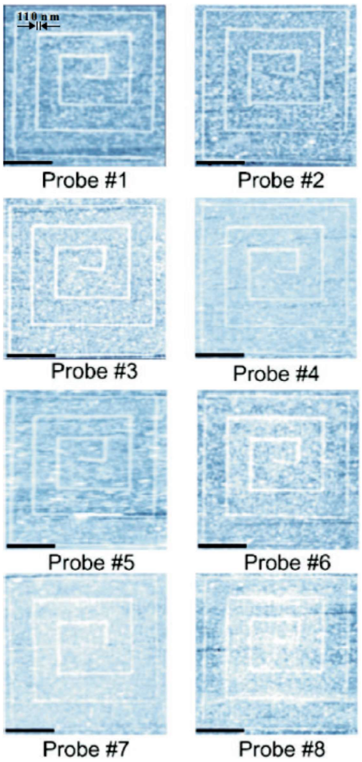


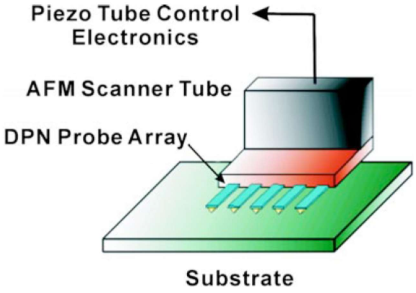
- With proper calibration complex patterns can be drawn over substrate.
  - Lateral Force microscopy images of pattern made by Dip Pen Nanolithography (DPN)

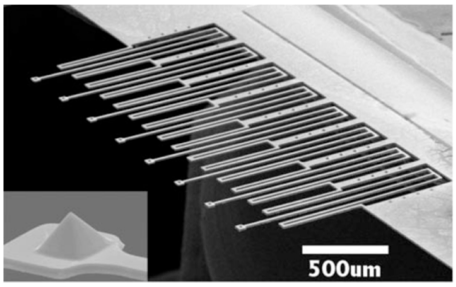
Images from "Surface Modification", © 2003 Pacific Nanotechnology, Inc.
< http://www.pacificnano.com/modifications-lithography_print.html > (Downloaded april 2005. Website no longer available online)

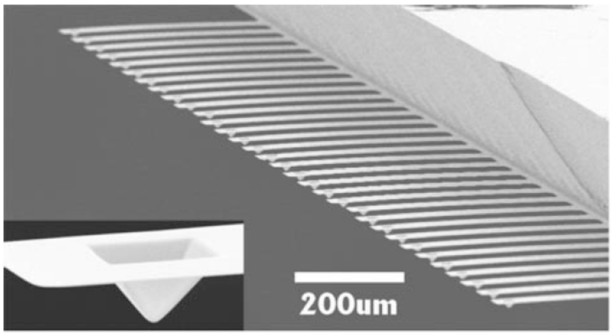
Dip Pen Nanolithography

- Arrays of DPN tips can be used for parallel writing of patterns









Images from: M. Zhang, D. Bullen, S.-W. Chung, S. Hong, K.S. Ryu, Z. Fan, C.A. Mirkin, C. Liu “A MEMS nanoplotter with high-density parallel dip-pen nanolithography probe arrays” Nanotechnology 13 (2002) 212–217

Artifacts in AFM Characterization

artifact |ˈärdəfakt |

New Oxford American Dictionary

2. something observed in a scientific investigation or experiment that is not naturally present but occurs as a result of the preparative or investigative procedure

Merriam-Webster Dictionary (m-w.com)

2. a product of artificial character (as in a scientific test) due usually to extraneous (as human) agency

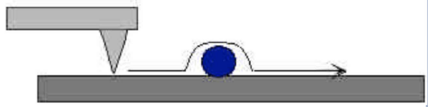
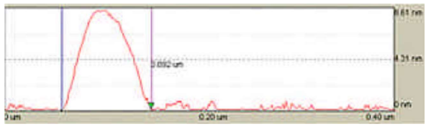
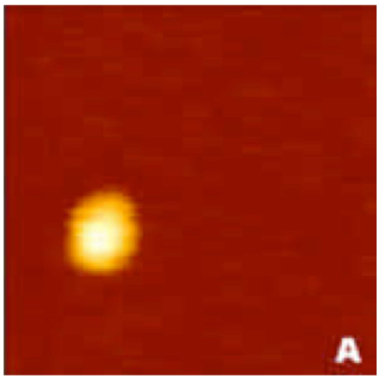
artefacto (artefacto o artificio)

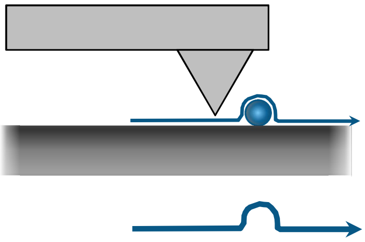
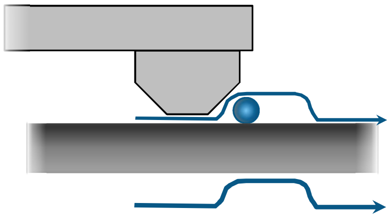
Diccionario de la Lengua Española (rae.es)

4. m. En un estudio o en un experimento, factor que perturba la correcta interpretación del resultado.

Probe Size Artifacts in AFM

- Features may appear larger when probe size is in the same order of the size of sample features, or larger
  - Example: 8 nm spheres
    - Height measured correctly as 8nm
    - Apparent diameter 92 nm, broadened by probe size and shape

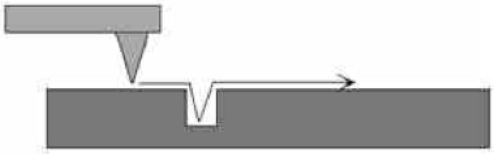




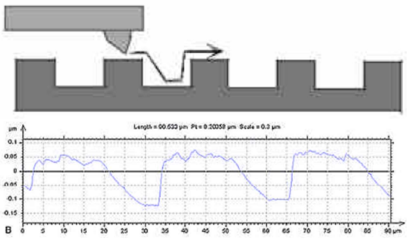
Images of AFM artifacts in this and subsequent pages (unless otherwise indicated) from: Paul West and Natalia Starostina "A Guide to AFM Image Artifacts", © 2003 Pacific Nanotechnology, Inc. < http://www.pacificnano.com/afm-artifacts_print.html > (Downloaded april 2005. Original website no longer online, archived at < http://web.archive.org/web/20061029204530/http://www.pacificnano.com/afm-artifacts_print.html >)

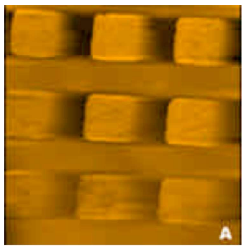
Probe Shape Artifacts in AFM

- Some large-aspect ratio features may appear too small due to probe size and shape
  - Example: rectangular trenches in a substrate require a long and thin tip to be imaged properly

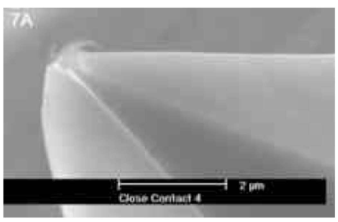


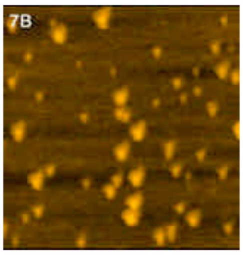
- Apparent shapes can be distorted if tip is damaged or misshapen

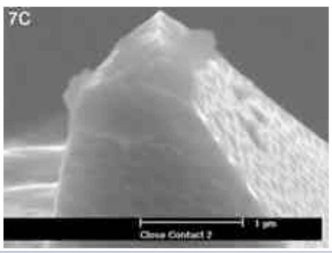


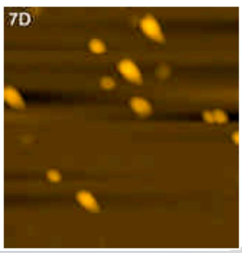


- Example: colloidal gold particles (below)
  - 5 nm spheres appear triangular due to probe shape
  - 28 nm spheres appear distorted due to irregular or dirty tip









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Probe Shape Artifacts

- Probe shape can limit lateral resolution in addition to depth resolution
  - Scanning known shapes can be used to get an idea of the tip profile that comes in contact with the surface

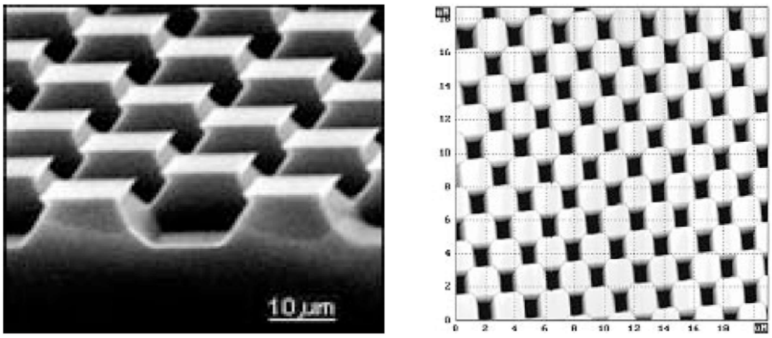


Fig. 36. Rectangular calibration lattice and its SFM image

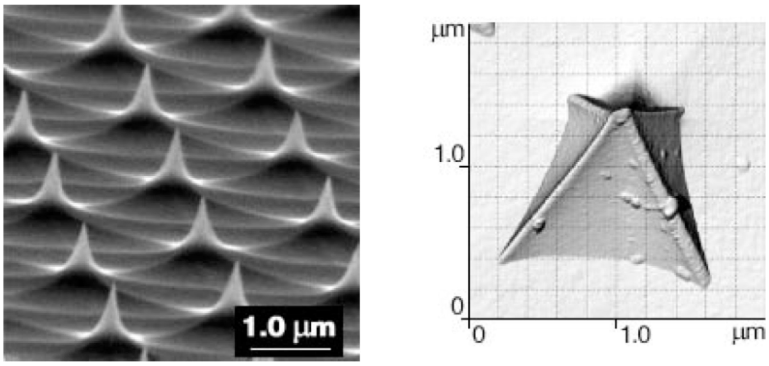
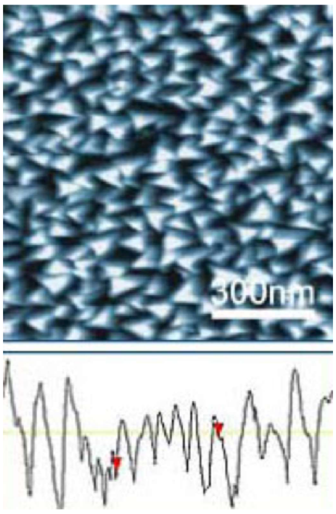


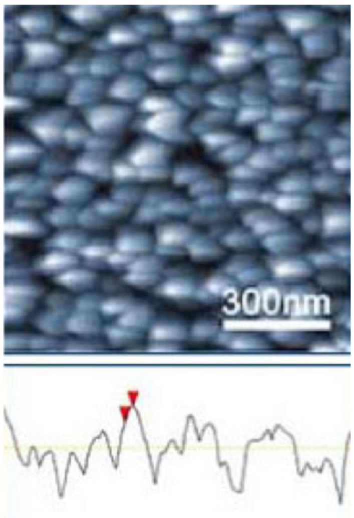
Fig. 37. Calibration lattice made of sharp pins and its SFM image obtained by a pyramidal tip

Figures from: V. L. Mironov, Fundamentals of Scanning Probe Microscopy, Institute of Physics of Microstructures of RAS, Nishny Novgorod, ©NT-MDT 2004 (downloaded from http://ipmras.ru/en/structure/people/mironov)

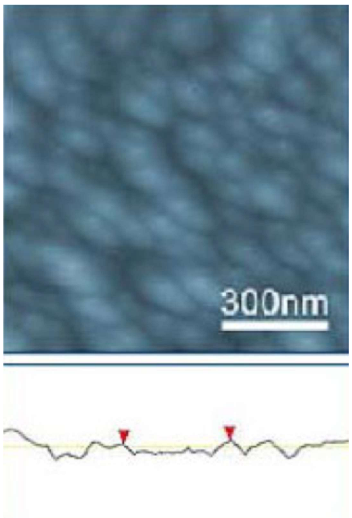
Tip Calibration standards



- Good tip



- Worn Tip



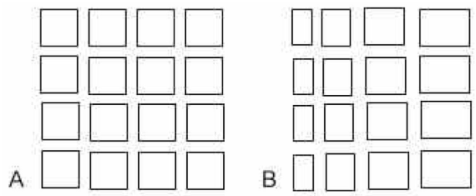
- Blunt or Broken Tip

- Standard material can show if tip remains usable or if it must be replaced

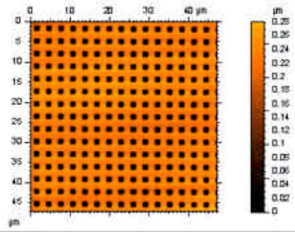
(images from: https://www.tedpella.com/calibration_html/AFM_SPM_Calibration.htm)

Some Scanner Artifacts in AFM

- Probe-sample angle
  - Ideally probe should be perpendicular to surface being scanned

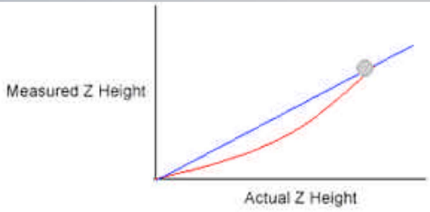


- Non-linearities of scan
  - Non-linear response of piezoelectric elements can introduces distortions in measurements of distances



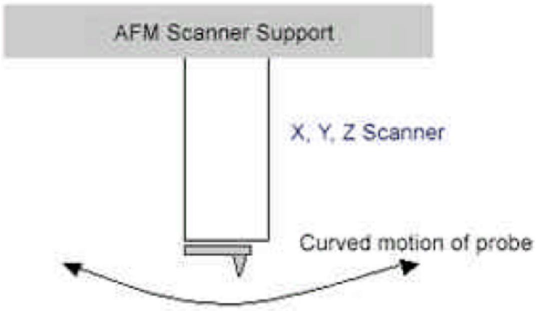
  - Square test patterns can be used to calibrate piezo-scanner and compensate for non-linearity

  - Non-linear responses in Z-axis mean that if calibration of heights is made at only one point actual measured heights may contain errors



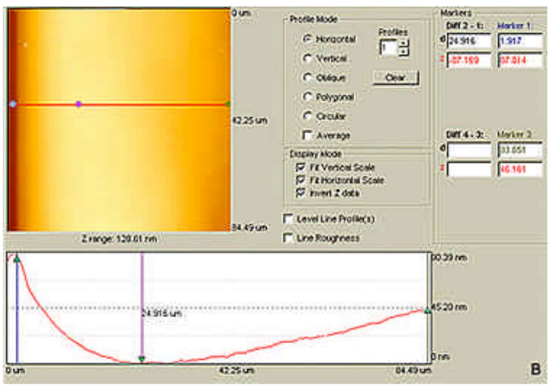
Some (more) Scanner Artifacts in AFM

- Background Bow
  - Scanner is fixed in one point, thus probe motion is non-linear in Z
    - X-Y scanning results in curving of piezo-scanner



- Background tilt
  - If probe is not perpendicular to surface due to piezo-scanner movement a flat surface may appear as a tilted plane

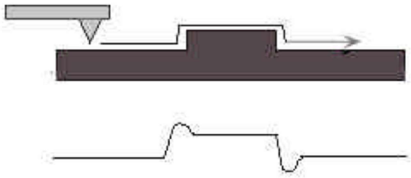
- Both effects can usually be compensated through the AFM software
  - Software applies a “baseline” correction to data

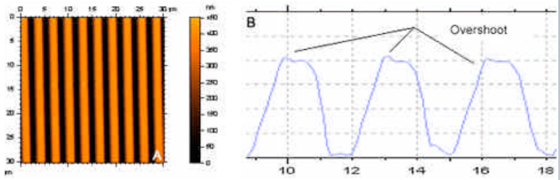


- Newer instruments may have configurations that minimize these problems

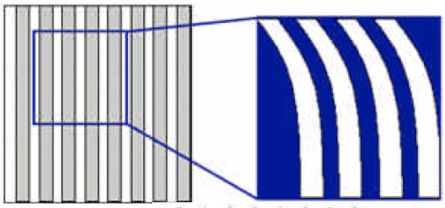
Some Scanner Artifacts in AFM

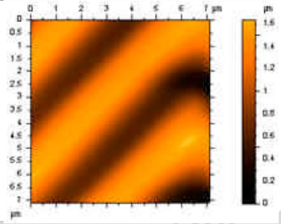
- Z-edge overshoot
  - Hysteresis in piezoelectric element may result in displacement of tip above the actual height of an edge and apparent displacement at the bottom of a step





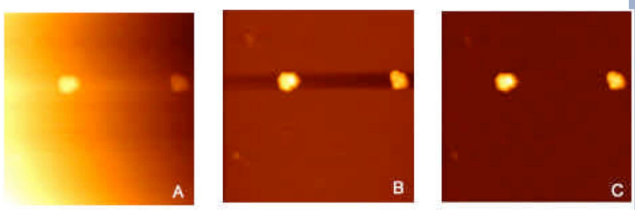
- Scanner Drift
  - When scanner is deformed a large amount the change requires additional time
    - "Creep" deformation signal has stopped but scanners keeps expanding or contracting slightly
  - When zooming or displacing scan to another region initial part of scan may look distorted





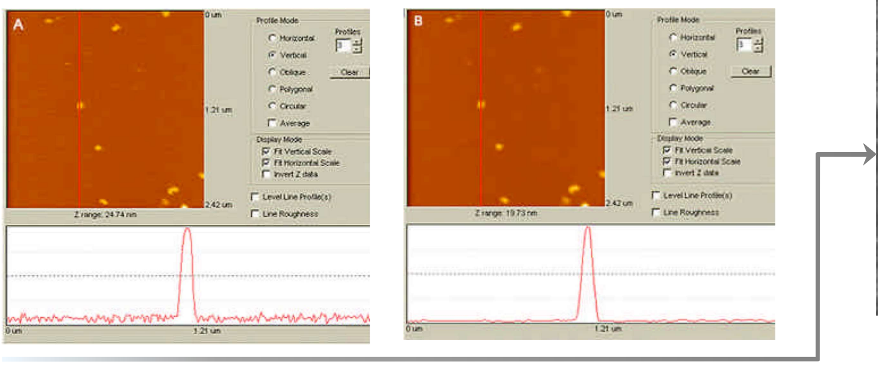
Some Image Processing Artifacts in AFM

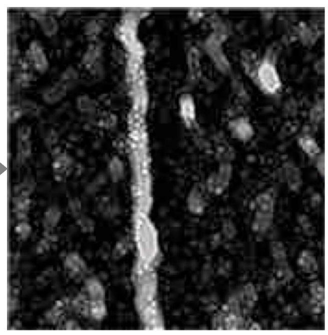
- This image originally has a tilt artifact
  - After a leveling process to remove tilt dark lines appear between the particles, these do not correspond to a real feature



- With different processing (excluding particles from background subtraction process) no leveling artifacts appear

- Smoothing / Filtering can reduce noise in image

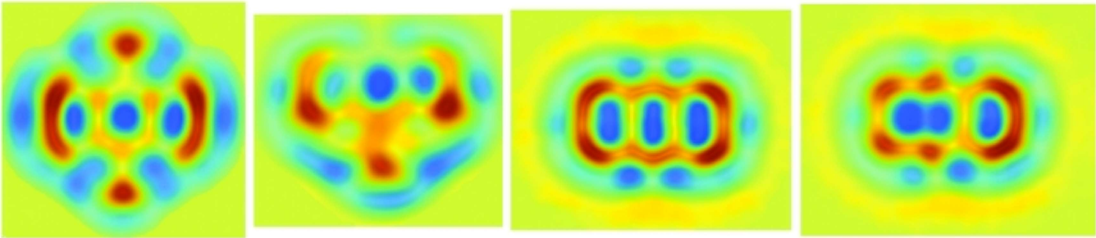


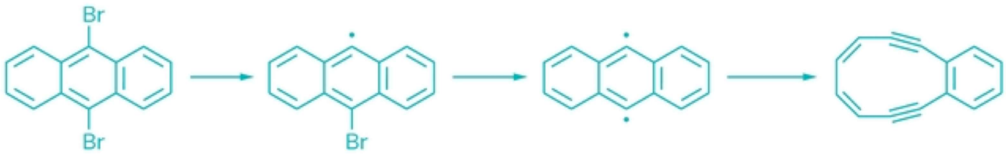


Filtering artifacts on this image introduced textured appearances not physically present in the sample

- Shapes of sample features may be distorted if filtering is not applied properly

APPENDIX: Chemical Bond Imaging (and rearrangement) with SPM





See the following links for articles about AFM imaging of reactions:
https://www.ibm.com/blogs/research/2016/01/30-years-of-atomic-force-microscopy-ibm-scientists-trigger-and-observe-reactions-in-an-individual-molecule/
http://news.berkeley.edu/2016/05/09/atomic-force-microscope-reveals-chemical-ghosts/
http://cen.acs.org/articles/94/i5/Chemists-Nudge-Molecule-React-Watch.html
http://cen.acs.org/articles/91/i22/Reaction-Snapshots.html
http://news.mit.edu/2015/new-microscope-real-time-videos-nanoscale-1214

Image taken from: http://cen.acs.org/articles/94/i5/Chemists-Nudge-Molecule-React-Watch.html