Fabrication and Characterization of Nanostructures Using AFM

NACK CENTER
Building College-University Partnerships for Nanotechnology Workforce Development

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PennState

AFM Lithography

Nanoshaving

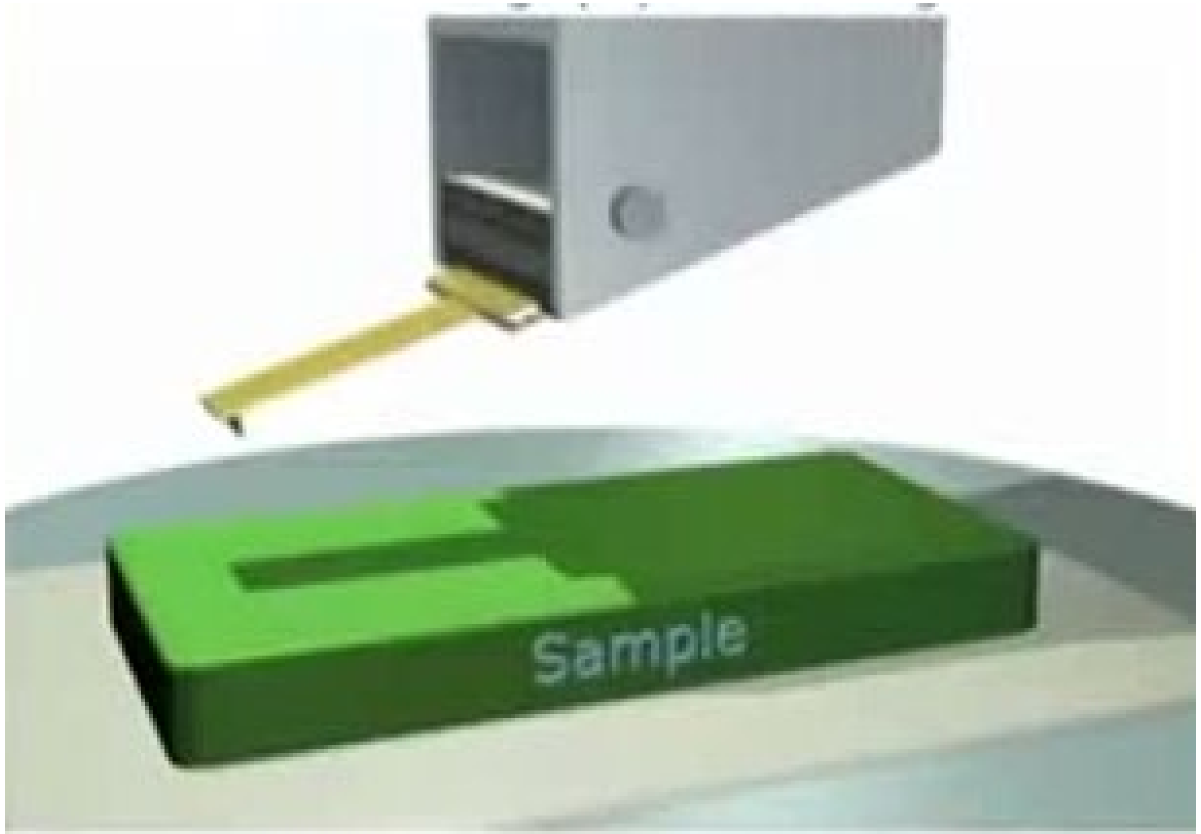
Nanografting

Dip-Pen Nanolithography (DPN)

Thermal DPN

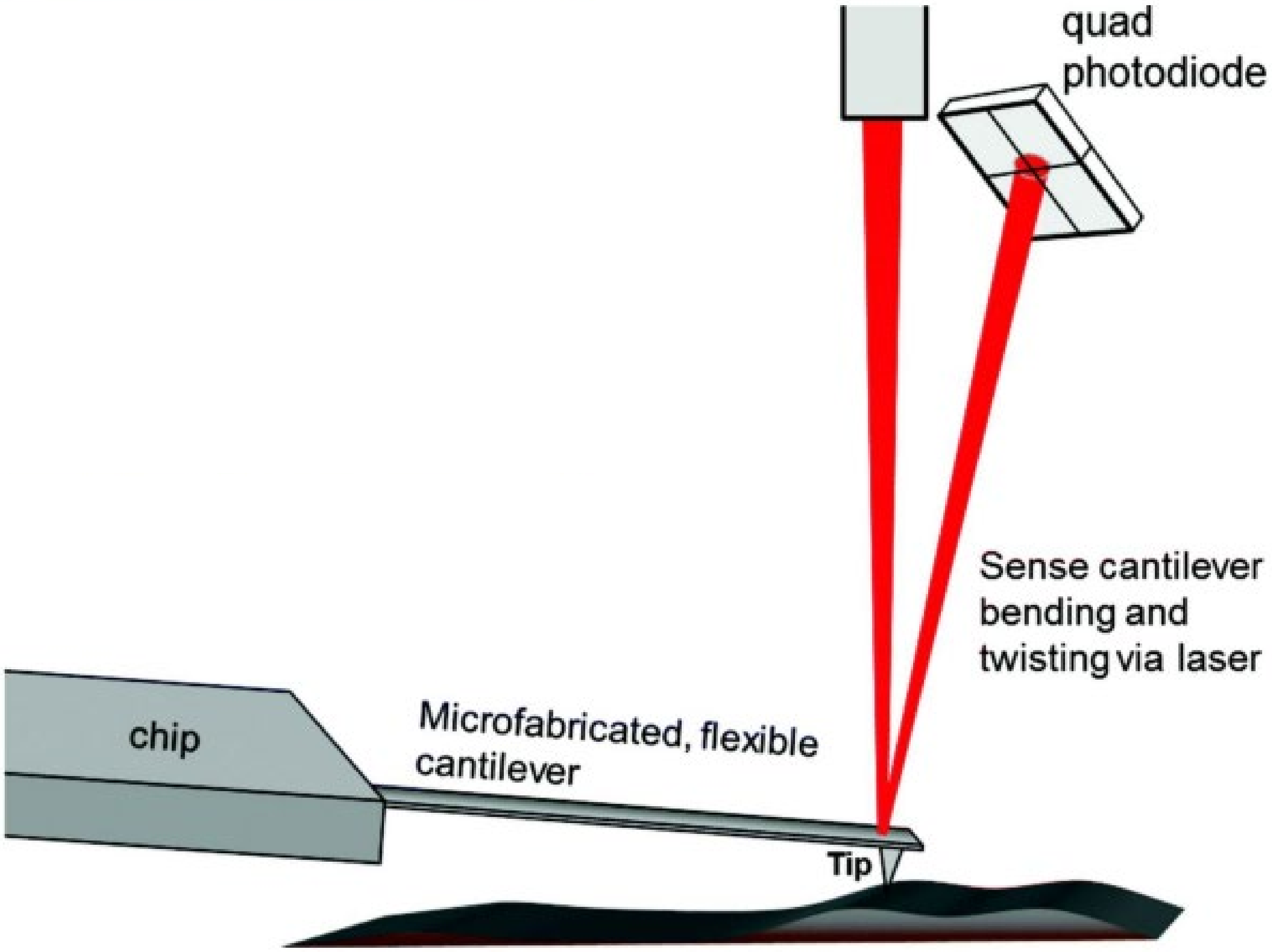
Electrochemical DPN

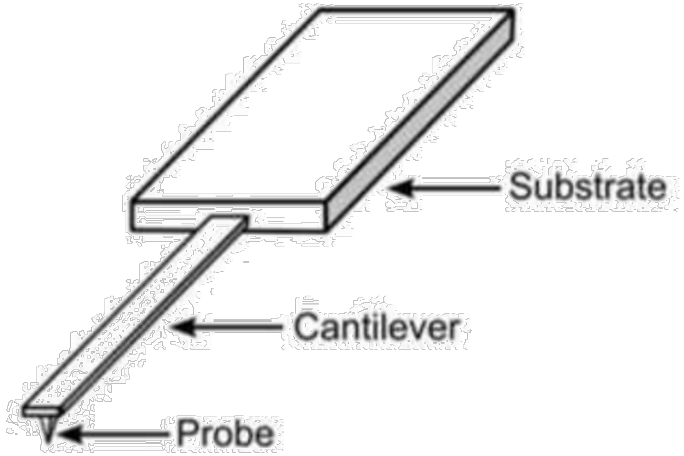
Anodization Lithography

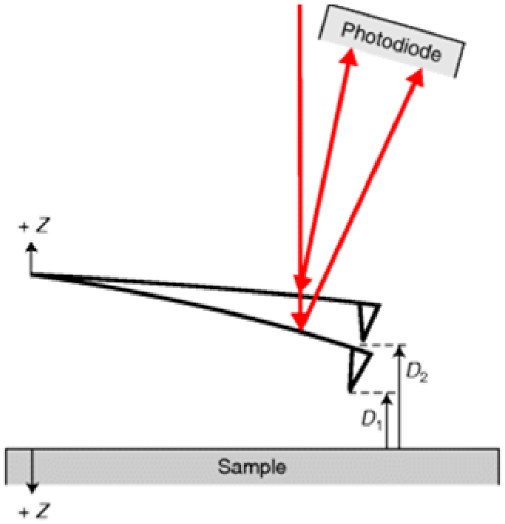


https://www.youtube.com/watch?v=mfulyT6ILdo

AFM Operation



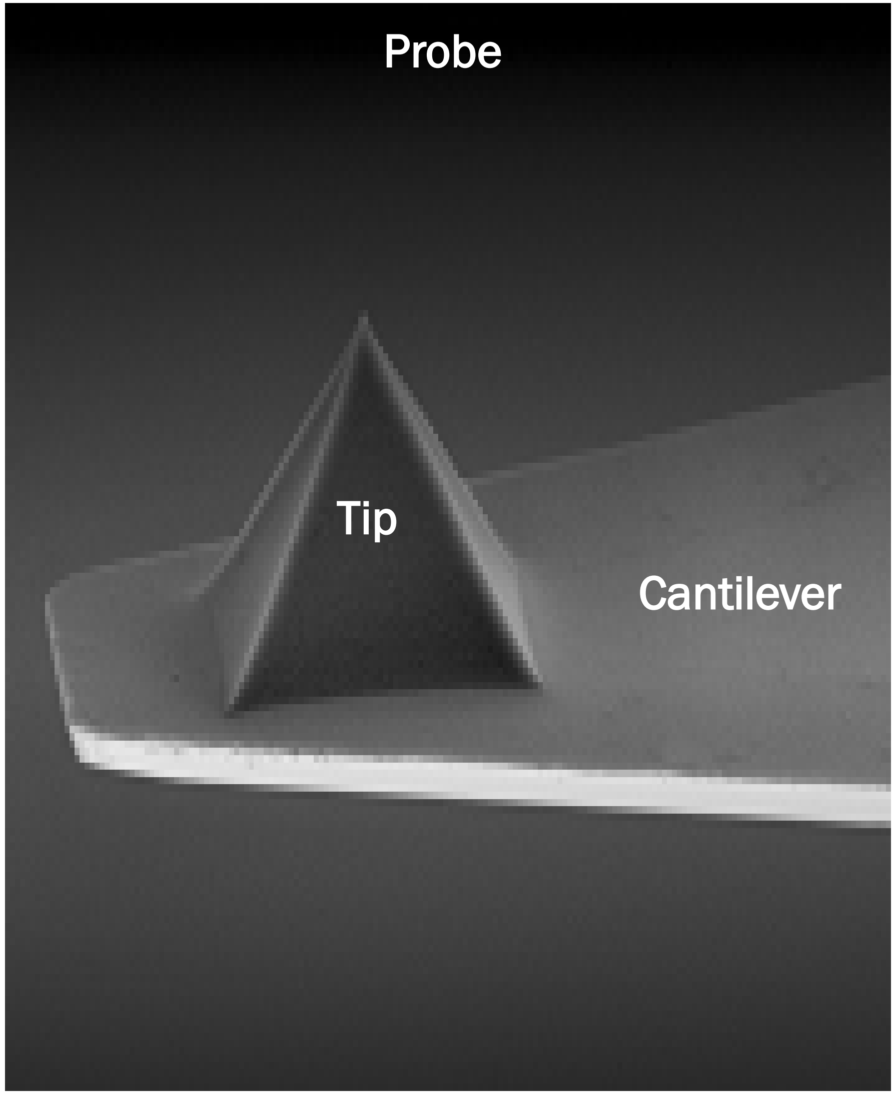




Patterning with AFM

SPM has also been used to manipulate atoms on metal surfaces and to fabricate nanopatterns.

This is due to the sharpness of AFM tips and strong and localized tip-surface interactions,

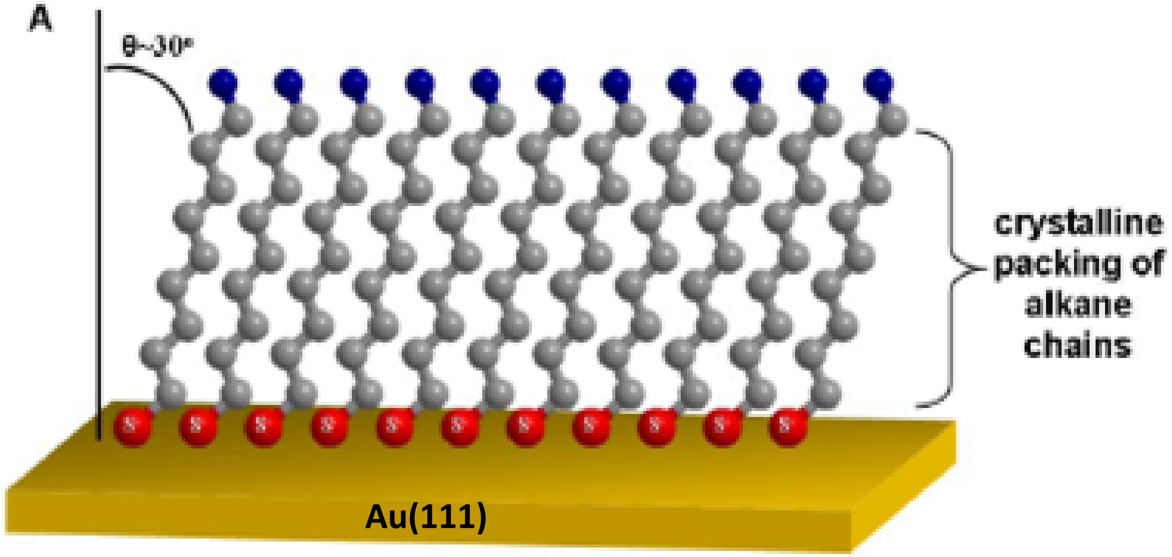


Yang, G. et al. Proceedings of SPIE Vol. 5220 Nanofabrication Technologies. 2003.

Self-Assembled Monolayers (SAMs)

Micro- and nano-fabrication of self-assembled monolayers (SAMs) on metal surfaces have attracted much attention due to potential applications in molecular electronics, chemical and biosensors, and in the control of biomolecular adhesion on surfaces.

Alkanethiol SAM

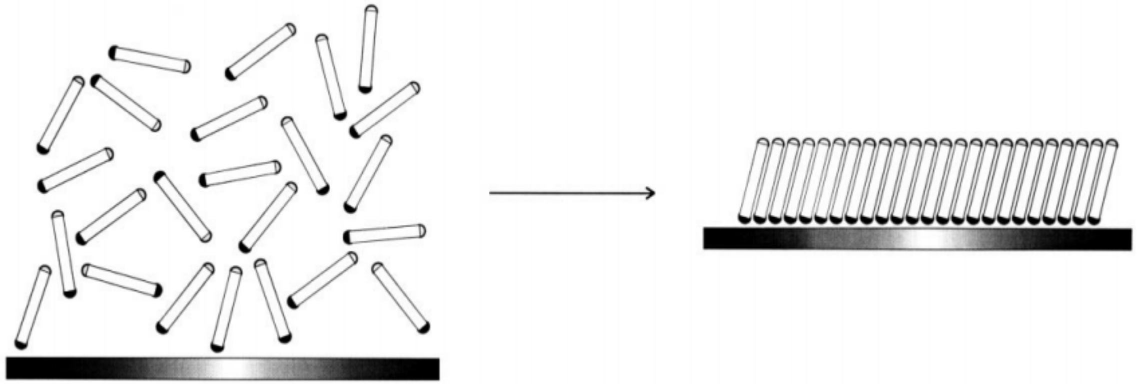


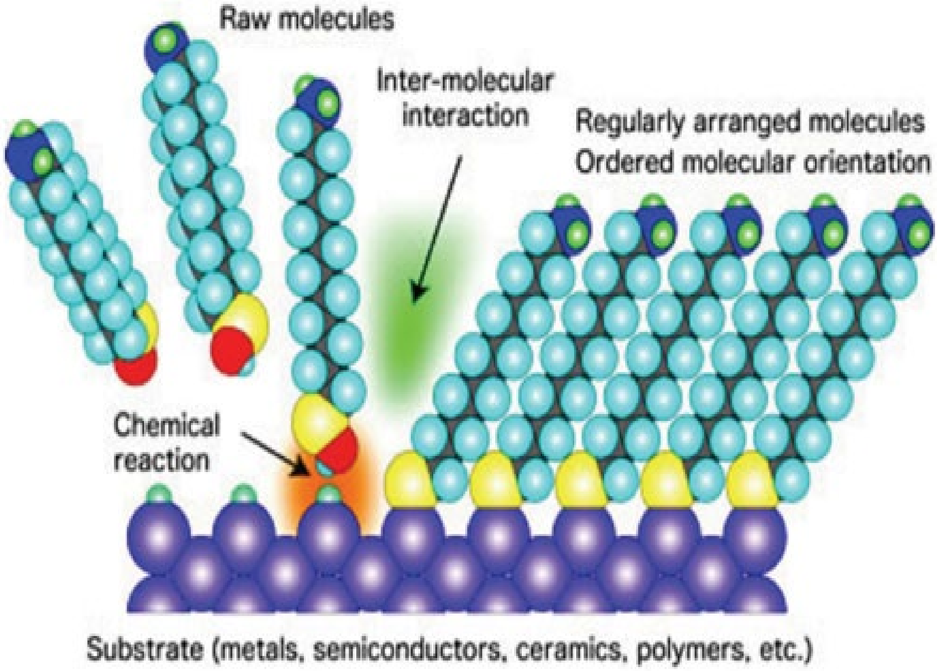
Creating nanopatterns of SAMs with molecular precision requires new fabrication strategies.

Yang, G. et al. Proceedings of SPIE Vol. 5220 Nanofabrication Technologies. 2003.

Self-Assembled Monolayers (SAMs)

Self-assembly is a phenomenon in which a number of independent molecules suspended in an isotropic state come together to form an ordered aggregate.

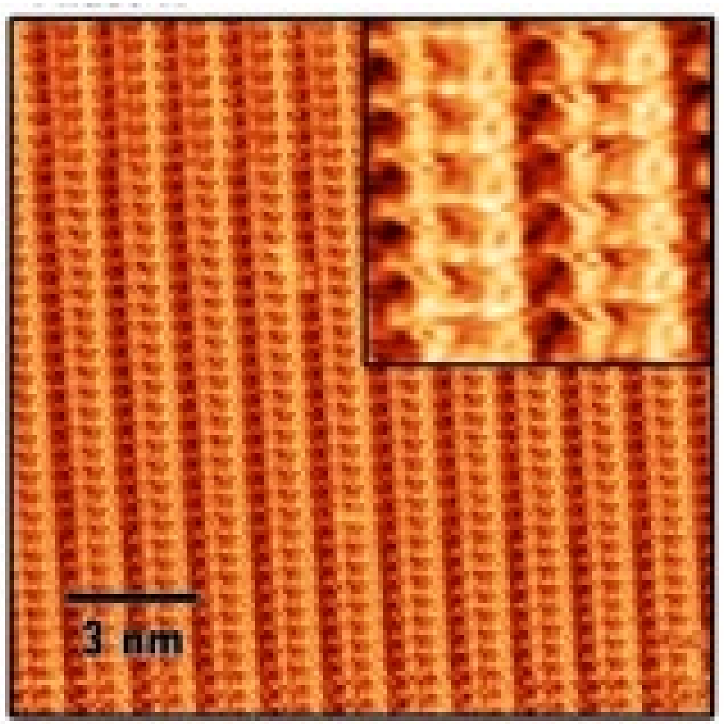




In the 1980's, scientists discovered that alkanethiols spontaneously assembled on noble metals.

Self-Assembled Monolayers (SAMs)

SAMs are crystalline-like monolayers formed on metal surfaces.



STM image of a 4-mercaptopyridine SAM assembled on gold

SAMs are critical components for stabilizing and adding function to preformed, nanometer-scale objects such as, thin films, nanowires, colloids, and other nanostructures.

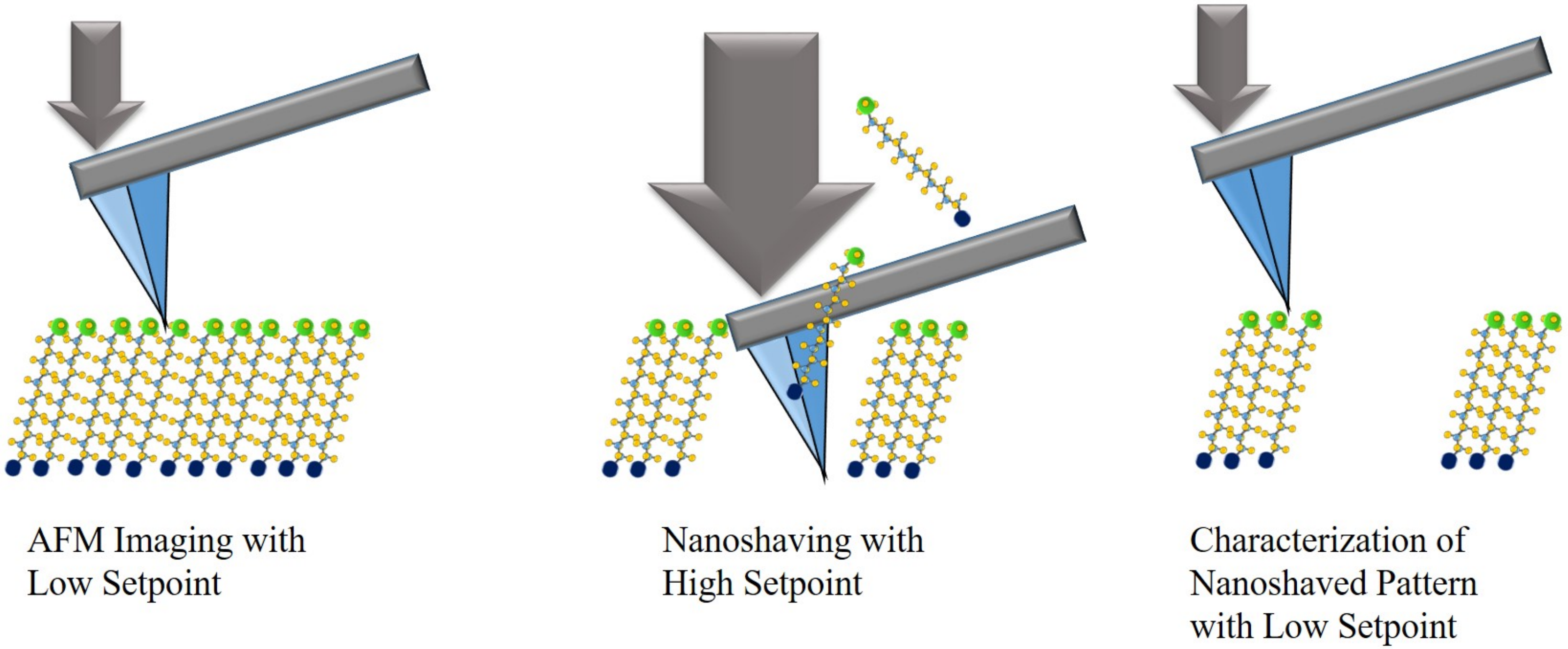
Herrrera, F. et al. *Langmuir*, **2017**, 33, 9565-9573.

AFM Lithography

https://www.youtube.com/watch?v=6J_v-C7Dozw

Nanoshaving

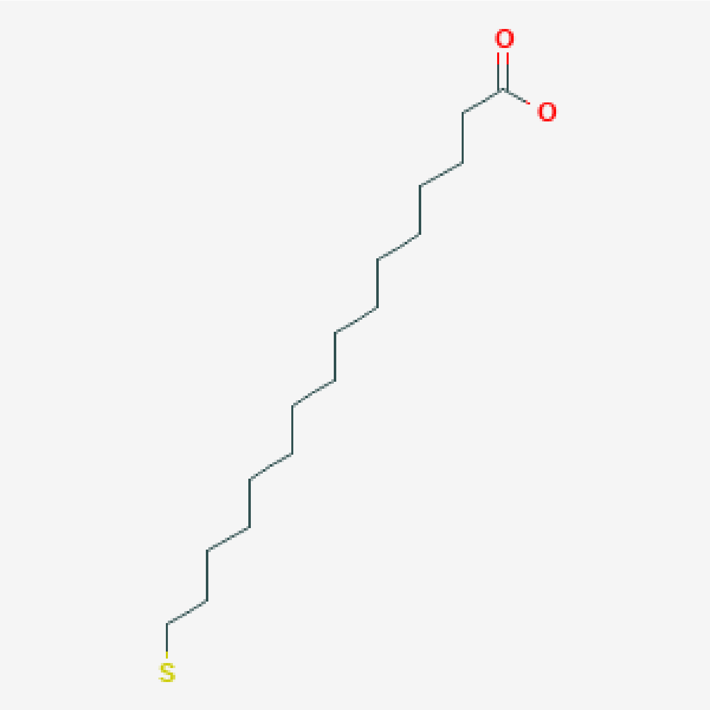
First, the surface structure is characterized under a low force or load. The second step is patterning SAMs under high force. In nanoshaving (Figure 6A, bottom), the AFM tip exerts a high local pressure at the contact. This pressure results in a high shear force during the scan, which causes the displacement of SAM adsorbates.



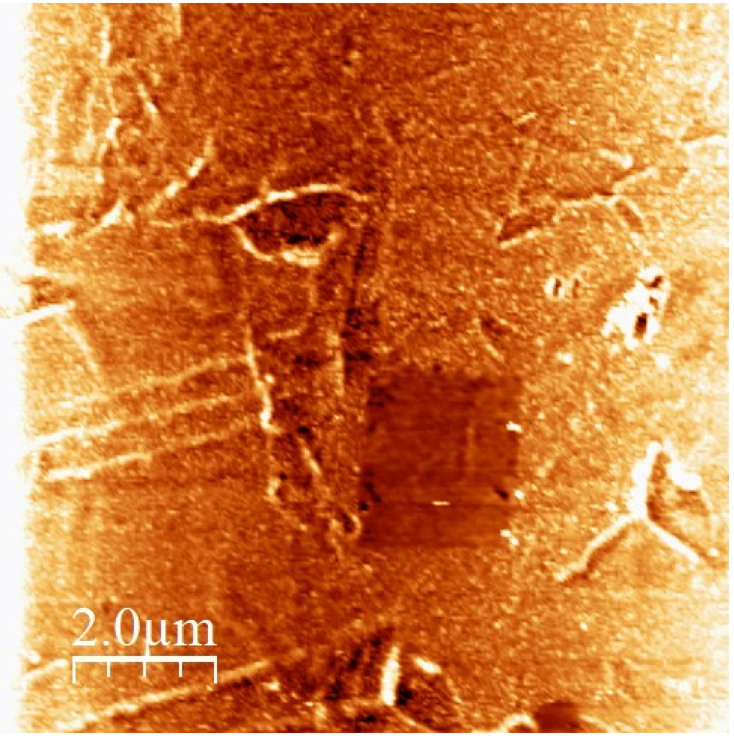
Yang, G. et al. Proceedings of SPIE Vol. 5220 Nanofabrication Technologies. 2003.

Nanoshaving

During nanoshaving, adsorbate molecules are displaced by an AFM tip during the scan at a load higher than the displacement threshold. Holes and trenches can be fabricated.



MHDA: Mercaptohexadecanoic Acid

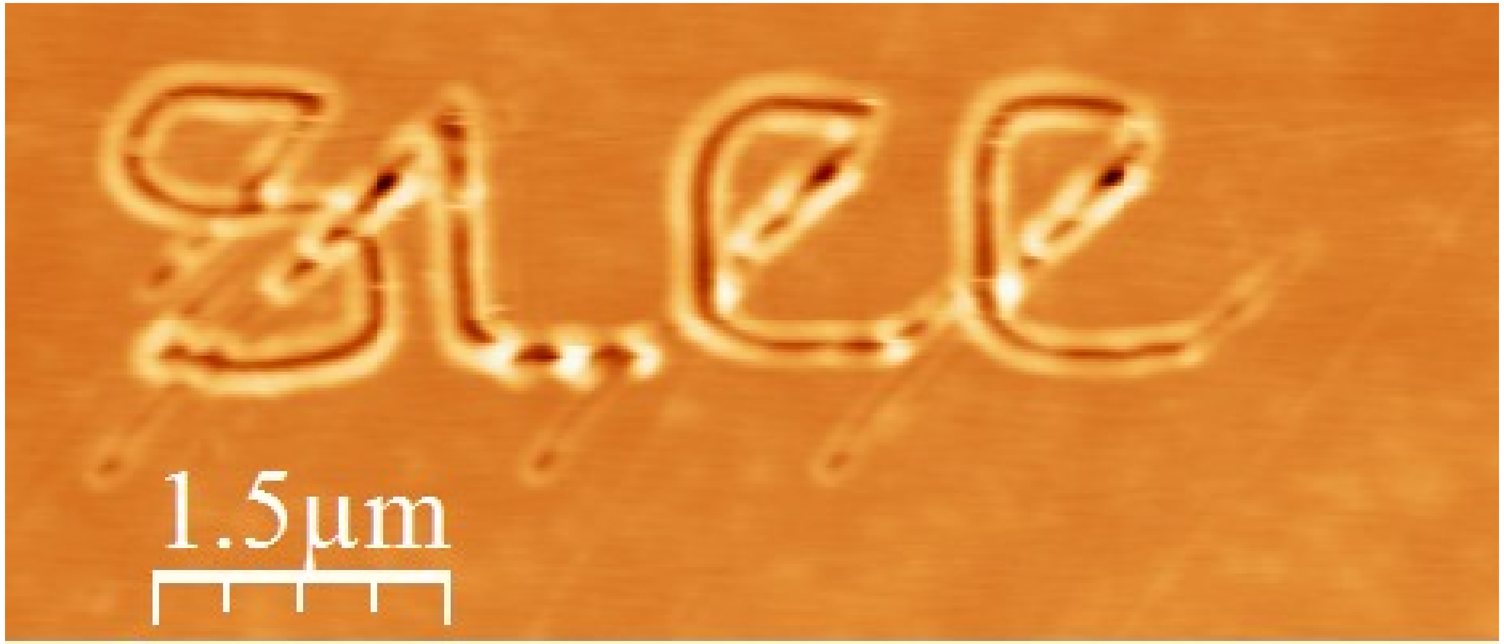


Yang, G. et al. Proceedings of SPIE Vol. 5220 Nanofabrication Technologies. 2003.

Nanoshaving

With an appropriate tip, 20 nm lateral resolution is possible

The use of SAM as a resist layer to increases resolution



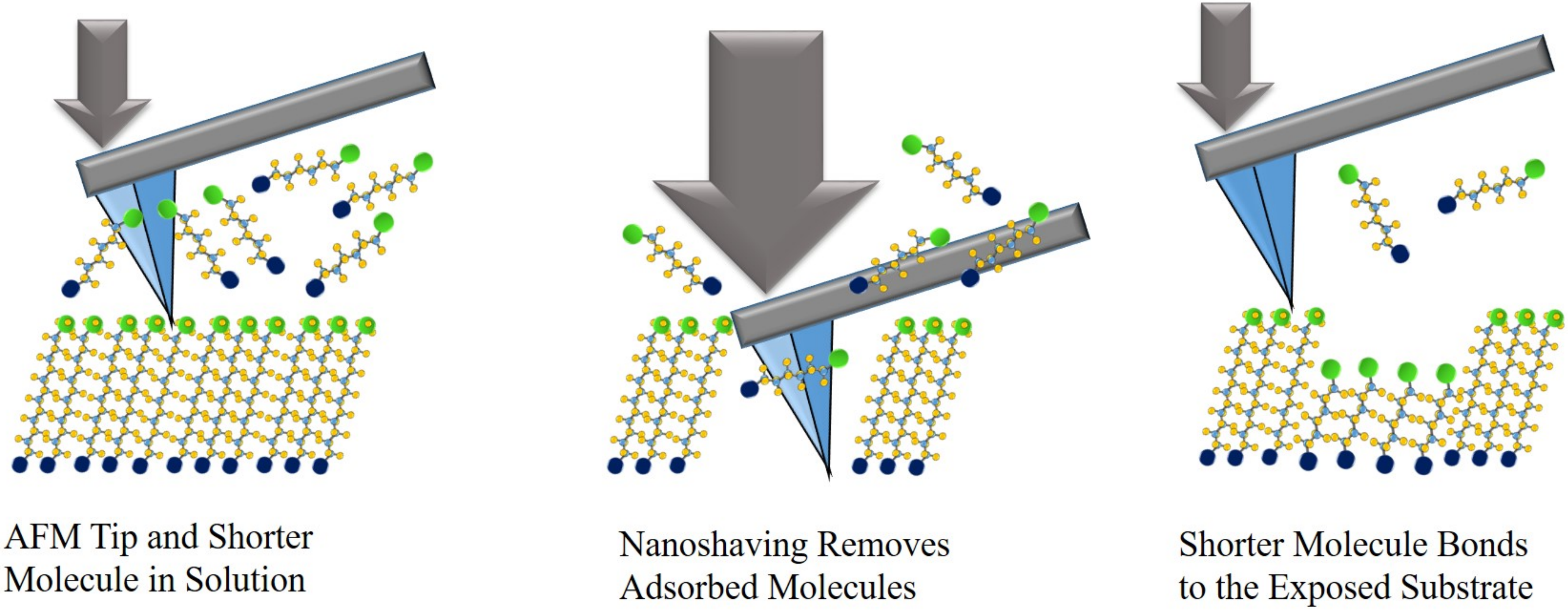
Pattern fabricated on polycarbonate substrate with nanoshaving

Peter Ainsworth - SLCC Student 2012

www.asylumresearch.com

Nanografting

In nanografting AFM tips are also used to shave thiol molecules from their adsorption sites. The SAM and the AFM cantilever are immersed in a solution containing a different thiol. The thiol molecules in the solution adsorb on the newly exposed gold surface as the AFM tip plows through the matrix SAM. The nanostructures can be characterized in the third step at reduced loads.



Yang, G. et al. Proceedings of SPIE Vol. 5220 Nanofabrication Technologies. 2003.

AFM Lithography

https://www.youtube.com/watch?v=qrV8Me9Q7b4

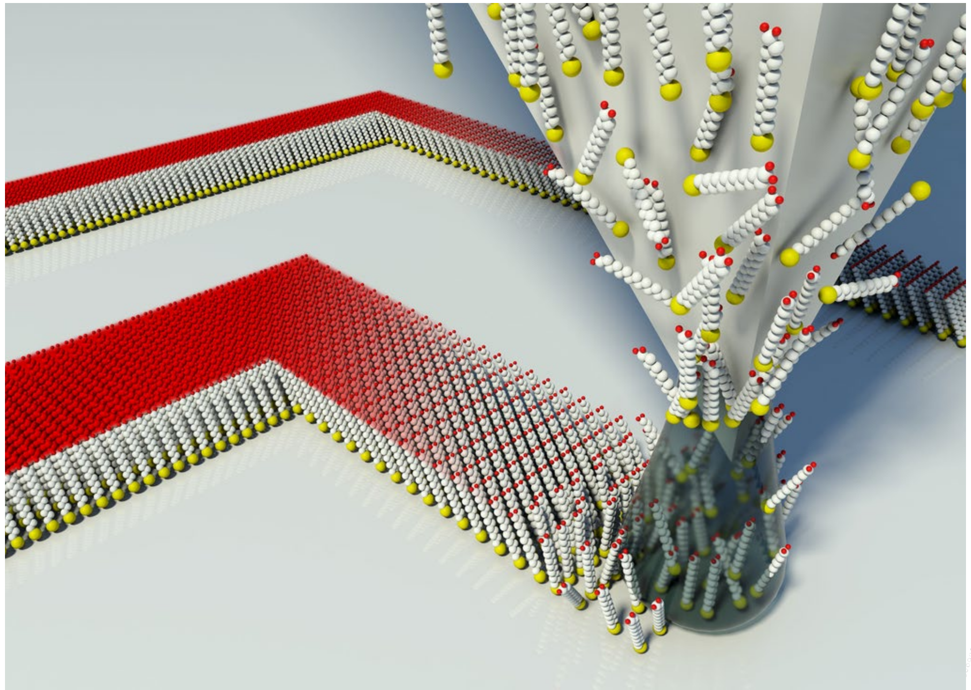
Dip – Pen Nanolithography (DPN)

Invented by Chad Mirkin (Northwestern University) in 1999.

Water accumulates on AFM tip and creeps onto surface, reducing resolution of AFM measurements

We can use “inks” on AFM tip to write spots and lines on the surface

Lines as thin as 15 nm can be deposited

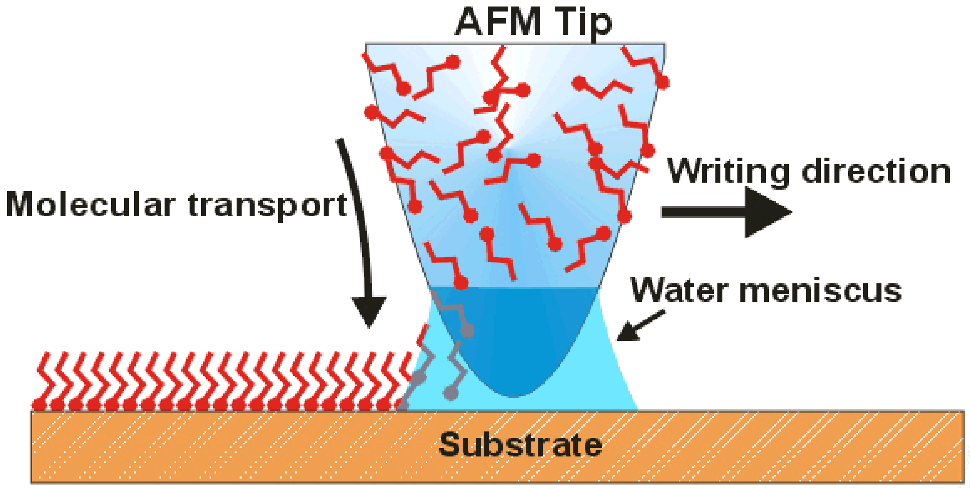


https://commons.wikimedia.org/w/index.php?curid=11994348

Piner *et al.*, *Science* **283**, 661 (1999)

Dip – Pen Nanolithography (DPN)

Direct write, positive printing technique using alkanethiols as diffusive inks.



Resolution depends on:

1 - tip radius

2 - substrate roughness

3 - contact time

4 - humidity (meniscus size)

5 - Grain size of the substrate

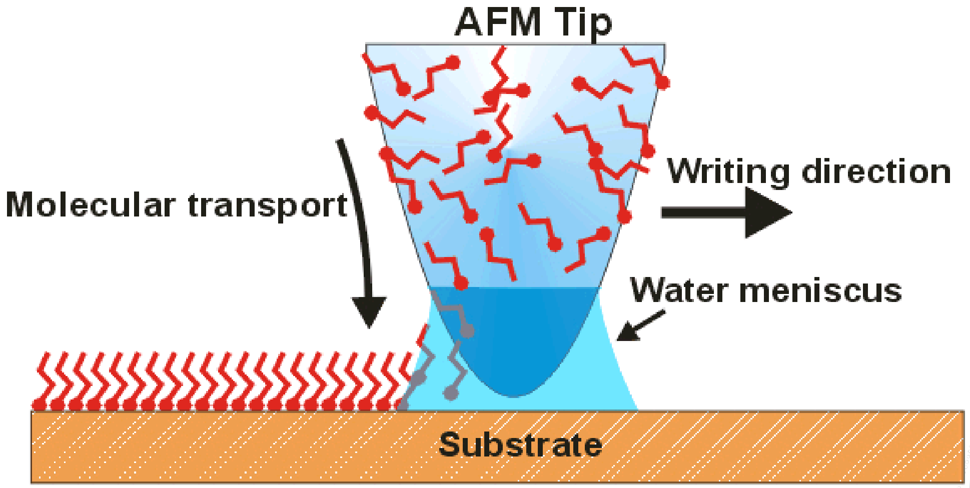
Dip – Pen Nanolithography (DPN)

The AFM tip (*pen*) is coated with the molecules to be written (*ink*), and a clean substrate serves as the paper.

Molecules are transported to the surface via capillary diffusion through the nanoscopic water meniscus formed between the tip and sample in an ambient environment.

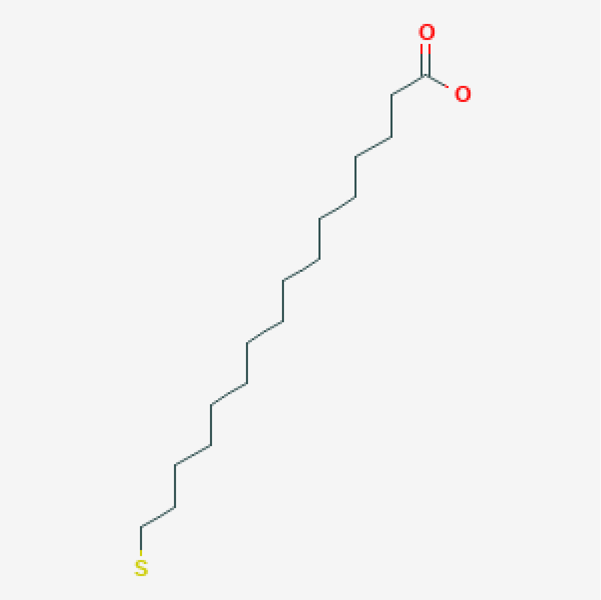
The transfer of the ink is dependent on the relative humidity, which affects the size of the water meniscus formed between the tip and the surface.

Tip is held in contact with the surface for certain time intervals.



Dip – Pen Nanolithography (DPN)

The molecular ink must have an affinity for both the AFM tip and for the substrate.



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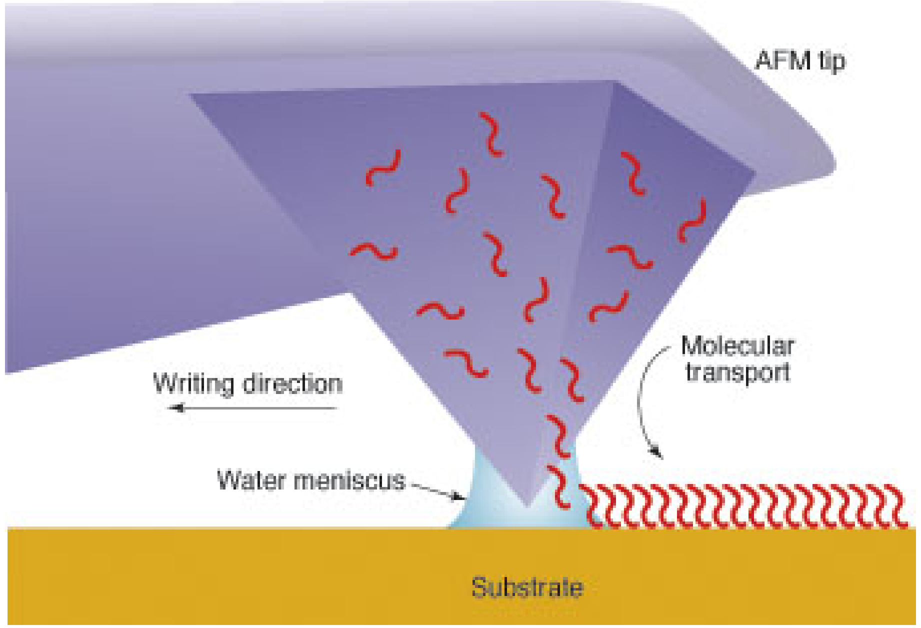
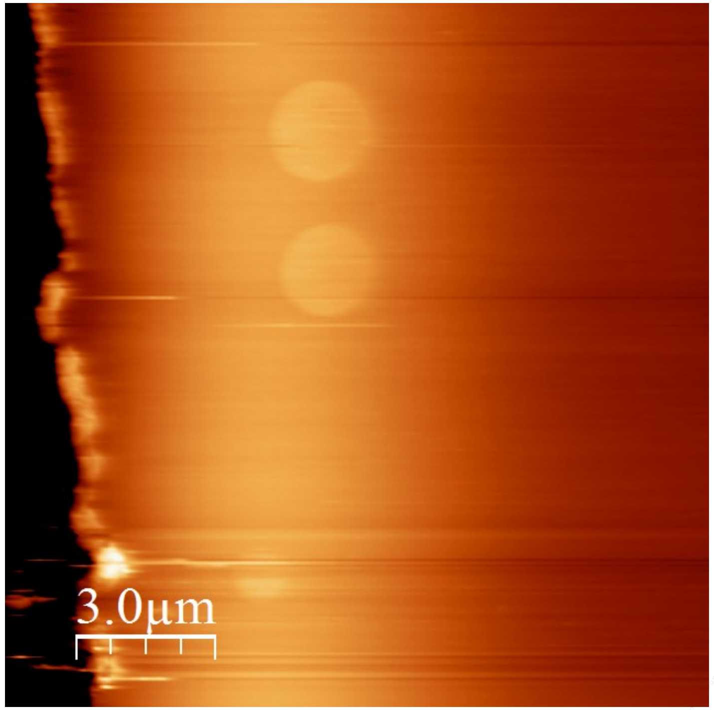




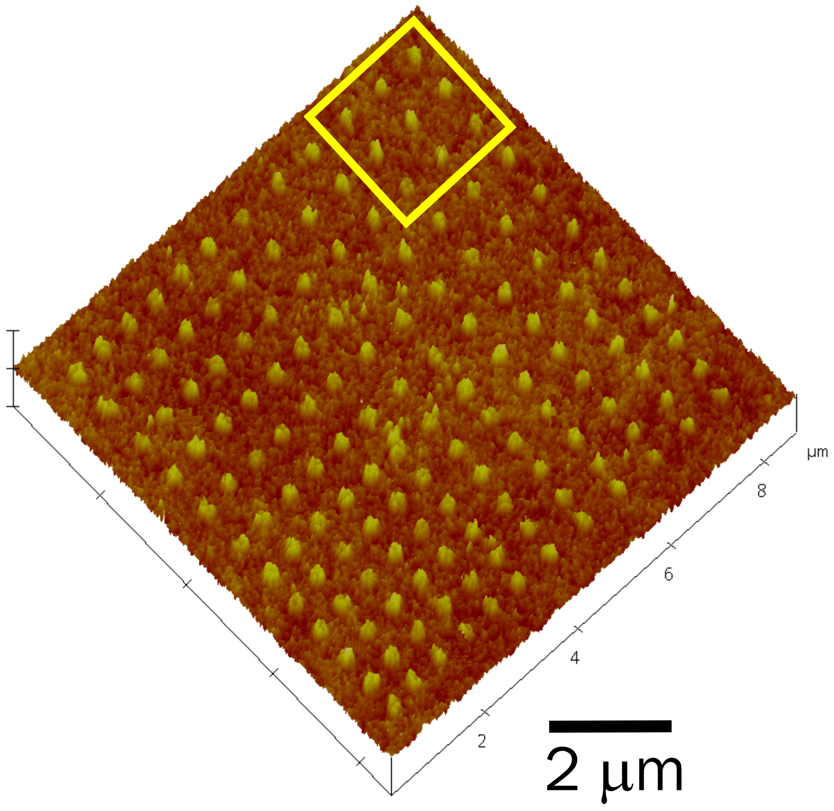
MHDA SAM nanopatterns on gold written with DPN

Alkanethiols attach to silicon nitride AFM tips through physisorption (physical adsorption) and bind to surfaces of certain metals through chemisorption.

Dip – Pen Nanolithography (DPN)

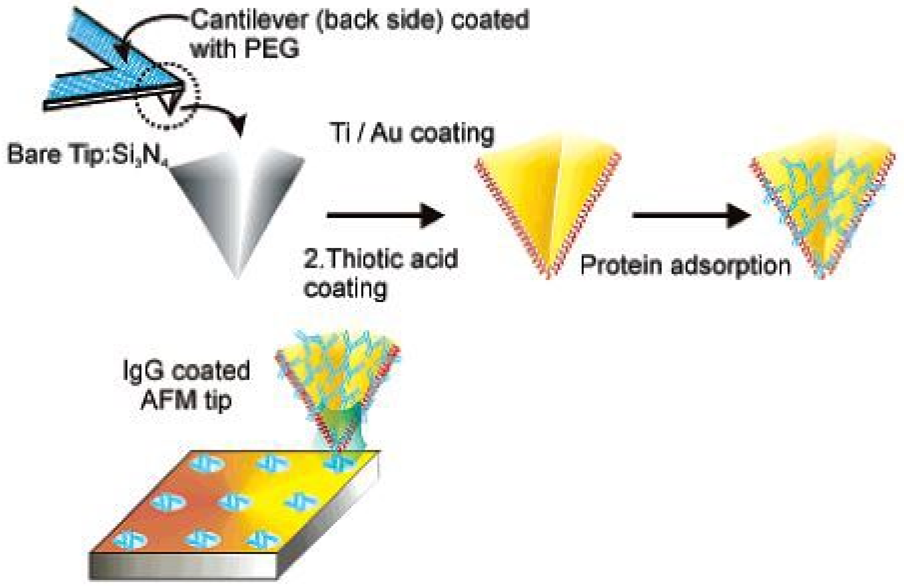
DPN can be used to construct protein nanoarray with several types of proteins

Protein Nanostructures (BSA)



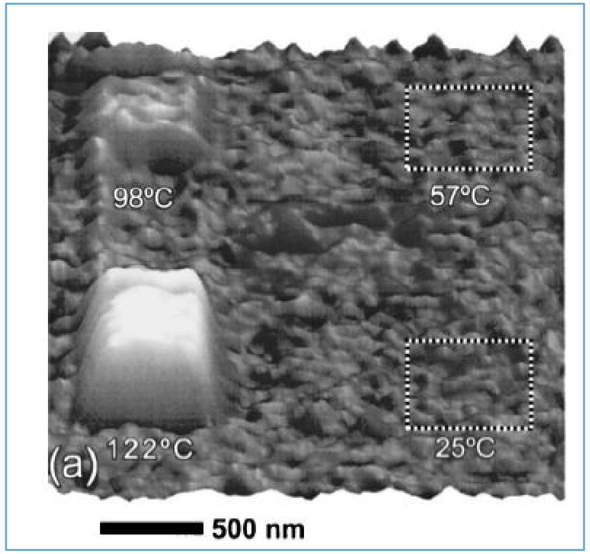
Zauscher *et al., Nanoletters,* **2002**, 2, 1203

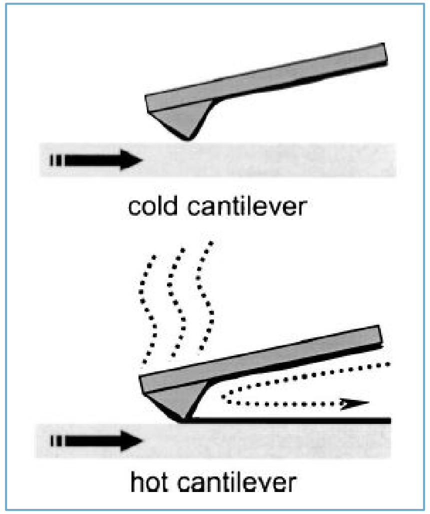
Lysozyme (Lyz) and rabbit immunoglobulin-gamma (IgG) nanoarray fabricated with DPN



Ki-Bum Lee et. Atl. *J. Am. Chem. Soc.*, **2003**, 125, 5588-5589

Dip – Pen Nanolithography (DPN)





Developed by William King (Georgia Tech) and Lloyd Whitman (Naval Research Lab)

Use solid inks – limit evaporation and run-off of the ink, result in sharper features

Use heated tips and polymer-based inks that melt around 100°C

Can be used in vacuum environment (thus compatible with conventional semiconductor manufacturing)

Sheehan, P. E. et al. *Appl. Phys. Lett.* **2004,** 85, 1589

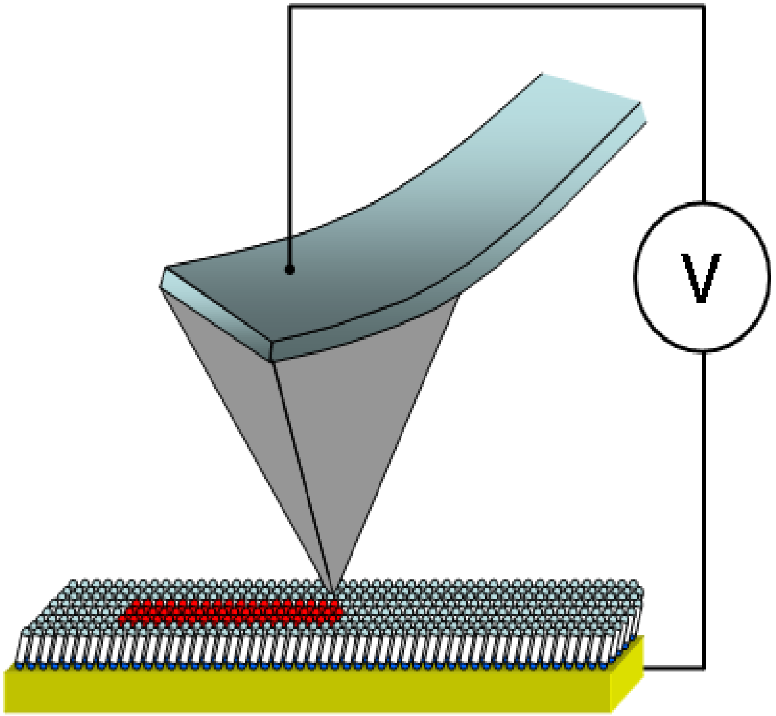
Electrochemical DPN

In this technique, the liquid meniscus is used as a nanometer-sized electrochemical cell in which metal salts can be dissolved, reduced into metals electrochemically, and deposited on the surface.

Li, Y. et al. *J. Am. Chem. Soc.* **2001**, 123, 2105-2106.

Anodization Lithography

Upon the application of small bias (typically between 2V and 20 V) an electrically-induced oxidation takes place under the AFM tip



Operating conditions:

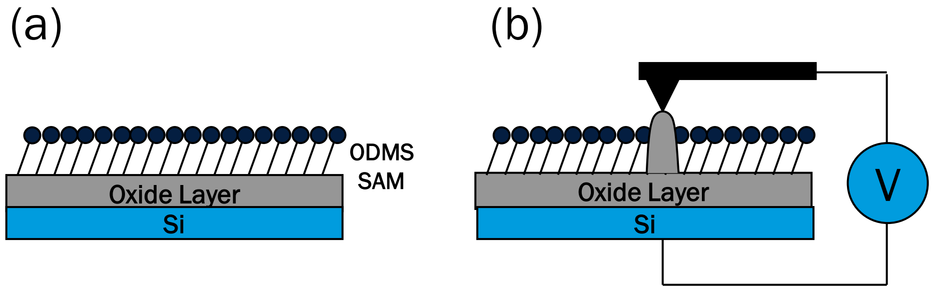
- Performed in air
- Tip is in direct contact with the sample during scanning

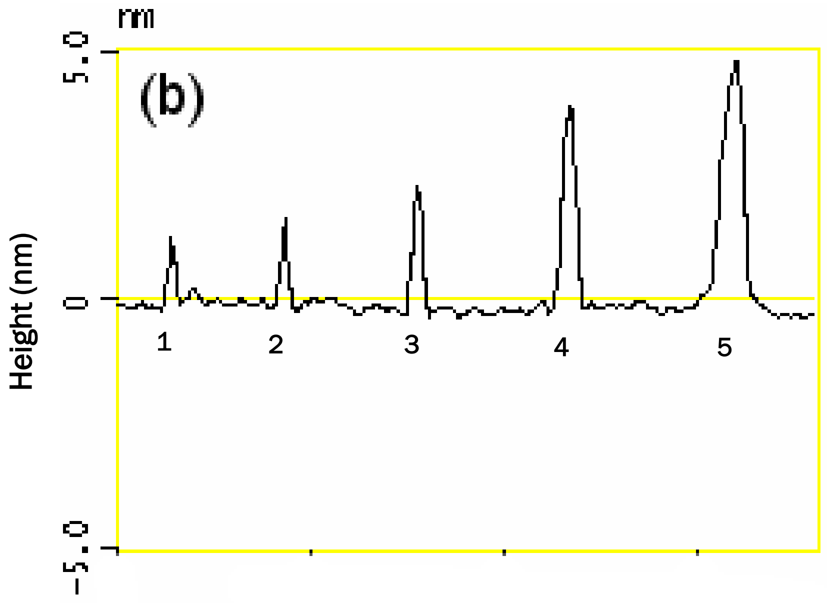
Gorman, C. et al. Chem. Rev. **2003,** 103, 4367.
Maoz, R. et al. Adv. Mater. **1999**, 11, 55.

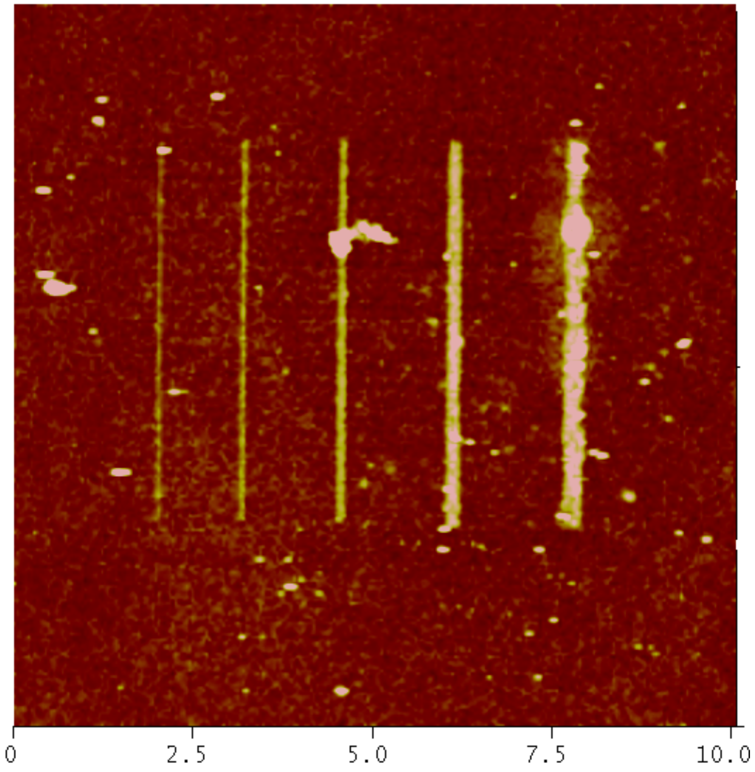
Anodization Lithography

When elevated bias voltages are applied, an electric field is generated between a conductive tip and a conductive/semi-conductive sample

Surface molecules beneath the tip will become oxidized or replaced.



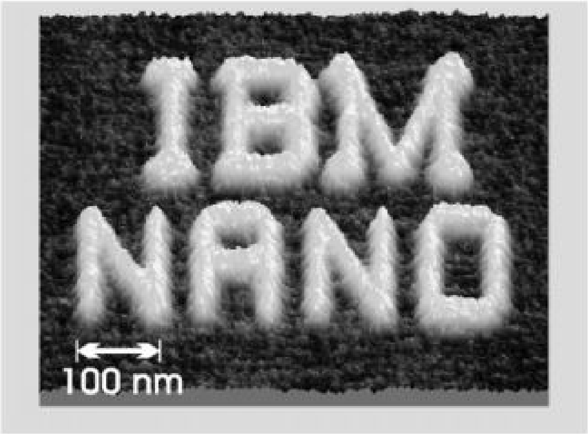




Lee, W. K. et Al. *Small*. 2006, 2, 848-853.

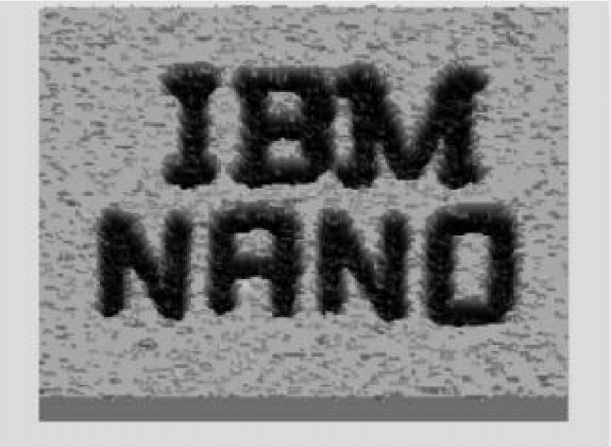
Anodization Lithography

This technique can be used to form raised patterns or trenches



Oxide can be used as a mask to etch the unprotected substrate

AFM-tip-induced oxide pattern on Si (100). Tip bias −10 V

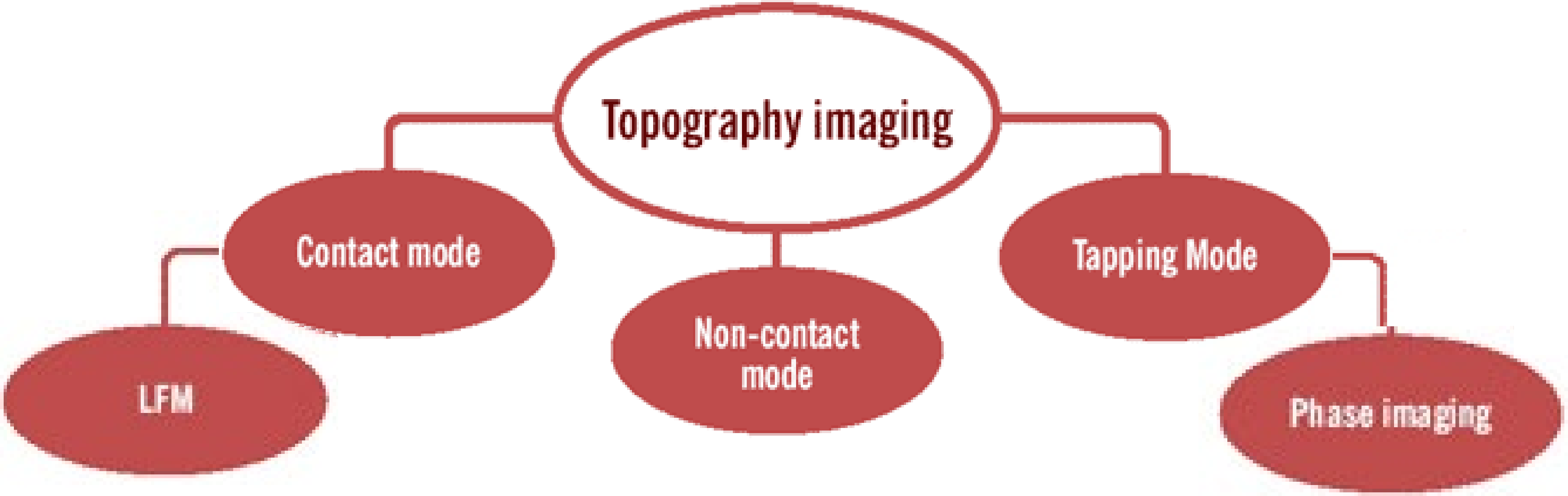


Removing the resulting oxide will leave the groove where the oxide used to be

After etching the oxide for 15 s using aqueous HF solution.

Avouris, P. et al. *Appl. Phys. A*, **1998**, 66, S659–S667.

Specialized AFM Operating Modes



Lateral Force Microscopy (LFM)

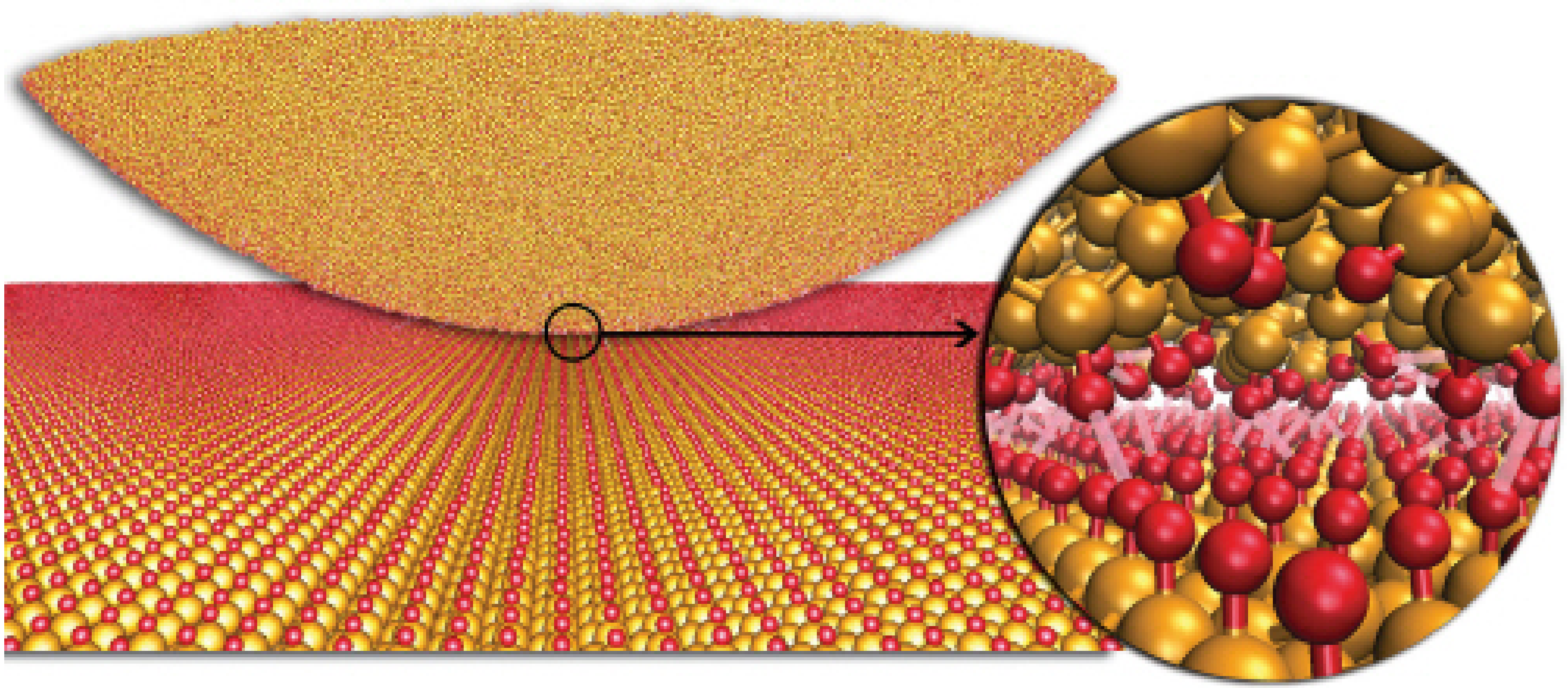
Lateral force microscopy (LFM) also known as frictional force microscopy (FFM) provides information about the mechanical interaction of the probe tip with the sample surface.

The lateral resolution allows to reveal tribological contrasts caused by material differences on heterogeneous surfaces.

https://www.youtube.com/watch?v=UKK9XoeeWBA

Nanoscale Friction

Nanoscale surfaces are rough, like a mountain range, where peaks correspond to individual atoms or molecules.



True contact area is due to the small fraction of tip-sample contact.

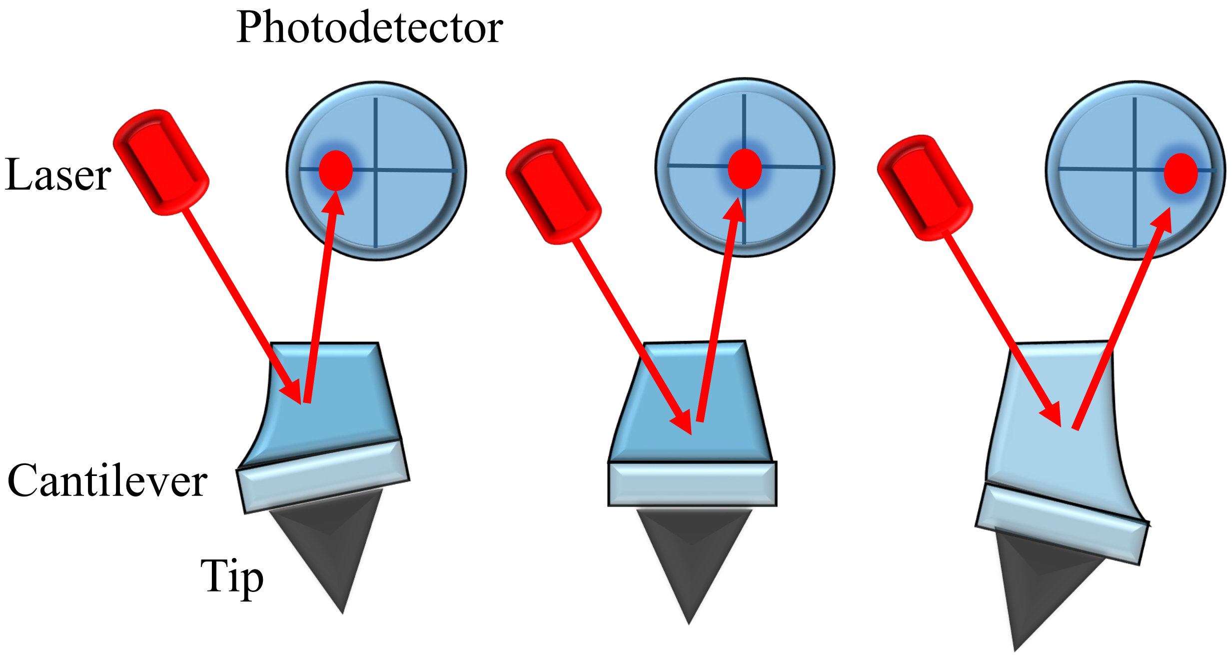
The force of friction is proportional to the number of atoms that interact between two nanoscale surfaces.

https://physicsworld.com/a/nanoscale-friction-thinking-big-helps/

https://nanohub.org/courses/AFM1/01a/outline/week4forcespectroscopy/l46forcespectroscopy-lateralforcemicroscopylfm

LFM – Probe Behavior

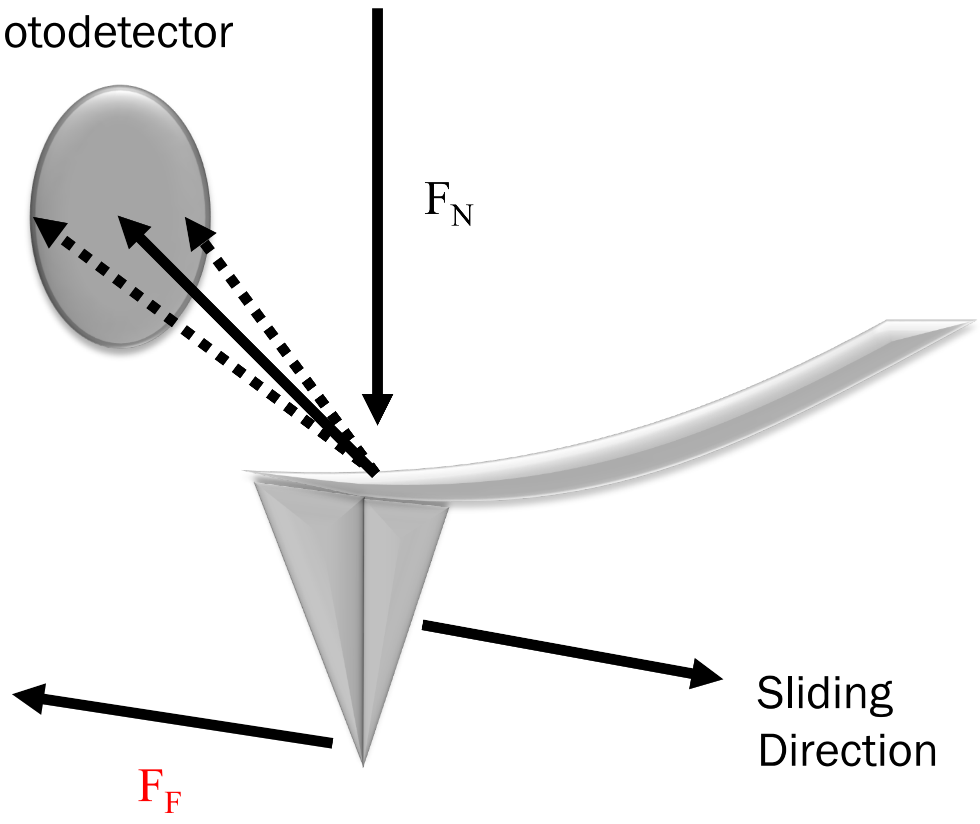
Lateral forces acting between the tip and sample causes the cantilever to twist. The twisting motion of the cantilever can be measured via the horizontal movement of the laser spot.



The lateral twisting of the cantilever is a measure of the friction encountered as the tip scans over the sample.

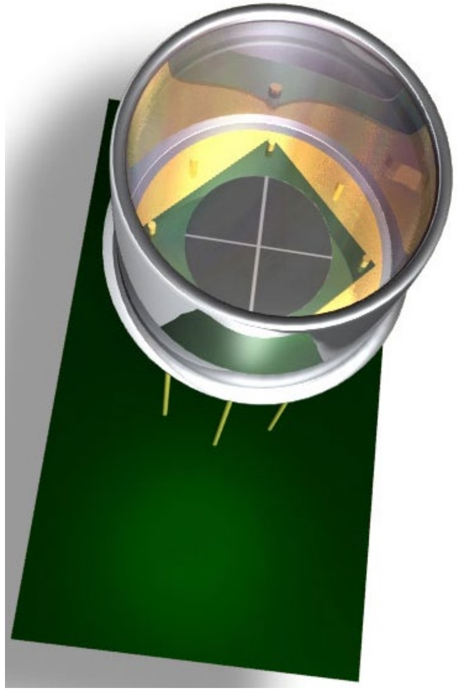
LFM – Probe Behavior

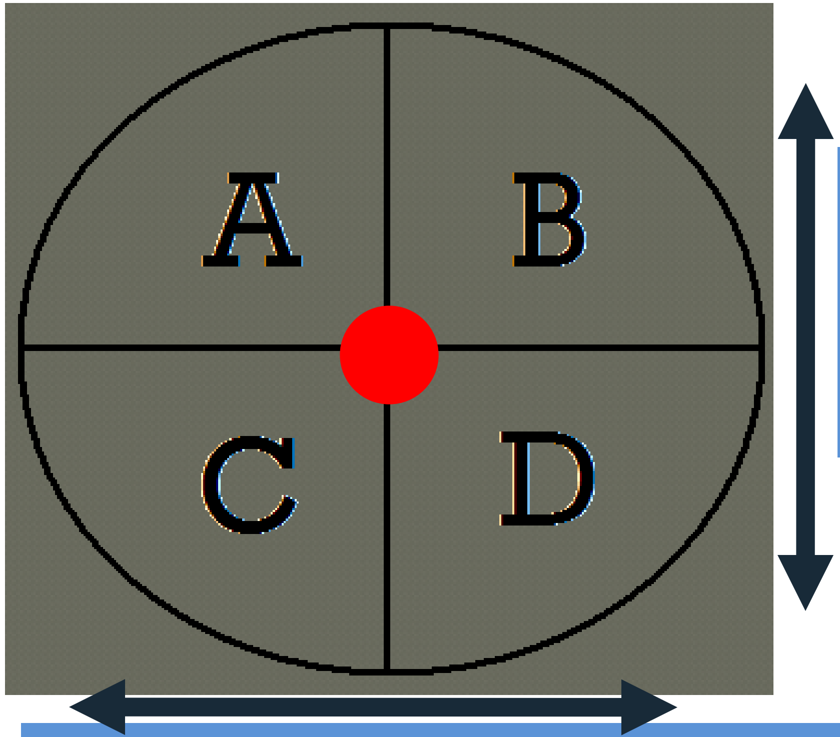
The cantilever will twist by a certain amount assuming there is some measurable lateral component to the tip-sample force (i.e. friction).



LFM – Photodiode Operation

The photodiode produces a signal based on the position of the reflected beam.

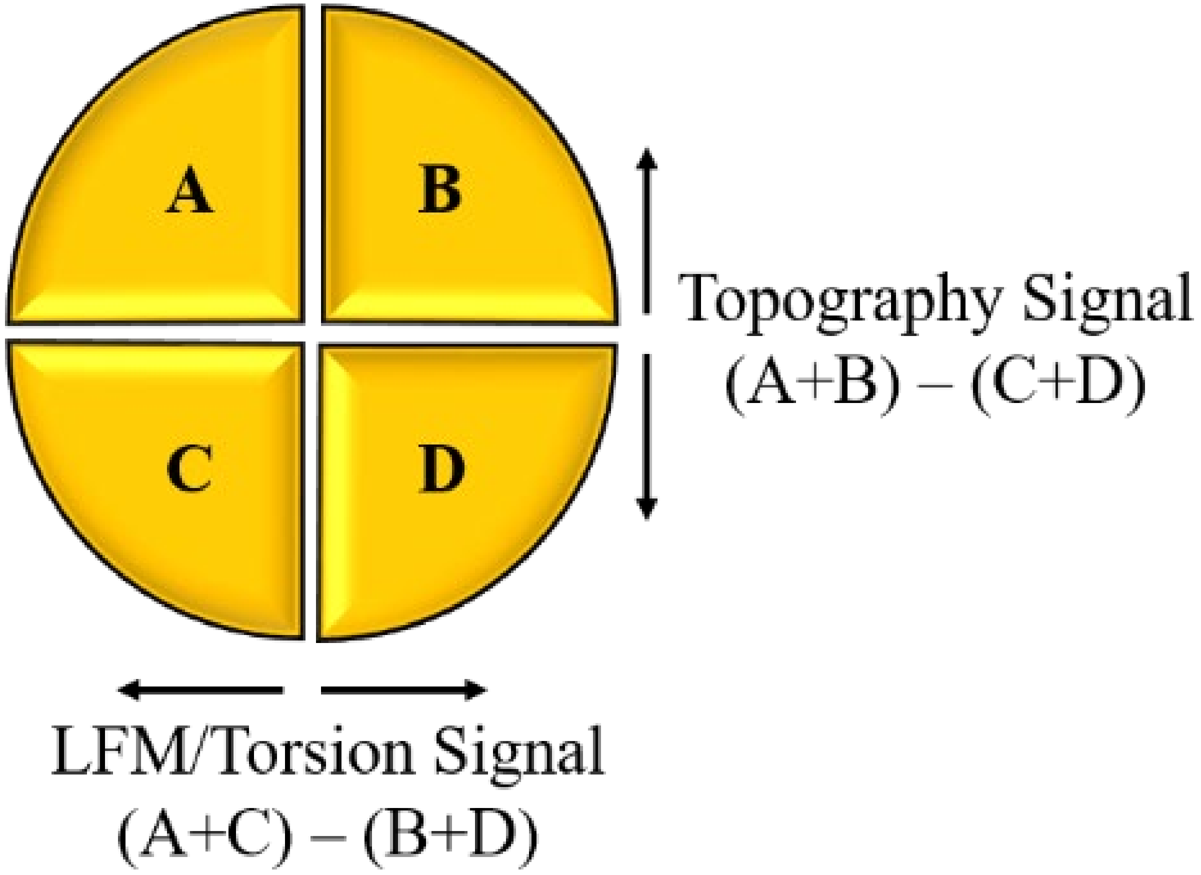




Deflection
Tip is moving up and down in response to surface contour.

Lateral Force
Tip is twisting. Used to produce a friction image.

LFM – Photodiode Operation



Topography Signal
(A+B) – (C+D)

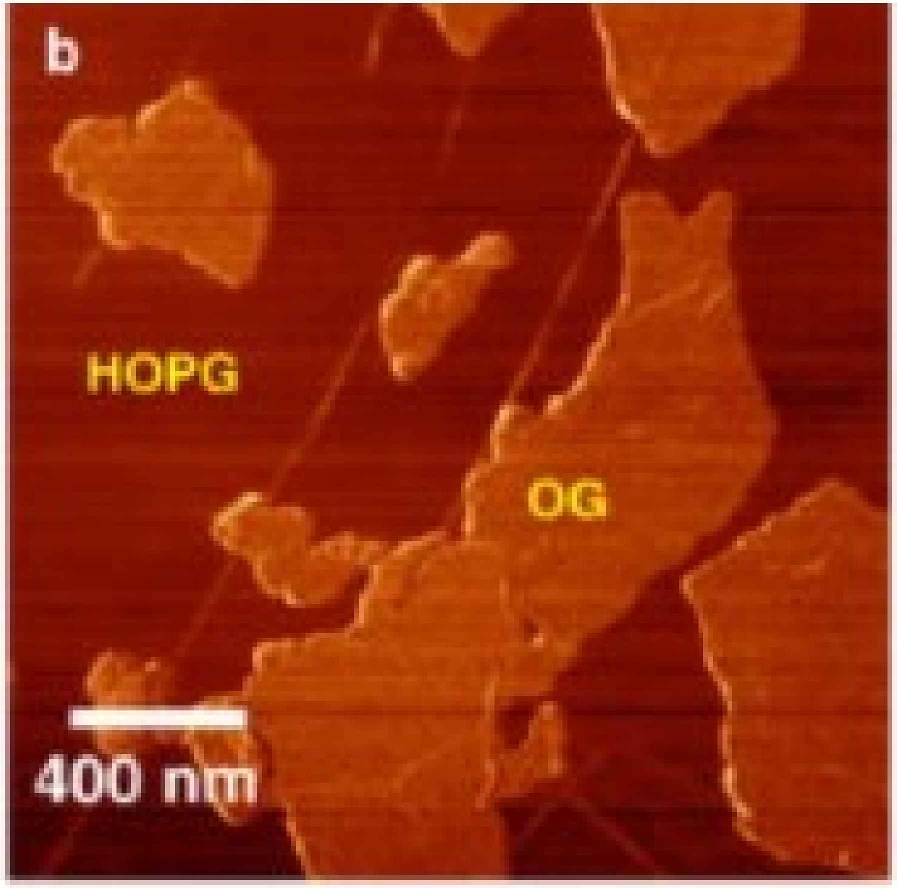
LFM/Torsion Signal
(A+C) – (B+D)

LFM – Applications

Heterogeneous surfaces produce images displaying significant contrast between different materials with high resolution.

Bright areas correspond to higher friction.

LFM can thus serve to identify partial coverage of a surface.



A lateral force image of oxidized graphene flakes on HOPG clearly indicates a difference between the lateral forces on HOPG and oxidized graphene.

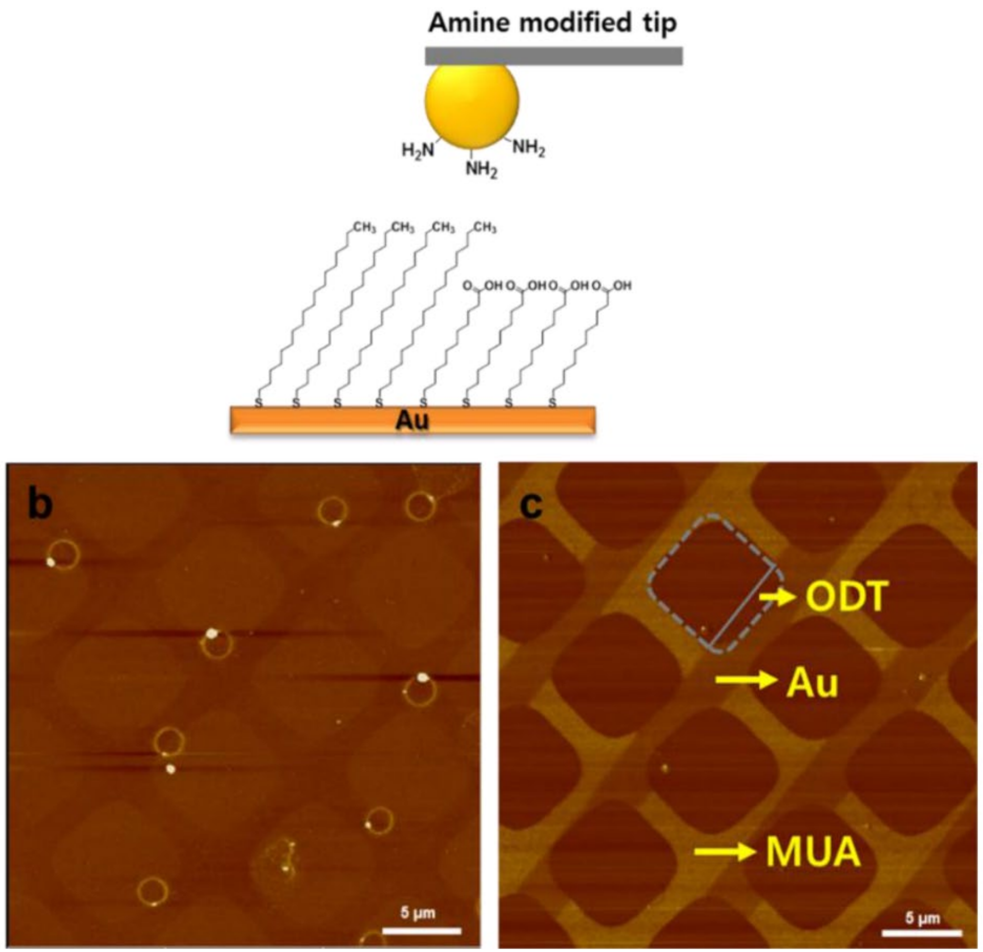
Pandey, D., et al. *Surf. Sci.* **2008.** 602, 1607-1613.

LFM – Applications

With appropriate functionalization, LFM mode can be used to distinguish between hydrophobic or hydrophilic areas on sample surfaces.

Similar chemical groups at the tip and the sample surface interact more than dissimilar groups.

A stronger interaction leads therefore to a higher friction between the tip and the sample (areas appear brighter).

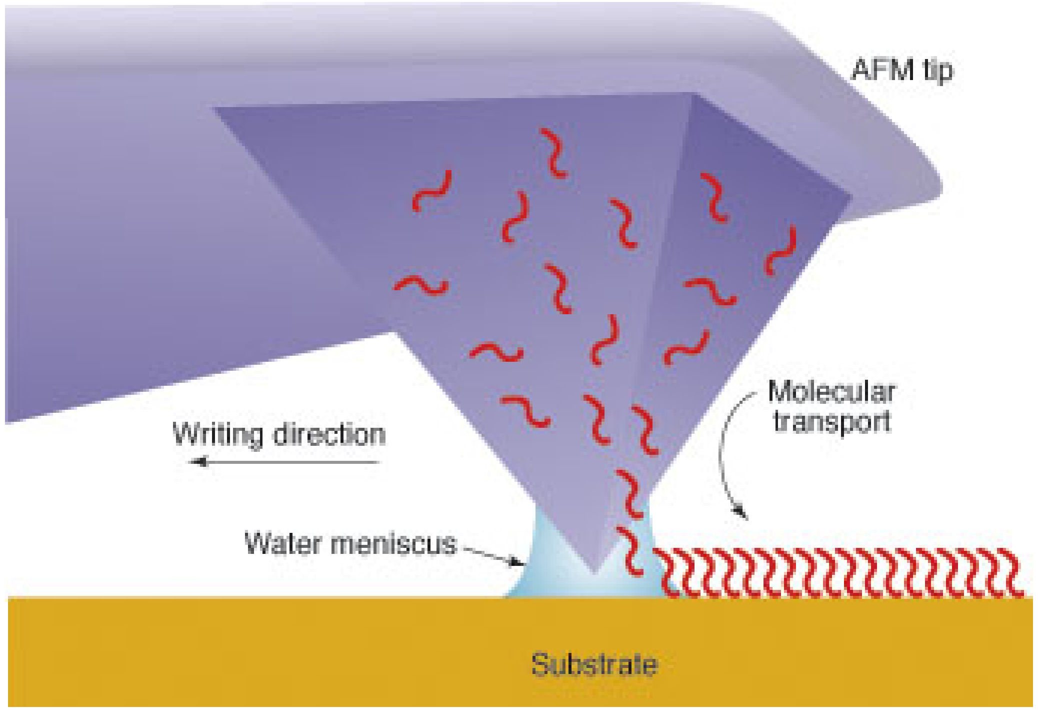


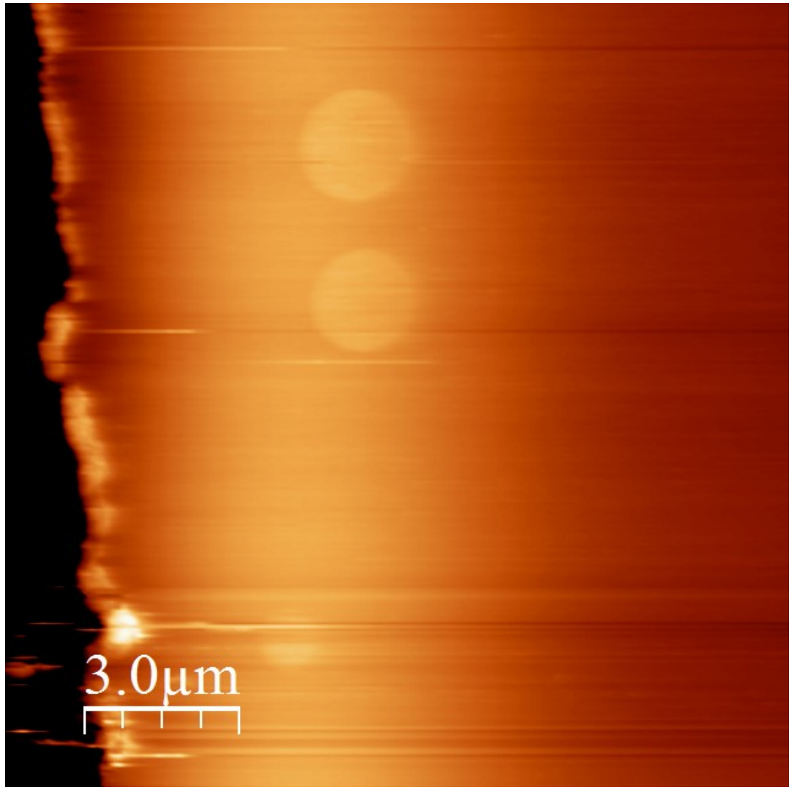
Chemical structure of the MUA/ODT pattern (**a**) Topography image (**b**) and Lateral force image (**c**) on the MUA/ODT pattern measured with an amine-modified ball tip (gray dash square: ODT pattern shape).

Lee, J. et al., *Sensors*. **2015.** 15, 30683-30692.

LFM – Applications

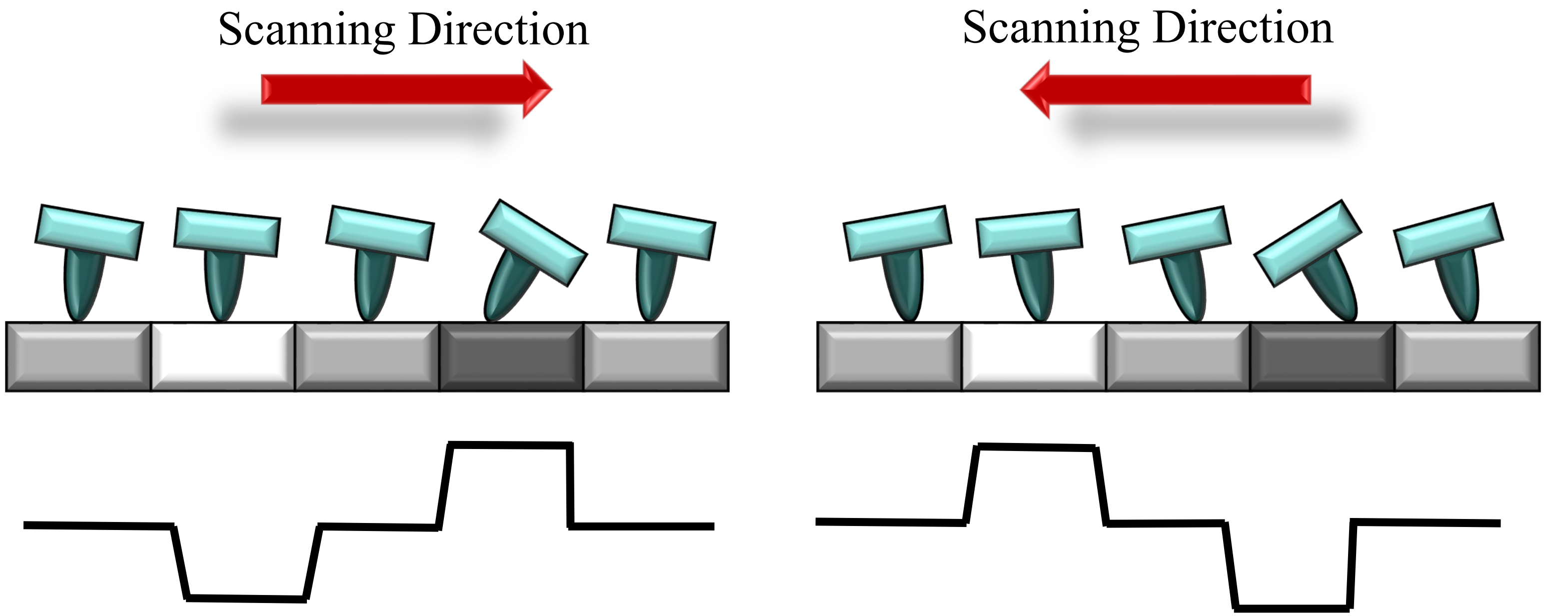
LFM is commonly used to image structures deposited by dip-pen nanolithography because the contrast is better than the topography image





LFM – Friction Loop

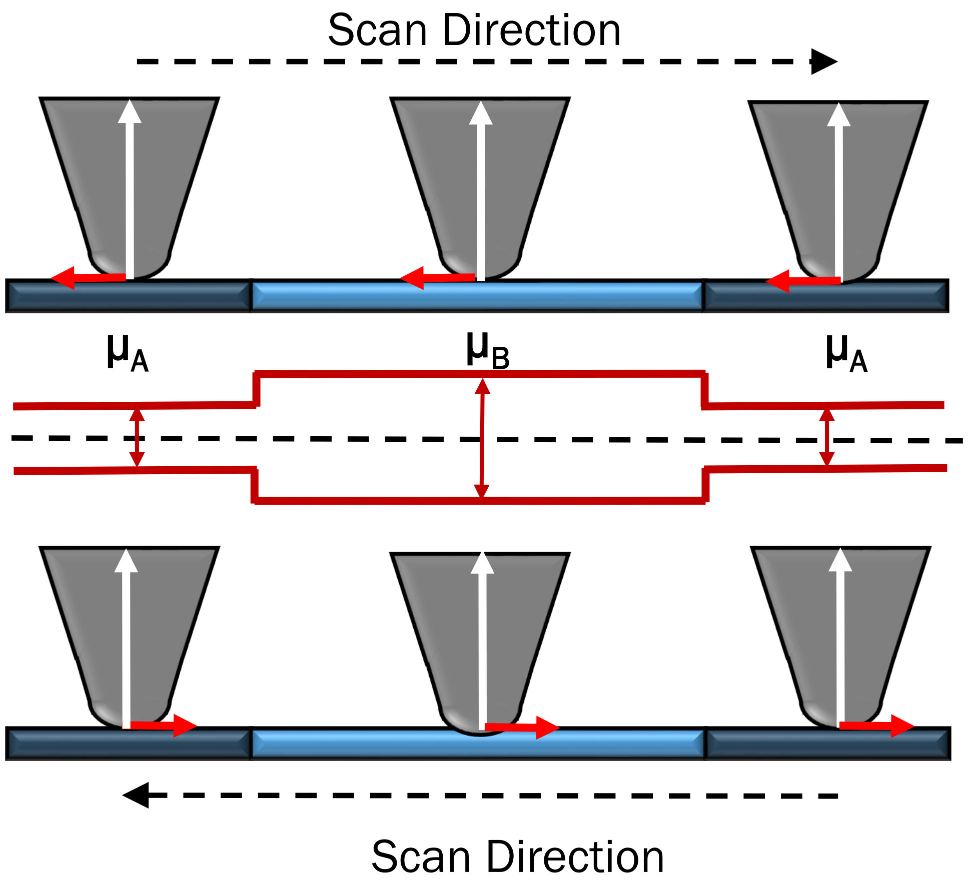
The lateral deflection signal will always be different in the forward and reverse scans.



Changes in friction due to material contrast will generate differences between the forward and reverse scans.

LFM – Friction Loop

Larger friction will give a greater difference between the forward and reverse scans, while lower friction will give a smaller difference.

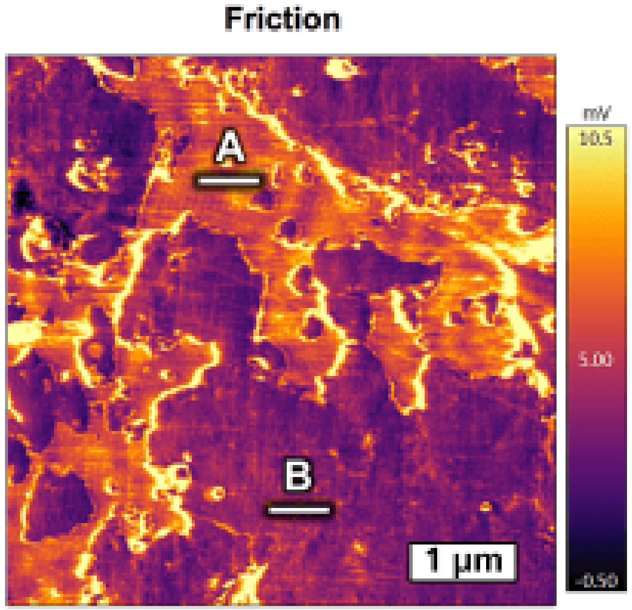


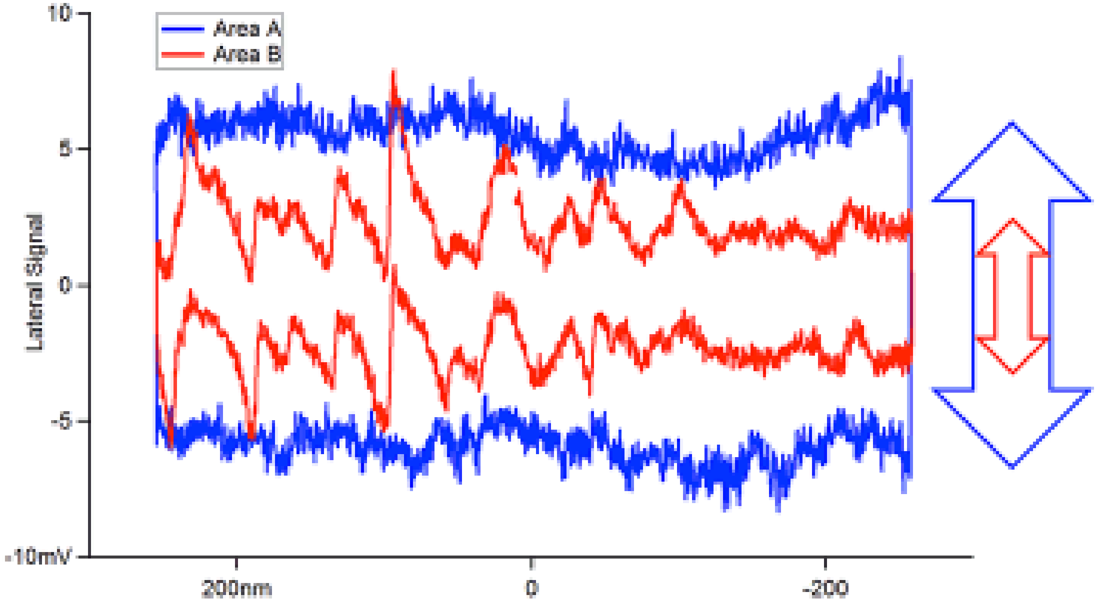
The actual friction measured is obtained by calculating the difference between the forward and reverse scans.

http://publish.uwo.ca/~hnie/spm.html

LFM – Friction Loop

Friction images reveals lower friction response on the raised film patches (i.e., plateaus B) versus the valleys (A).





Valleys (A) show a wider friction loop, indicating higher friction, while plateaus (B) show a tighter friction loop (lower friction)

This shows that the valleys have a different material composition

https://afm.oxinst.com/learning/view/article/there-is-the-rub-an-afm-investigation-of-tribofilm-formation

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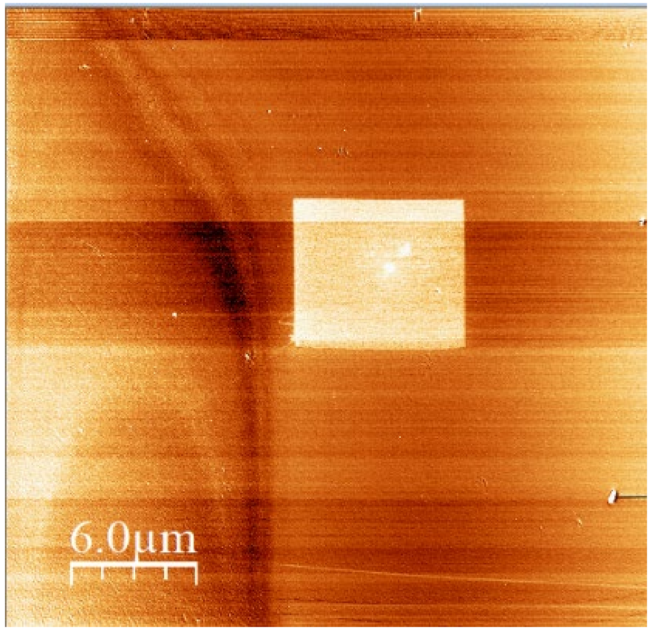
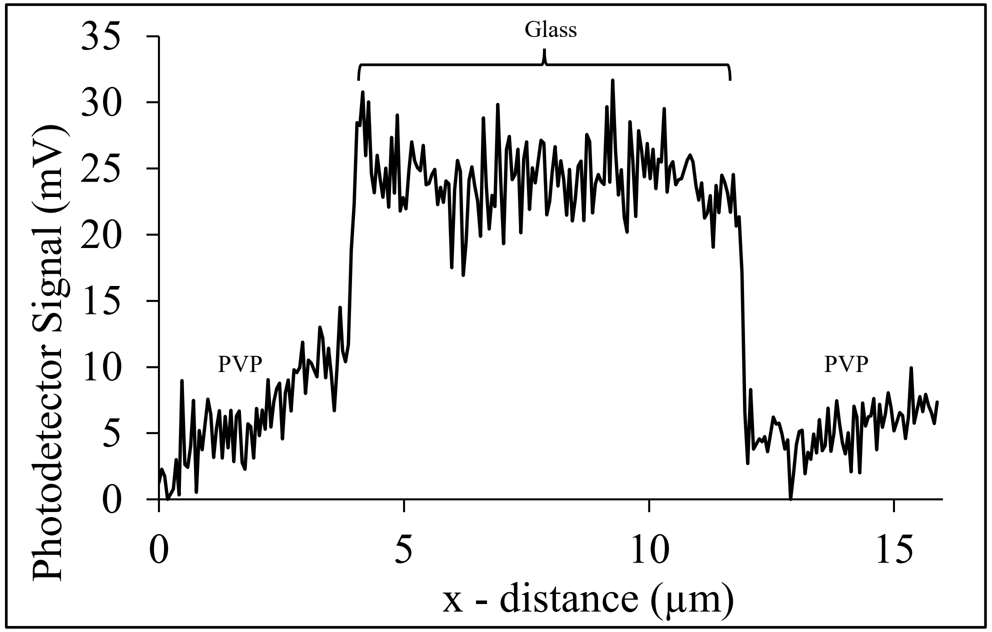
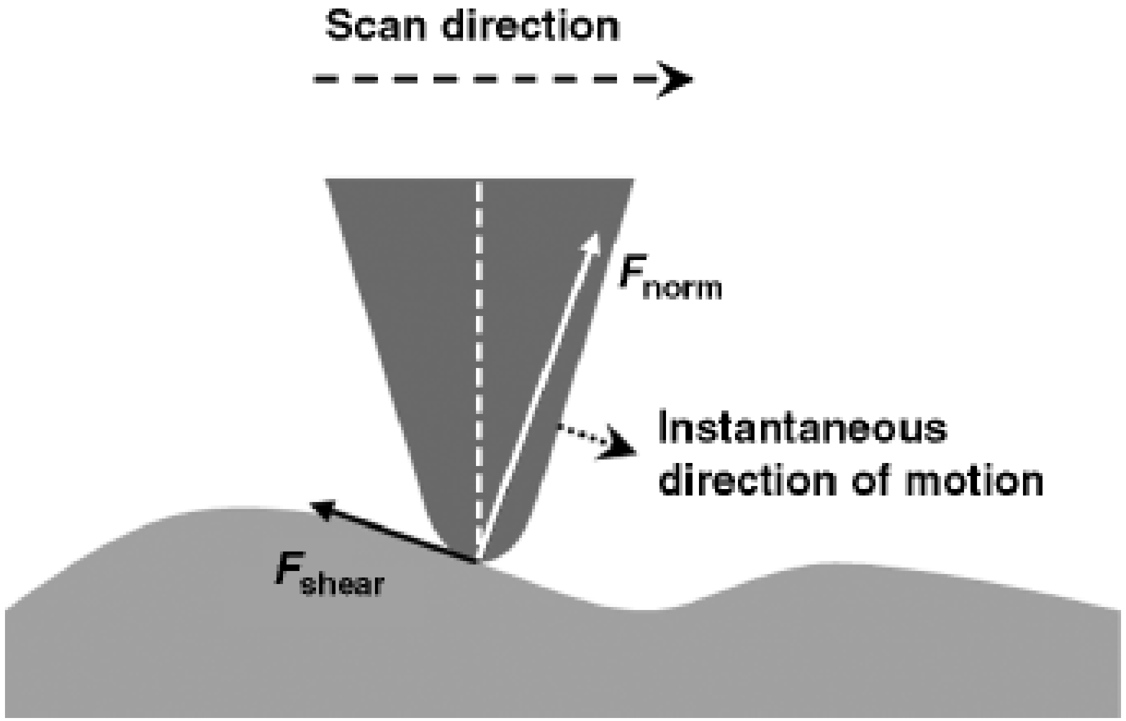




Brighter areas correspond to higher friction.

LFM Calculations

Friction signal arises from normal tip-sample forces and tangential shear forces.

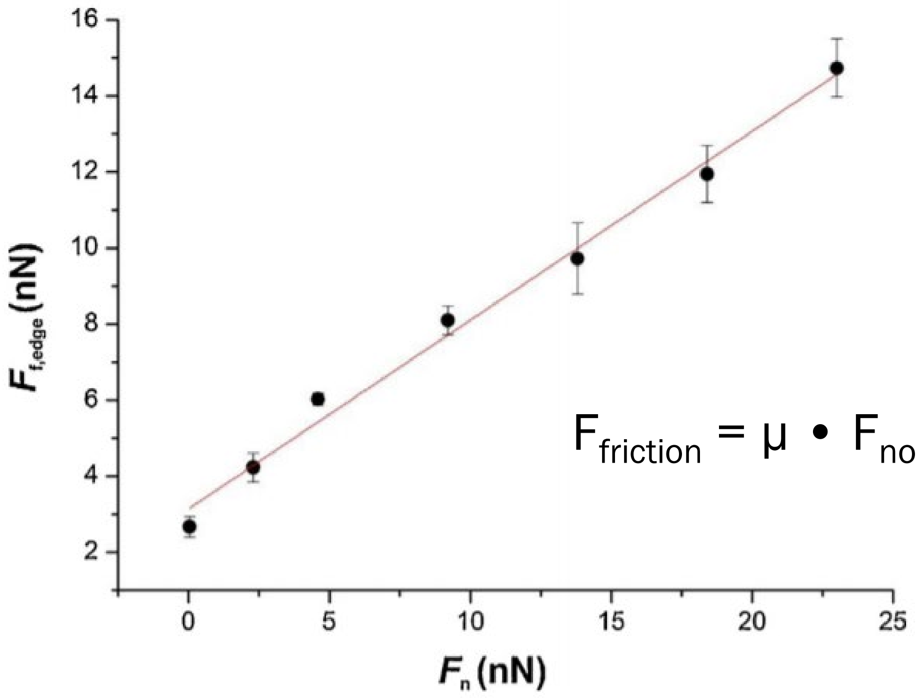


For a constant F_{norm}, the relationship between the magnitudes of these forces is:

$$F_{friction} = \mu \cdot F_{norm}$$

LFM Calculations

Coefficient of friction (μ) determination.



$$F_{friction} = \mu \bullet F_{norm}$$

Fig. 8. Experimental data demonstrating the dependence of increased friction forces at AuNP edges ($F_{f,edge}$) on normal load (F_n) for a representative AuNP of 128 nm height. As expected from analytical calculations regarding the *ratchet* effect occurring during AFM measurements on sloped surfaces [38], $F_{f,edge}$ increases substantially with increasing F_n, following a reasonably linear trend.

E. Cihan et al., *Appl. Surf. Sci.,* **2015,** 354, 429-436.

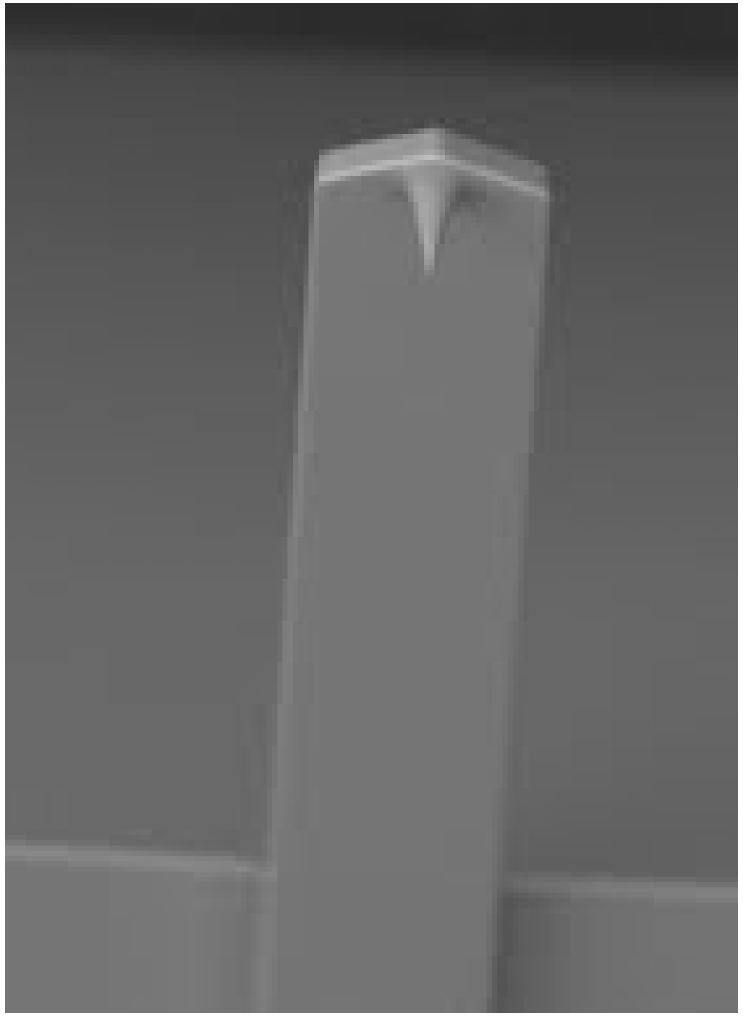
LFM Calculations - Cantilever Spring Constant

Vertical Spring Constant (k): Cantilever stiffness

$$k = \frac{Et^3 w}{4l^3}$$

E = Young's modulus
t = thickness
w = width
l = length

The stiffness of the cantilever is very important probe parameter that affects the image quality; when the AFM operating mode is changed, a different stiffness is required.



LFM Calculations - Cantilever Spring Constant

To determine frictional forces (F_f), the torsional spring constant of the cantilever (k_t) must be determined:

$$k_t = w \times \frac{t^3}{l} \times \frac{1}{(H + \frac{t}{2})^2}$$

k_t = torsional spring constant

w = cantilever width

t = cantilever thickness

l = cantilever length

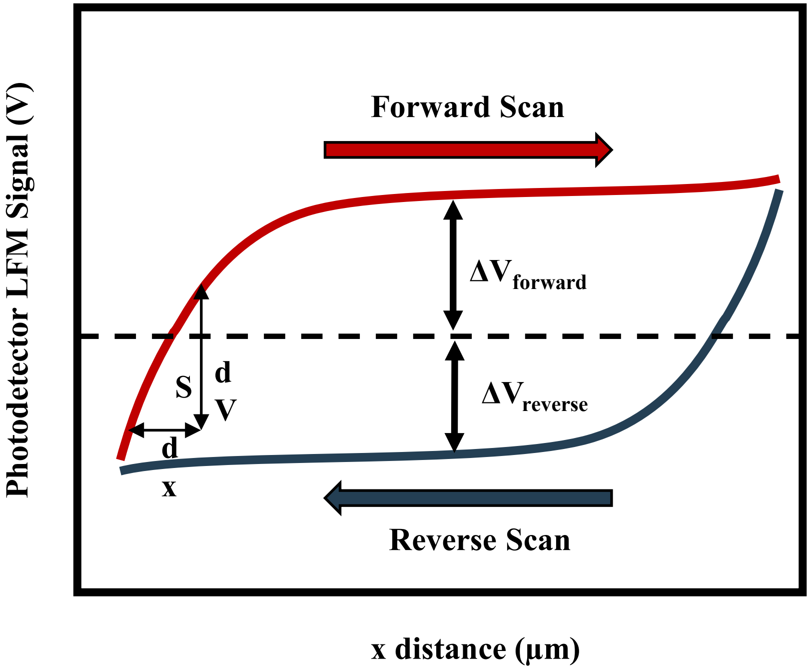
H = tip height

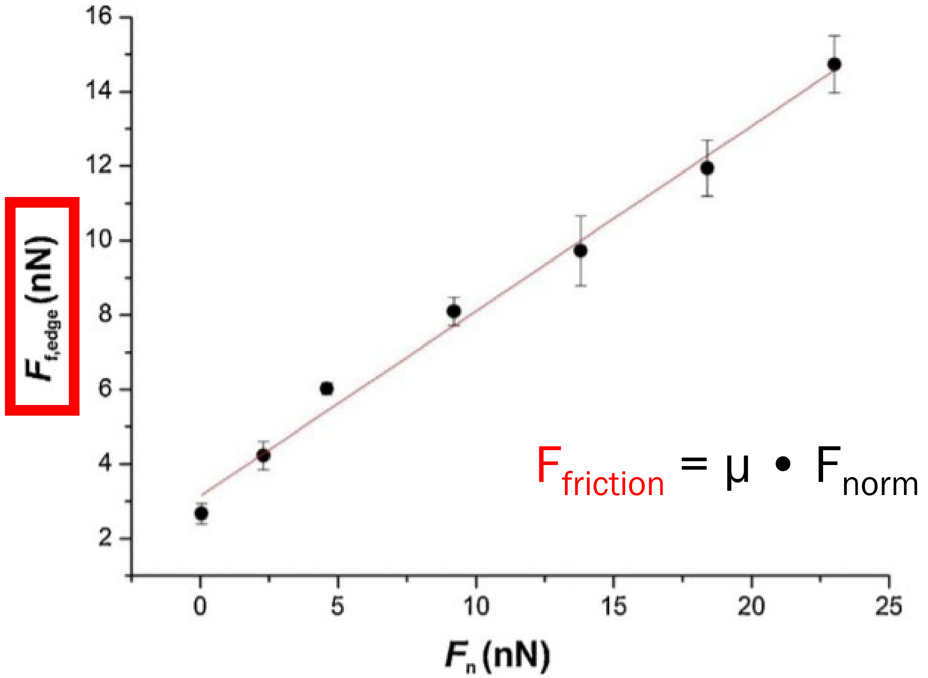
$$F_f = \frac{\Delta V \times \boldsymbol{k_t}}{S}$$

LFM Calculations

Use the torsional signal difference **(ΔV)** in V, cantilever torsional sensitivity **(S)** in m/V, and cantilever torsional coefficient **(k_t)** in N/m to determine the frictional force **(F_f)**.

$$F_f = \frac{\Delta V \times k_t}{S}$$

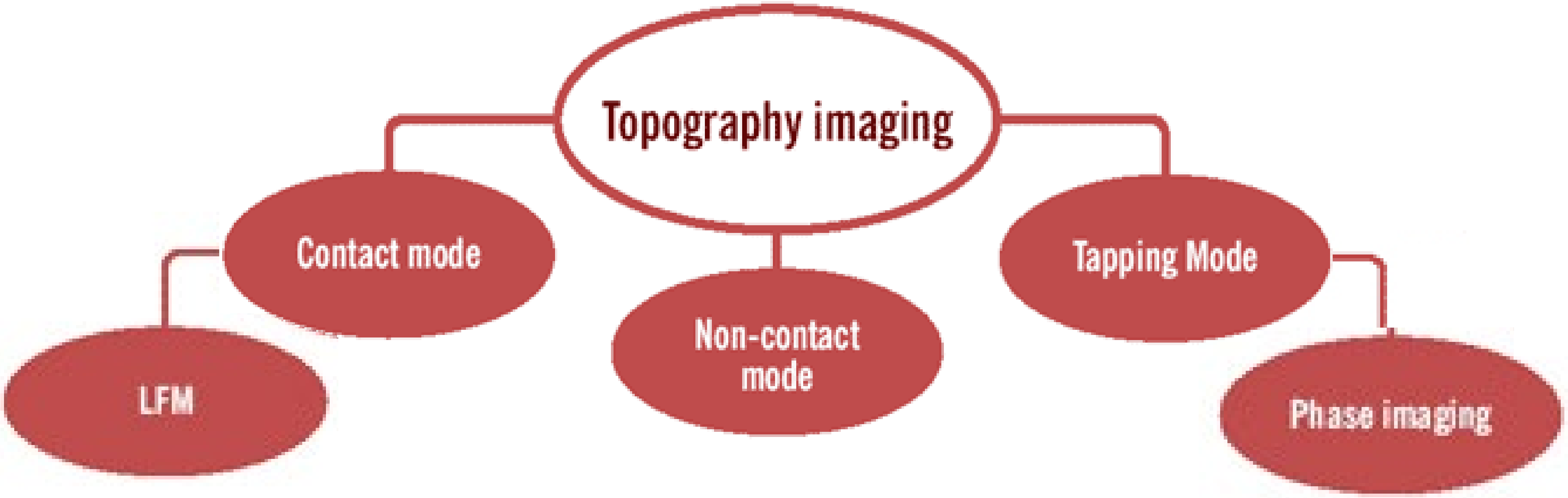




$F_{friction} = \mu \bullet F_{norm}$

Fig. 8. Experimental data demonstrating the dependence of increased friction forces at AuNP edges ($F_{f,edge}$) on normal load (F_n) for a representative AuNP of 128 nm height. As expected from analytical calculations regarding the *ratchet* effect occurring during AFM measurements on sloped surfaces [38], $F_{f,edge}$ increases substantially with increasing F_n, following a reasonably linear trend.

Specialized AFM Operating Modes



Tapping Mode

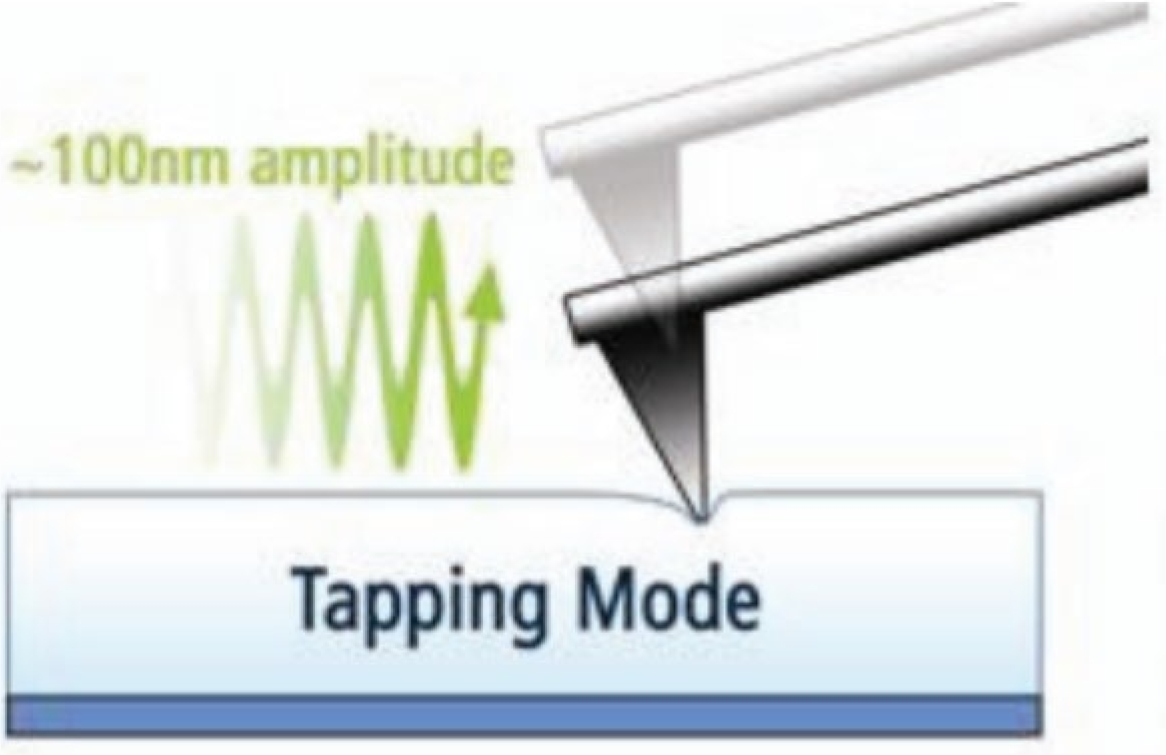
The cantilever vibrates at or near its resonance frequency (100 – 400 kHz).

The “resonance frequency” is defined as the driving frequency at which vibrational amplitude (A) is maximized.

Resonance frequency (f) :

$$f = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

m = mass
k = spring constant



Tapping Mode

A piezoelectric transducer shakes the cantilever holder at or near its resonant frequency.

Cantilever resonant frequencies are generally between 100-400 kHz.

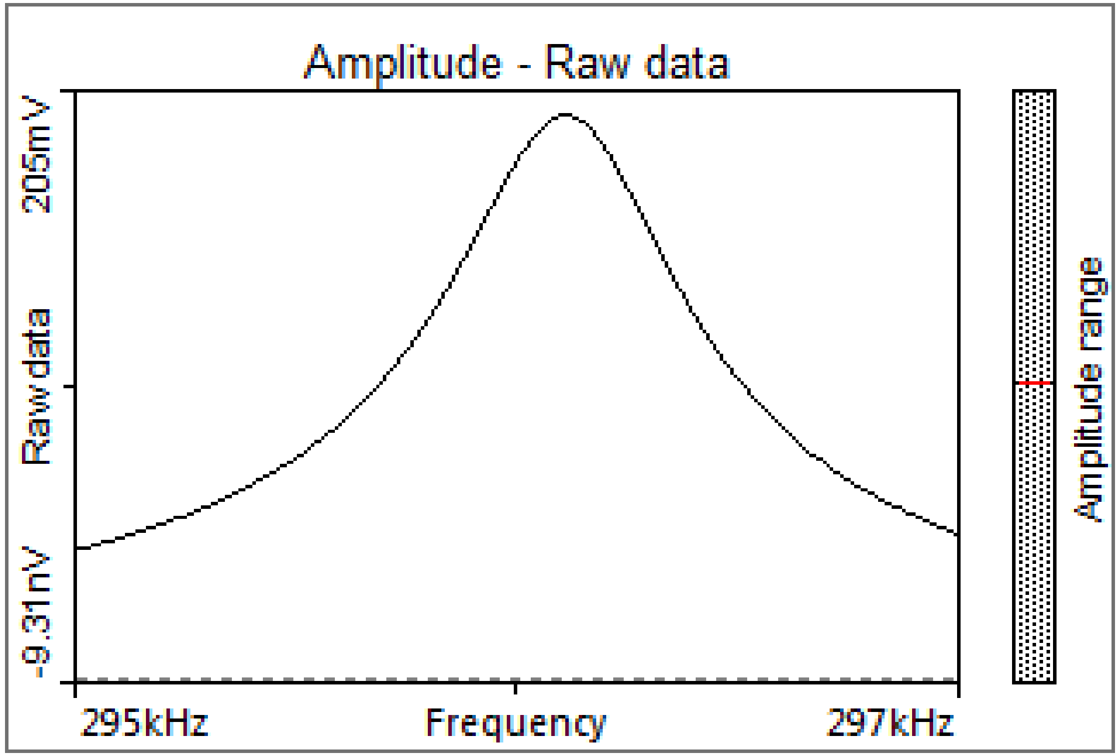
The “resonance frequency” of the oscillator is defined as the driving frequency at which vibrational amplitude (A) is maximized. The resonant frequency (f_o) of the tapping mode cantilever is determined using:

$$f_o = \frac{1}{2\pi}\sqrt{\frac{k}{m_{eff}}}$$

where m_{eff} is the is the effective mass and k is the spring constant (Wang 2013).

Resonance Frequency

In dynamic mode, the cantilever is generally driven with a shaker piezo and starts vibrating at the excitation frequency.

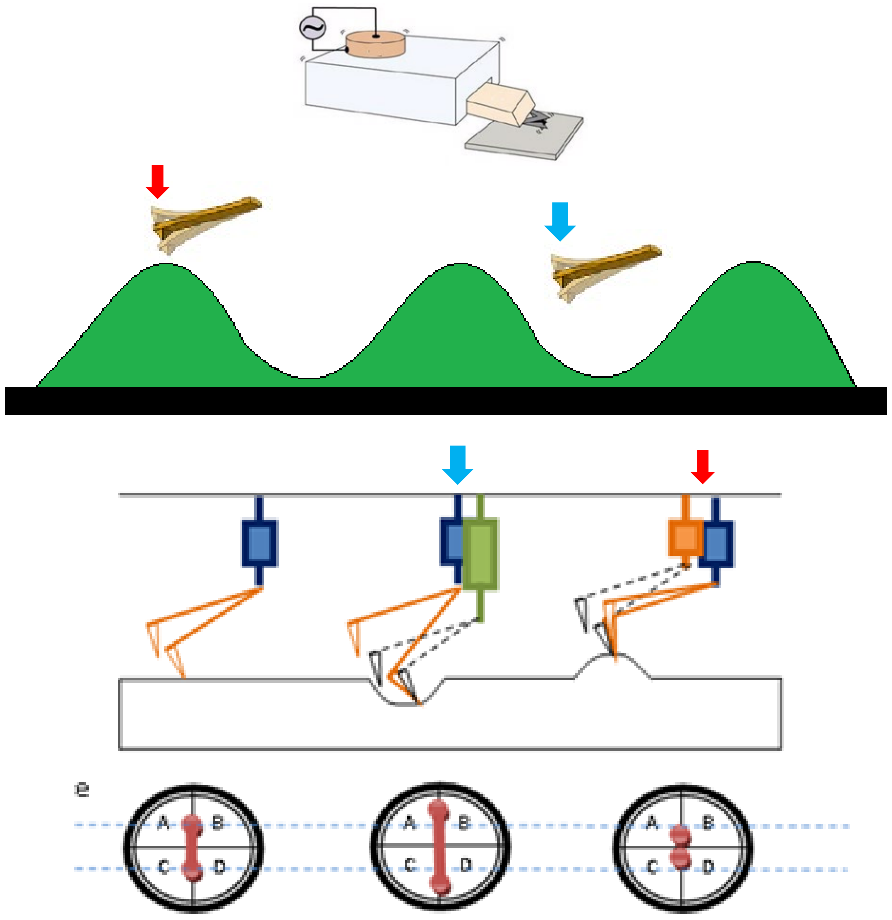


By sweeping the frequency across a suitable range, the peak in the frequency spectrum that corresponds to the resonance frequency of the cantilever can be found.

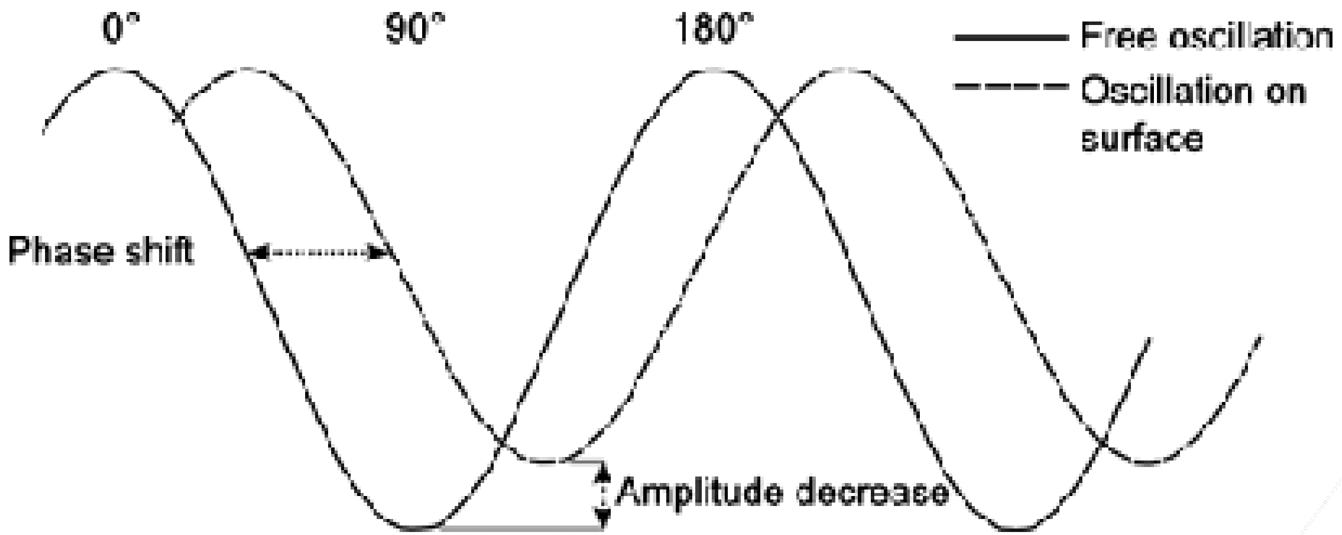
https://www.nanosurf.com/en/support/afm-modes#dynamic

Vibrational/Oscillation Amplitude

Cantilever is oscillated at its resonant frequency



As the oscillating cantilever is brought closer to the surface, the cantilever cannot oscillate at its full amplitude anymore and the amplitude of oscillation is reduced.

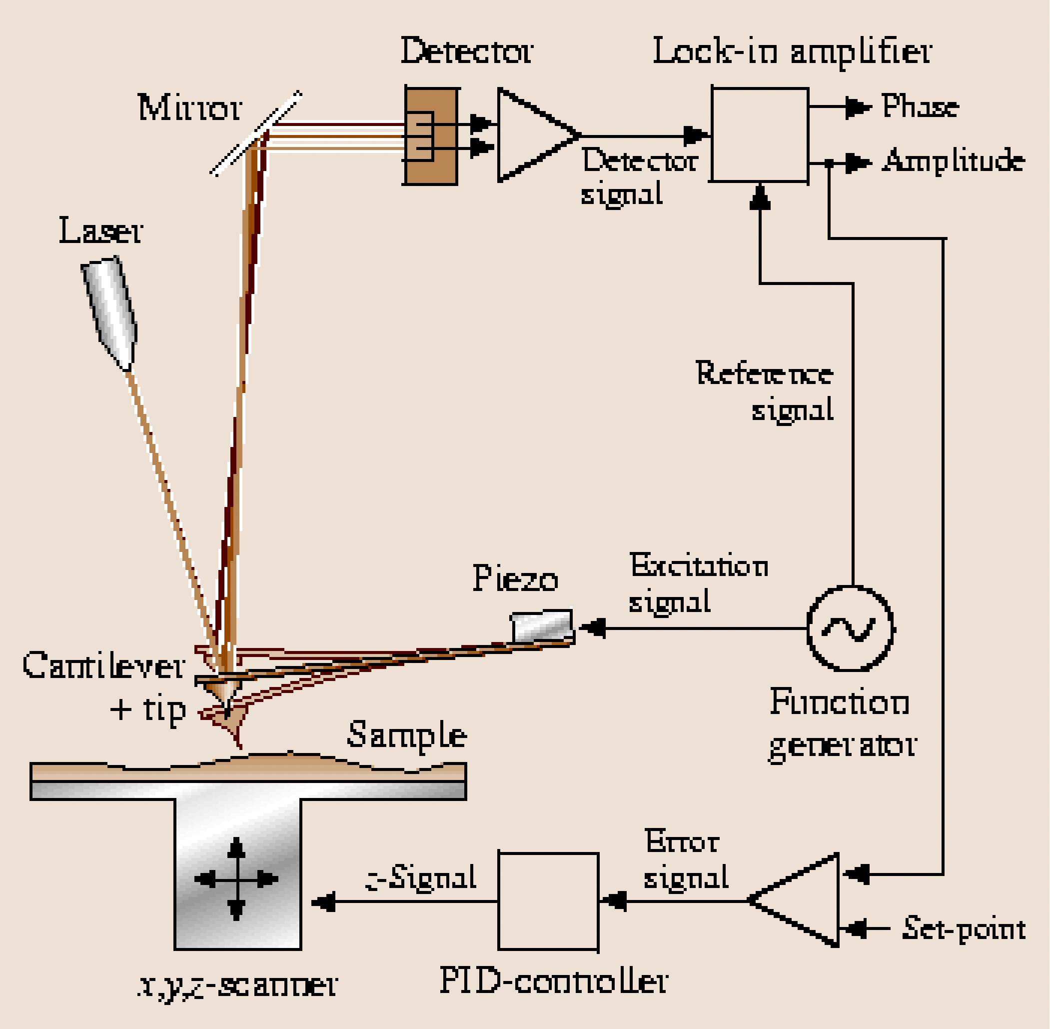


Feedback Loop

During tapping mode AFM, a shift in resonance frequency and a change in vibrational amplitude is detected using a feedback system.

The most commonly measured signal in tapping mode is the oscillation amplitude and is kept constant via the feedback mechanism.

The feedback loop matches the measured amplitude to the setpoint value by changing the *z*-position of the sample.

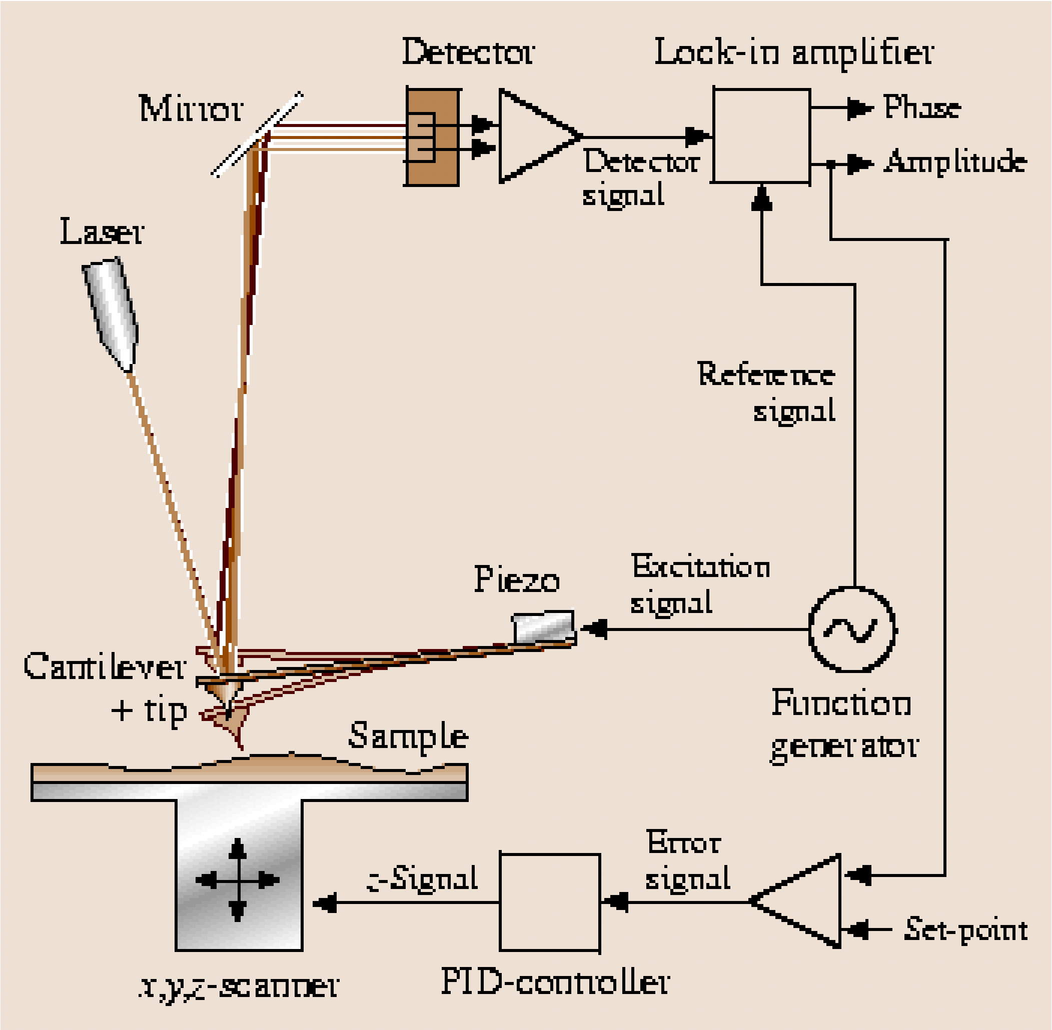


Feedback Loop

Raising or lowering the z-piezo adjusts the oscillation amplitude to restore the original set point value.

As the feedback loop maintains a constant oscillation amplitude throughout a scan, the feedback signal corresponds to a height profile.

Thus, the *z*-feedback signal is used to map topography during data acquisition.

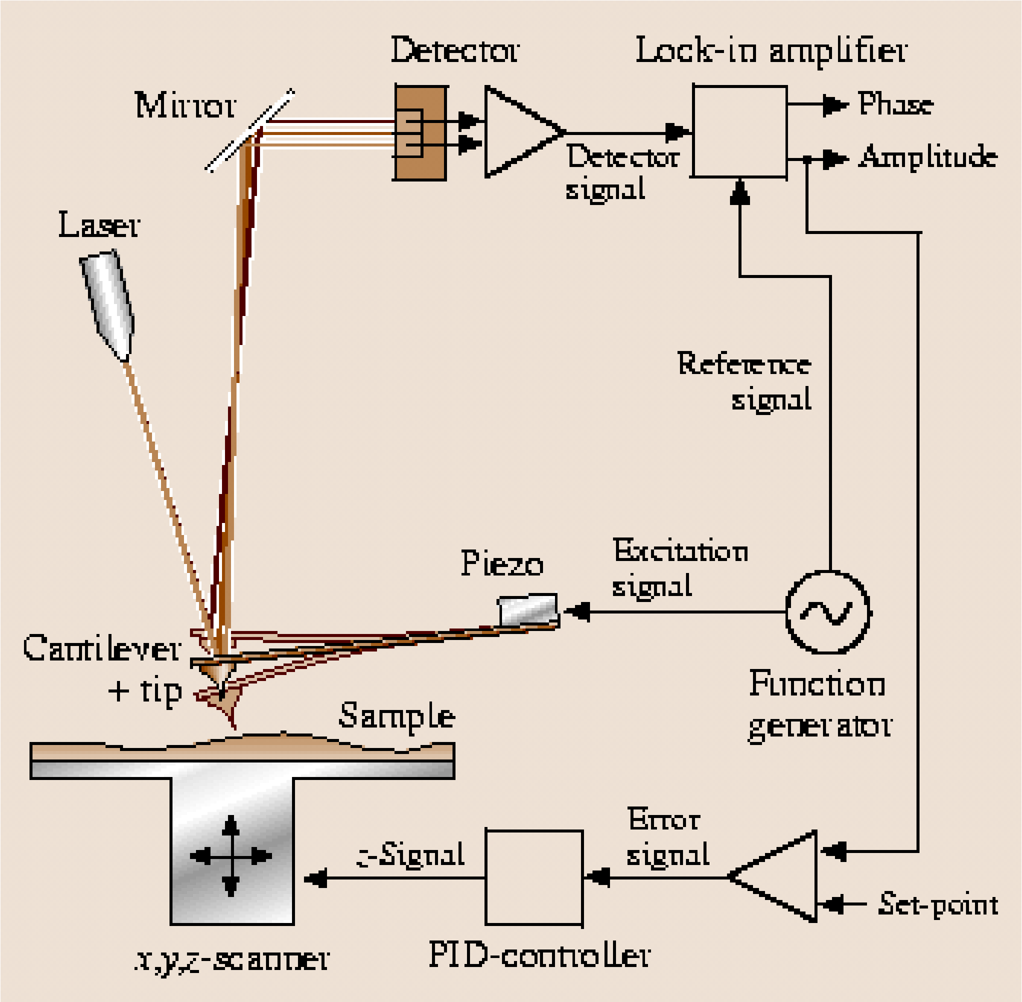


Lock-In Amplifiers

Typical Tapping Mode operation is carried out using amplitude modulation detection with a lock-in amplifier.

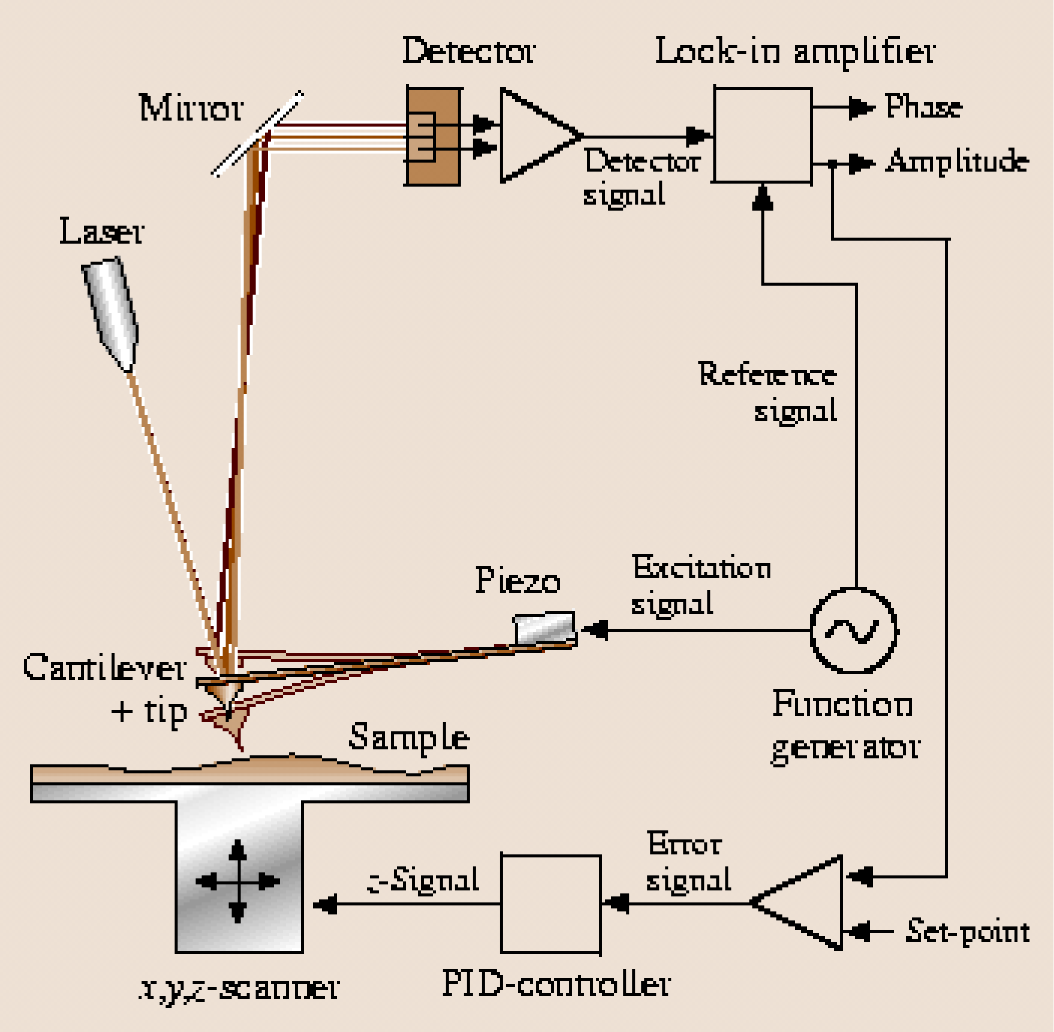
Lock-in amplifiers are used to detect and measure very small AC signals

Lock-in amplifier set-up: The lock in amplifier compares an input signal to a reference signal $V_r(t)$ to determine the amplitude (R) and phase (θ).



http://www.physik.uni-augsburg.de/~guenter/fp12/3_SR830_28-56.pdf

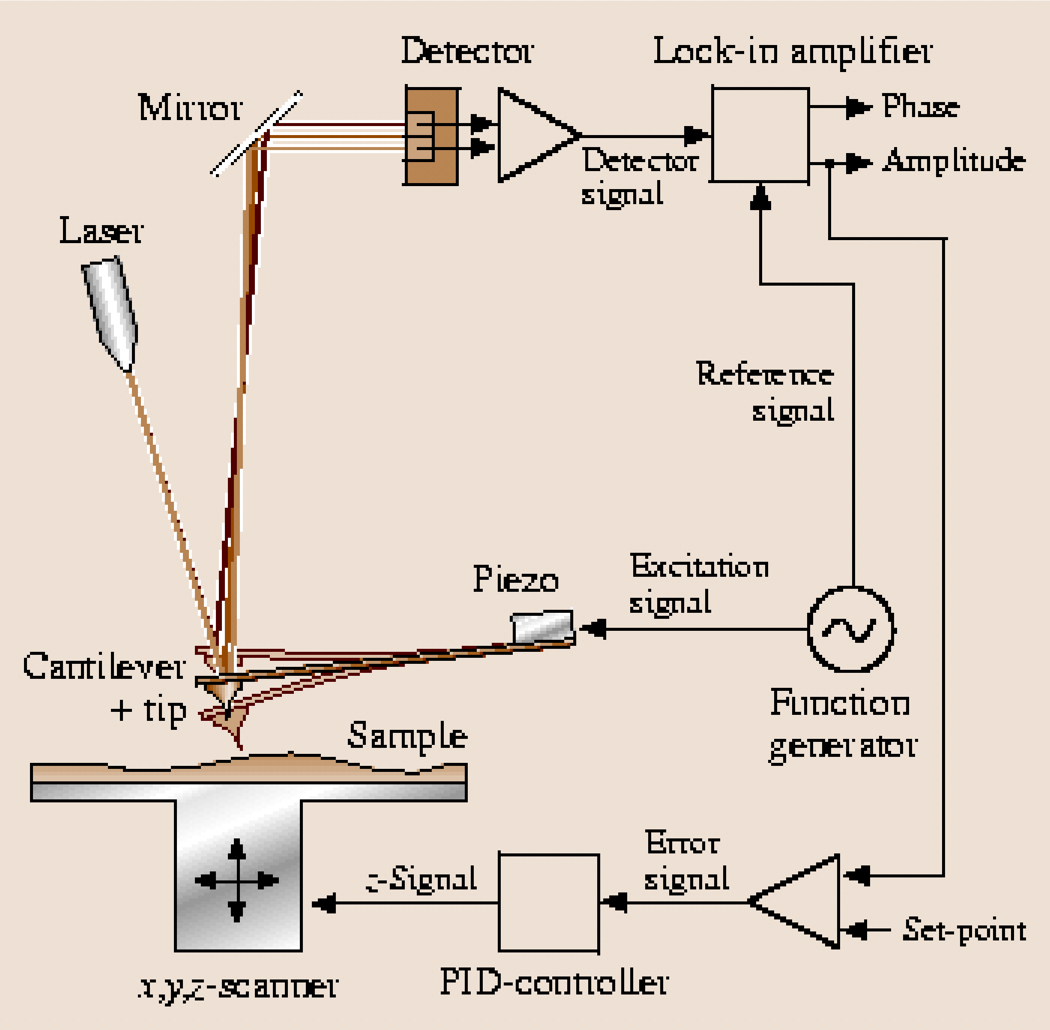
Lock-In Amplifiers



Determination of the amplitude and phase is achieved using a dual-phase demodulation circuit.

The input signal is split and separately multiplied with the reference signal and a 90◦ phase-shifted copy of it.

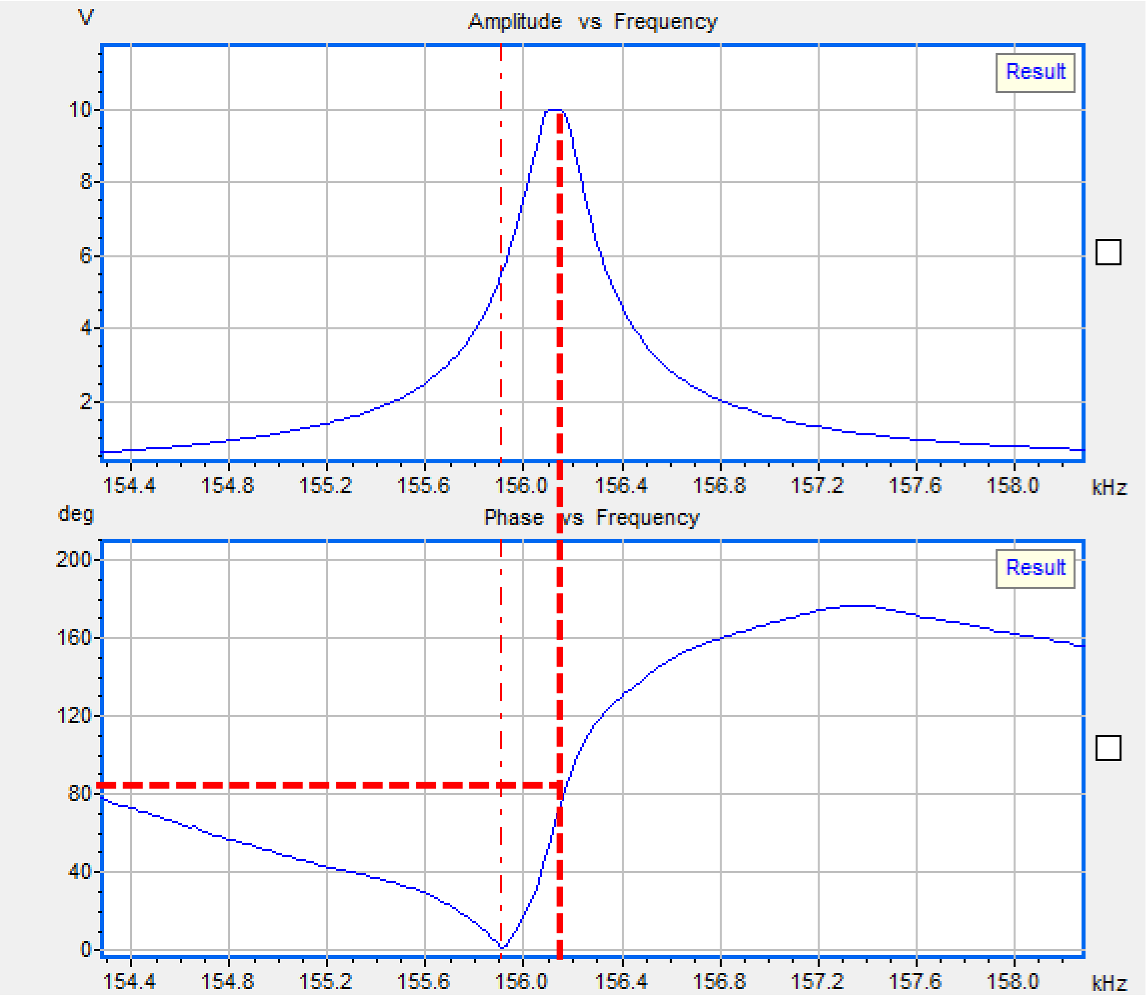
Lock-In Amplifiers



The signals are filtered to reject the noise and finally converted into amplitude (R) and the phase θ signals.

Tuning the Cantilever

The phase angle is 90˚ at the resonance frequency.



This occurs when the probe is far from the sample and there is no interaction between the AFM tip and the sample.

Oscillating Mode Parameters

1. **Cantilever spring constant:**

The stiffness of the lever must be appropriately suited to image the material. Often some empirical trial and error is required to find a suitable cantilever. If the cantilever is too stiff, the result may be destructive to the sample or cause tip wear. If the cantilever is too soft, it may not be able to interact with the sample to generate any contrast or it stays in contact with the surface.

Contact Mode	0.2 N/m
Tapping Mode	50 N/m

https://www.nanosurf.com/en/support/afm-modes#dynamic

Oscillating Mode Parameters

2. Vibrational amplitude:

This is the amplitude of the oscillation by the cantilever when the cantilever is vibrating in free space away from the sample. This parameter is set in units of millivolts. Rougher samples require a larger free vibration amplitude.

3. Setpoint:

This is the reduced target amplitude, which results after the tip is in intermittent contact with the sample (see schematic above). The setpoint is expressed as a percentage of the free vibration amplitude. **Lower amplitude setpoints will favor a more aggressive tip-sample interaction**.

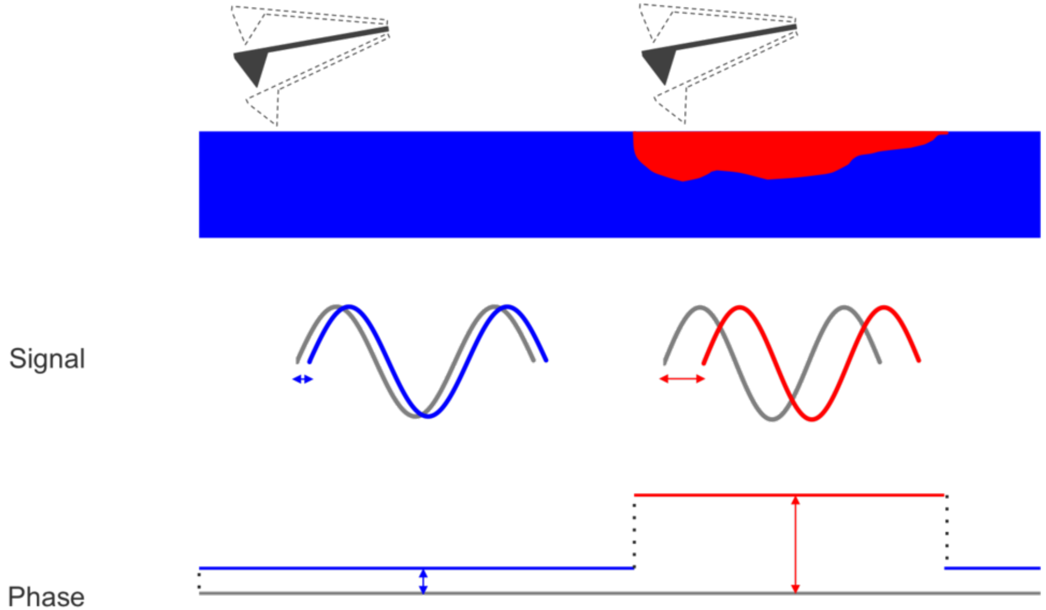
https://www.nanosurf.com/en/support/afm-modes#dynamic

Phase Imaging

Phase imaging is one of the most common AFM imaging methods used to obtain contrast based on material properties.

Oscillating probes interacting with the surface will exhibit a phase shift (φ) between the drive and the response, as defined by the equation:

$$\varphi = \tan^{-1}\left(\frac{\omega\beta}{\omega_0^2 - \omega^2}\right)$$



given that,

ω_o = natural frequency of the cantilever

ω = measured frequency of the cantilever

β = b/m, where b is the damping coefficient

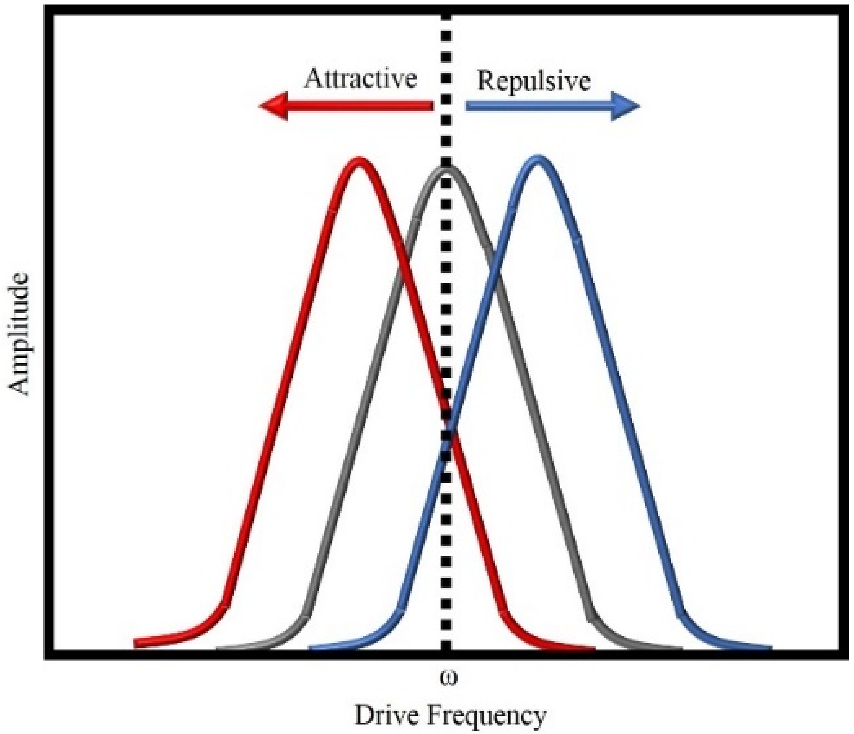
(coefficient of friction) and m is the cantilever mass

https://www.icspicorp.com/blog/afm-phase-images

https://afmhelp.com/index.php?option=com_content&view=article&id=84:what-is-phase-imaging

Phase Imaging

When the interaction between an oscillating cantilever and a sample changes, the resonance frequency of the cantilever will shift to lower frequencies for attractive forces, to higher frequencies for repulsive forces.

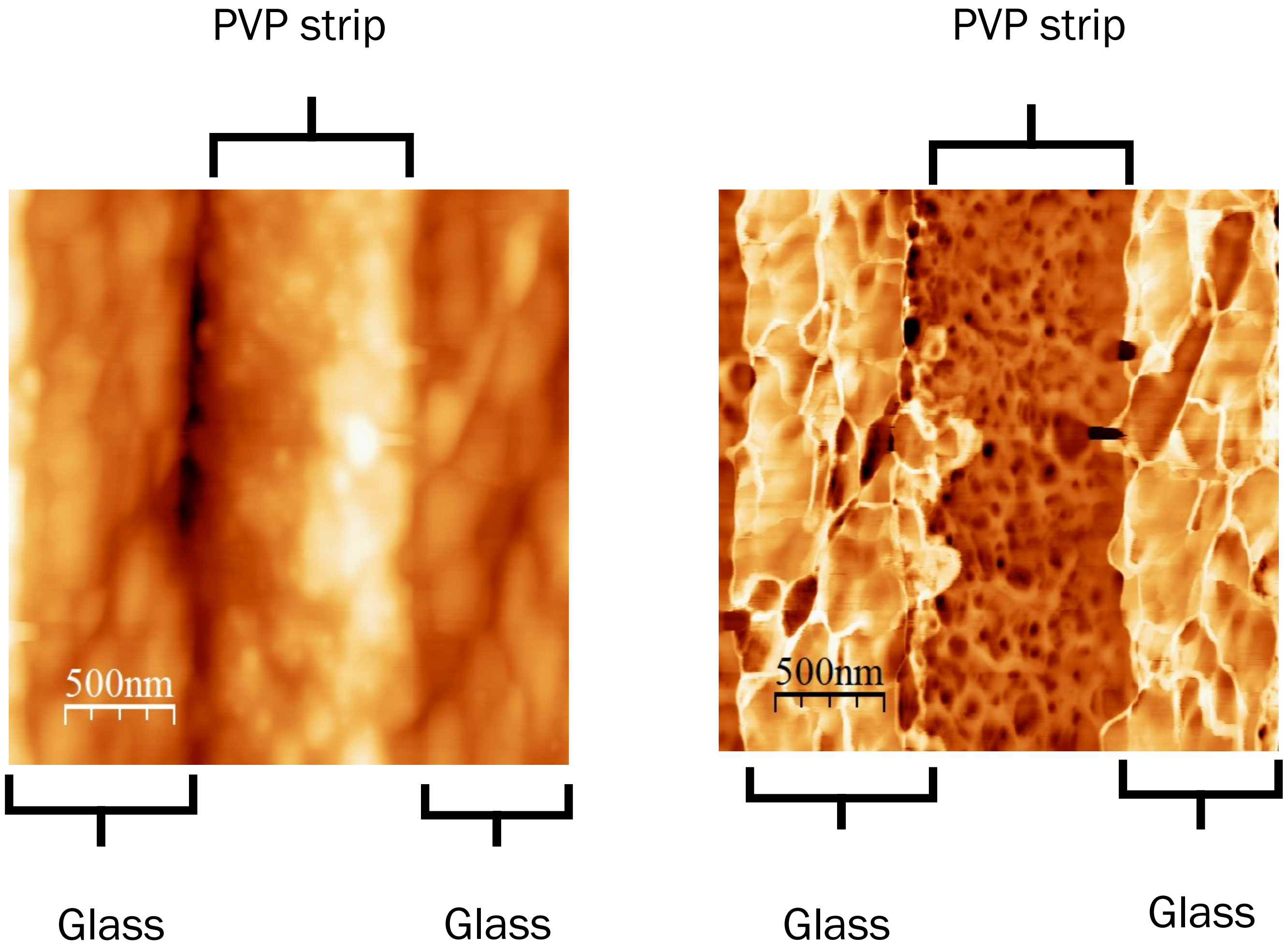


AFM phase image appears dark when the probe phase angle decreases and appears bright when the phase angle increases.

https://www.nanosurf.com/en/support/afm-modes#dynamic

Phase Imaging

Over the regions with a higher elastic modulus, more repulsive forces are observed. More damping is observed over the more viscous regions.



Hence, the areas with higher elastic moduli segments appear bright and the more viscous samples appear dark.

Phase Imaging - Applications

- Identification of contaminants;
- Mapping of different components in composite materials;
- Differentiating regions of high and low surface adhesion or hardness;
- Mapping of electrical and magnetic properties with wide-ranging implications in data storage and semiconductor industries.

Building College-University Partnerships for Nanotechnology Workforce Development

Thank you!

For additional lecture content and AFM information contact Wesley Sanders

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glen.johnson@slcc.edu