LAB UNIT 1: Introduction Scanning Force Microscopy

Specific Assignment: Setup of scanning force microscopy experiment and first contact measurements

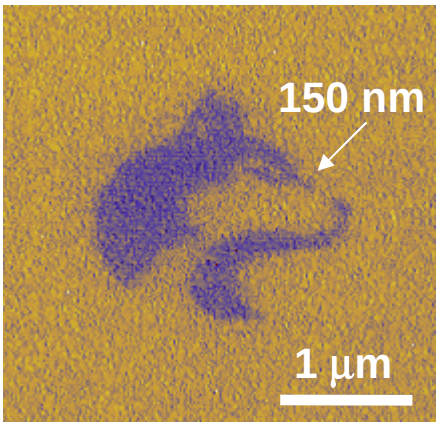
Objective The student will become familiar with contact mode Scanning Force Microscopy (SFM) as an imaging technique.

Outcome At the end of this lab, you will be familiar with the basic principle and technique of contact mode SFM. You will be able to mount a cantilever tip, approach the tip to a surface, image the surface and conduct force displacement measurements.

Synopsis This lab unit serves as an introduction to SFM.

Materials Smooth surfaces, such as graphite, mica, uncoated compact disc (CD), microfabricated calibration test grids

Techniques Contact mode SFM



Nanolithographically Patterned
Alkanethiols on a Gold Surface

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1. Assignment

In this lab, you will use the Scanning Force Microscope (SFM), also known as Atomic Force Microscope (AFM), as both an imaging tool, and a force measuring tool. As an imaging tool, you will use the most basic SFM imaging method: contact mode imaging. Employing force-displacement curves you will be measuring probe-sample forces and determine "true" normal loads.

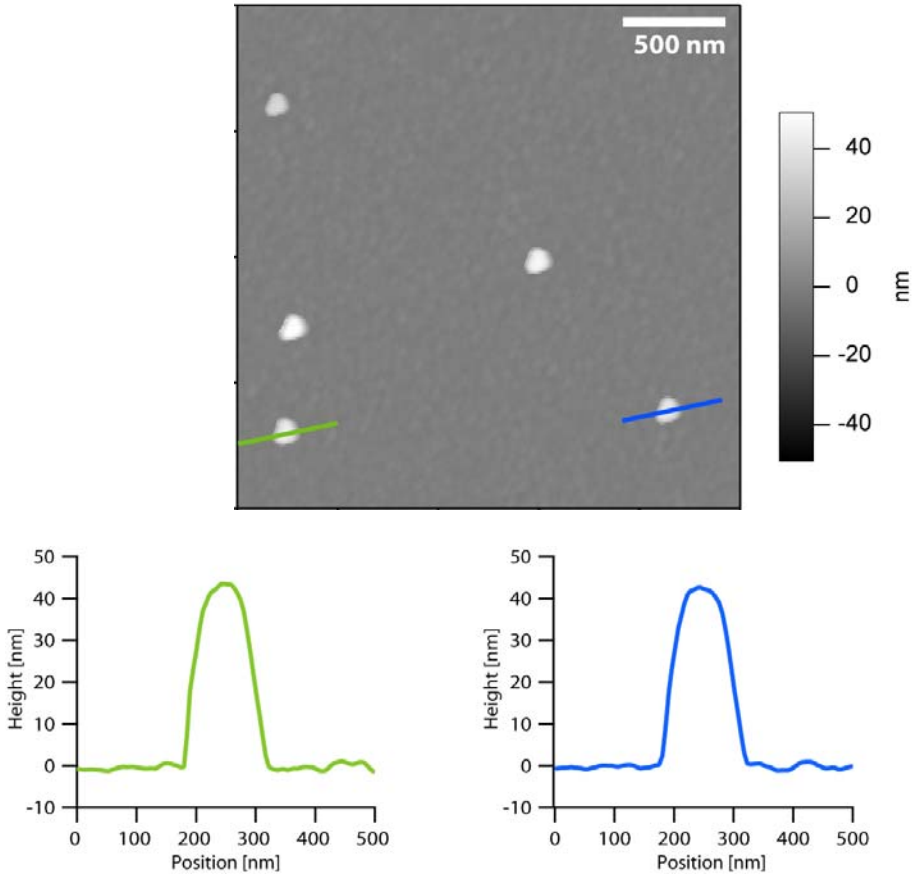
1. (***pre-lab)*** Read background information of Scanning Probe Microscopy in section 4
2. Take the quiz on your theoretical understanding in section 2
3. Learn on how to mount SFM tips
4. Image the samples provided
5. Conduct force displacement curves as function of the approach/retraction speed on three different samples. Compare the adhesion forces.

2. Quiz

2.1 Background Questions

(1) How many hydrogen atoms would you have to line up to make one nanometer?

(2) A student takes a SFM image like the one shown below to measure the size of some gold nanoparticles attached to a surface. What are the dimensions of the nanoparticles?



(3) A student takes an SFM like the one shown below. Explain what has gone wrong.

(4) A) What is the force constant of the cantilevers you will be using in this lab?
B) How much force does it take to deflect such a cantilever by 1nm?
C) Provide an order of magnitude estimate of how much force is needed to break a covalent bond (remember typical ~1 Angstrom long, ~80 kcal/mol).
D) Calculate the force that a 1 mW beam of 830 nm photons exerts on a mirror.

(5) Using the same SFM cantilever as in problem (4) the deflection set point is set to 10 nN.
A) How far is the cantilever deflected from equilibrium?
B) What is the pressure beneath the SFM tip if the contact area is 30 nm in diameter?

(6) How does the SFM scan the tip across the surface?

(7) If you are scanning an area of 80 μm by 80 μm with 512 lines and 512 points per line, what is the resolution of your image (specify in both μm and nm)?

3. Experimental Assignment

3.1 Goal

At the end of this lab, you should understand the concept and operation of SFM contact mode.

Specifically perform the following:

(1) Image the materials provided on various scales by SFM.
(2) Analyze your data by processing images and performing cross-section analysis.
(3) Control the "normal load" via the force displacement curves.

3.2 Safety

- Refer to the General rules in the SFM lab

Warning: The AFM contains a Class 1 laser (830 nm wavelength). Although class 1 lasers are deemed safe for brief exposure, you should NOT look directly into the laser beam behind the cantilever alignment chip. The laser is infrared, meaning your blink reflex will not protect you.

3.3 Instrumental Setup

- Easy Scan 2 AFM system with contact mode AFM tip (Vista probes; CL-25) with 0.2 N/m spring constant, resonant frequency of 12 kHz, and the tip radius of ~10 nm

3.4 Materials

- Smooth surfaces: Graphite, Mica, microfabricated silicon calibration grids

3.5 Experimental Procedure

Read the instructions below carefully and follow them closely. If you are uncertain about anything, please consult your TA first.

(i) Preparation – Coarse Approach

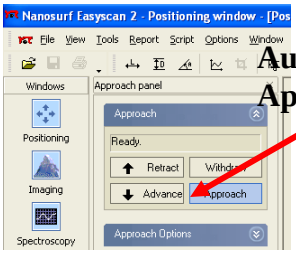
(1) System set-up: follow the start up procedure in Easy Scan 2 AFM System SOP (Standard Operational Procedure).
   a. Use a contact-mode cantilever (CLR-25)
   b. Operating mode: static force (contact mode)
   c. Lower the stage by clicking *Advance* in the Approach panel until you see the shadow of your cantilever.

(ii) Coming to Contact

(1) Once the cantilever is approximately 1mm from its shadow, automatic approach is used to bring the cantilever into contact.
(2) Open the Z-Controller Panel by clicking the icon right in the Navigator bar.
(3) Set the set point to be 5 nA. Use the default values for the P-Gain, I-Gain, and D-Gain.

(4) Click the Positioning icon (right) and under Approach options uncheck 'Auto start imaging' (below left).
(5) In the Approach panel in the Positioning window (see below right) click 'Approach'.
(6) The software lowers the SFM tip till it comes in contact with the sample surface.
(7) Once the approach is complete a message 'Approach done' appears and the imaging panel automatically appears in the active window.
(8) Look at the Probe Status Light on the Controller. If it is NOT green, it is not operating correctly. Immediately come out of contact by clicking Withdraw in the Approach Panel. Consult a lab assistant.

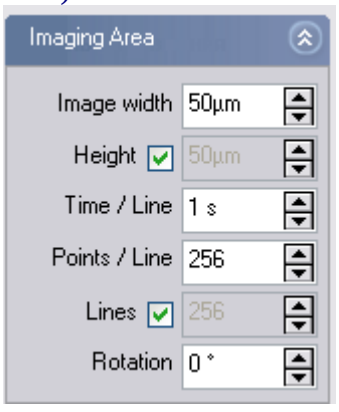
Click off the Auto start imaging



Automatic Approach

(iii) SFM Imaging

(1) Scan the selected area by going to the Imaging Panel by clicking on the Imaging icon (right). Select the desired scan size (image width), speed (Time/Line) and resolution in the 'Imaging Area' panel (below).



(2) When you have an acceptable image you wish to save, ensure that you click the 'photo' icon (right) before the image is complete. This will

bring up a separate box with the completed image. To save the image go to File→Save As, create your own file on the desktop and save the image there.

(3) Process image and perform cross-section analysis using the options under the *Tools*. Keep in mind that you want to obtain the following information,
- Cross-section profile of surface structures
- Dimensions of your structures (report average diameter and height with standard deviation)
- Determine the surface roughness

(iv) Procedure for force spectroscopy measurement

(1) Follow the procedure described in Easy Scan 2 force distance measurement SOP.

(2) Record for the each reading;
a. Adhesion force in units of nm,
b. The temperature and the humidity
c. Any other observations that might be relevant in interpreting the results

(v) AFM shut down

(1) Follow the *Easy Scan 2 AFM System SOP Shutdown Procedure*

4. Introduction to Scanning Force Microscopy (SFM)

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4.1 Historic Perspectives

In 1982, Gerd Binnig and Heinrich Rohrer of IBM in Rüschlikon (Switzerland) invented scanning tunneling microscopy (STM). Although STM is not the focus of this lab, it is the ancestor of all the variations of scanning probe microscopy (SPM) that followed: although the mechanism of image contrast may vary, the idea of building up an image by scanning a very sharp probe across a surface has endured. As the name suggests, STM scans a sharp tip across a surface while recording the quantum mechanical tunneling current to generate the image. STM is capable of making extremely high resolution (atomic resolution) images of surfaces and has been extremely useful in many branches of science and engineering. For their invention, Binnig and Rohrer were awarded the Nobel Prize in Physics in 1986[1].

Although STM is able to obtain images with better than atomic resolution (some scientists even use it to image the electron orbitals around atoms in molecules), one limitation is that STM can only be used to image conductive surfaces. In an effort to overcome this restriction, Gerd Binnig, Christoph Gerber, and Calvin Quate at IBM and Stanford Univeristy developed scanning force microscopy (SFM), also known as atomic force microscopy (AFM), in 1986. SFM is a surface imaging technique that images both conductive and nonconductive surfaces by literally "feeling the surface", i.e. measuring the force between a surface and an ultra sharp tip (typically 10 nm in radius). Fig. 4.1 shows a SFM image of a lipid bilayer.

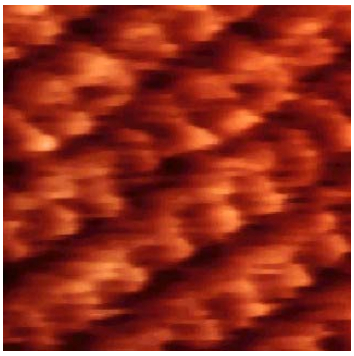

Figure 4.1. SFM Image of Lipid Bilayer (scan size: 10 nm)

4.2 Scanning Force Microscopy (SFM)

4.2.1. Contact Mode

As noted above, an SFM acquires an image by scanning a sharp probe across a surface. This can be done by contacting the surface (contact mode) or by a variety of other scanning modes (intermittent contact and others are covered in more detail in separate lab modules). Contact mode imaging is perhaps the most straightforward SFM mode, and is the technique you will use in this lab. In contact mode, a sharp tip attached to the end of a long flexible cantilever is brought into contact with a surface (Fig. 4.2). The harder the tip presses into the surface, the more the cantilever bends. The tip moves in regardless of the sample in the x-, y- and z-directions using a piezoelectric actuator. The actuator contains a piezoelectric crystal that expands and contracts as an external voltage is applied across its crystal faces (voltages of a few hundred volts may be applied to move the sample tens of microns).

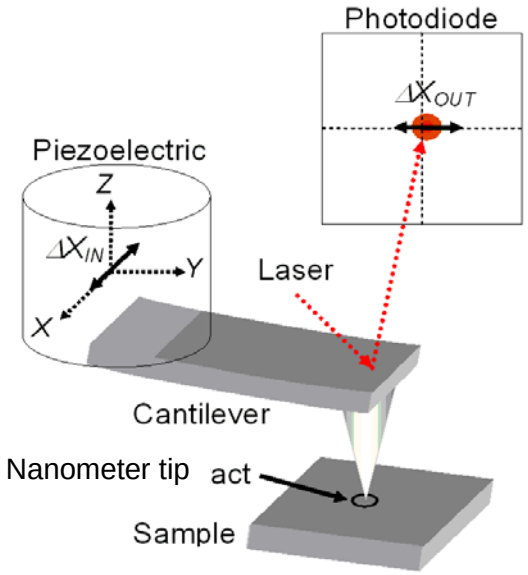

Figure 4.2. Schematics of scanning force microscopy (also known as atomic force microscopy, AFM) operated in contact mode

The deflection of the cantilever is most commonly monitored by a laser-beam deflection scheme. A laser is reflected off the back of the cantilever tip onto a segmented photodiode (top and bottom segments for vertical deflection) or a four-quadrant photodiode (for both vertical and lateral detection of the cantilever deflection). One way to acquire an image is to use the piezo to scan the tip in the x-y plane and record the deflection of the tip as a function of position. As the tip moves over a bump, the deflection of the cantilever increases, which increases the tip-sample force. If the bump is too large the tip may scratch the surface, or the lever may break. This scanning mode is called “force mode.” For a topographical imaging mode, a feedback loop (Fig. 4.3) is implemented to keep the cantilever deflection constant by changing the tip height (z) while scanning in x and y. In this way, a nearly constant force is maintained between the tip and sample, and the topographical image is created by recording the voltage applied to the z-piezo as a function of the x and y position. As the tip is scanned, lateral force are achieved on the lever on the lever due to friction causing the lever to torque. The motion can be with 4-quadrant segmented photodiodes.

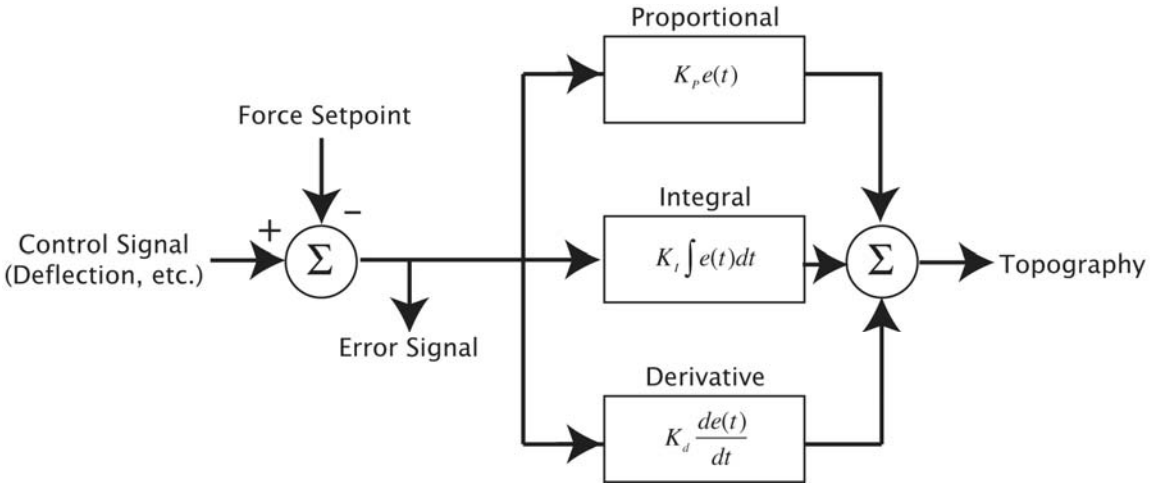

Figure 4.3. Block Diagram of an SFM Feedback Loop. K_c is proportional gain; K_i is the integral gain; K_d is the derivative gain; *e* is the error.

4.2.2. AC Mode Imaging

The SFM can also image a surface without continuously touching the surface. Such imaging modes—which can be classified as non-contact or intermittent-contact (Tapping Mode™ imaging by certain manufacturers)—are widely used, and are particularly suited to imaging soft surfaces such as polymers or biological samples. AC mode imaging gets its name from the fact that the tip is raised slightly above the surface and the cantilever is driven to vibrate near its resonant frequency (by yet another piezoelectric crystal). The amplitude, phase, and/or frequency of the cantilever are then monitored as the tip is scanned across the surface. The forces between the tip and the sample change the properties of the cantilever resonance, which can be used to generate a feedback signal and thus create an image. AC Mode imaging will be covered further in other lab modules so we will not discuss it further here.

4.2.3. Applied Force: Cantilever Deflection and Hooke's Law

The dimension, shape, and material of the cantilever tip can affect its resolution and sensitivity to different forces. In addition, tips with different coatings can be used in different applications of SPM. A conductive coating is required for electrostatic force microscopy (EFM), conductive atomic force microscopy (c-AFM), and etc. The most common commercial SFM tip is microfabricated from silicon or silicon nitride using conventional photolithography and semiconductor processing techniques, processes similar in many ways to those used to generate silicon computer chips. Hundreds to thousands of cantilever tips can be fabricated on a single wafer at once. The tip (with a tip radius of ~10 nm) is located at the free end of the cantilever that is typically 100 to 200 micron long (refer to Fig. 4.2). Shorter or thicker cantilevers have higher spring constants and are more stiff. The cantilever acts like a spring and can be described by Hooke's law:

$$F = -k_N z \qquad \text{Eq. (1)}$$

where F is the force, k_N is the normal spring constant, and z is the cantilever normal deflection. Typical spring constants available on commercially manufactured SFM cantilevers range from 0.01 N/m to 75 N/m. This enables forces as small as 10^{-9} N to be measured in liquids or an ultra-dry environment with the SFM. Analogous, lateral forces acting on the lever can be expressed as the product between a lateral spring constant k_x and a lateral deflection x.

For a bar-shaped cantilever with length L, width W and thickness t, and an integrated tip of length r, the normal and lateral spring constants, k_L and k_x, are related to the material stiffnesses, as

$$k_N = \frac{EWt^3}{4L^3} \quad \text{and} \quad k_x = \frac{GWt^3}{3Lr^2}.$$

where E and G respresent the normal Young's modulus and the shear modulus, respectively.

The thickness of the cantilever, typically poorly defined by the manufacturers, can be determined from the first resonance frequency of the "free" cantilever using the following empirical equation:[2]

$$t = \frac{2\pi f_1}{(1.875104)^2} L^2 \sqrt{\frac{12\rho}{E}}$$

The Young's modulus and density of silicon cantilevers are around E = 1.69×10^{11} N/m^2 and $\rho=2.33\times10^3$ kg/m^3.[2]

4.2.4. SFM Tips

The lateral imaging resolution of SFM is intrinsically limited by the sharpness of the cantilever. Most commercial cantilevers have a tip with a 10 nm radius of curvature, although more exotic probes (such as those tipped with carbon nanotubes) are also available. Keep in mind that the resolution is also limited by the scanning parameters. For instance, if you take a 10x10 micron scan with a resolution of only 256x256 points, the size of each image pixel represents a lateral distance of $1\text{x}10^{-6}$ m / 256 = 39 nm.

As SFM images are generated by scanning a physical tip across the surface, this can lead to several image artifacts. One type of imaging artifact results from tip convolution. When the tip size is larger than the imaging feature size, the resulting image will be dominated by the shape of the tip. In this case, the observed features from the topography images will have very similar shapes despite the fact that the real features might be different (think of it as taking a picture of the tip with each of the surface features). Fig 4.4 shows two different sized tips scanned over a substrate with both small and large features. Also, damaged tips can often lead to distorted images. A tip with a piece of dirt stuck to it, or one that has been broken near the end can yield, for instance, doubled features as illustrated in Fig 4.5. One way to check for tip-induced artifacts is to rotate the scan angle by 90 degrees. If the shapes you are seeing do not rotate, the tip might be damaged!

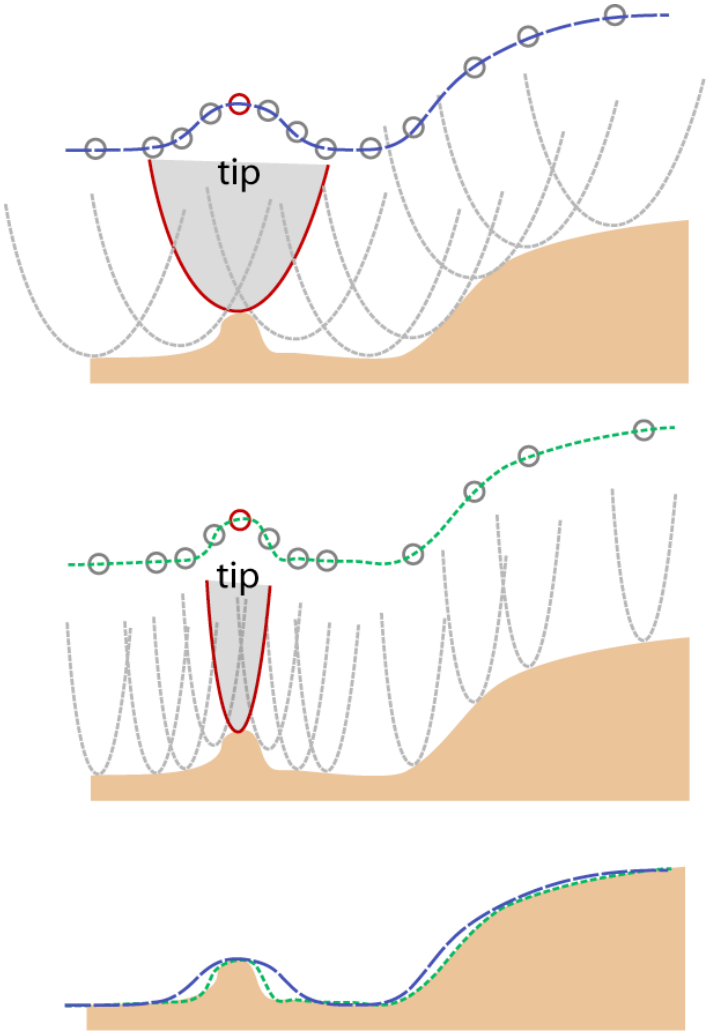

Figure 4.4. Limitations of Tip Size. (Top) The large tip is much bigger than the small substrate feature. Each circle on the figure represents the position of the z-piezo recorded by the SFM as it moves across the sample. (Center) A small tip tracks both surface features better. (Bottom) The two line traces (large tip is dashed blue; small tip dotted green) from each tip are shown with the actual surface topography.

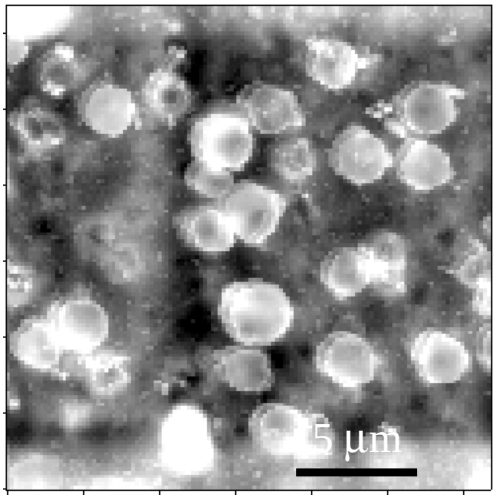

Figure 4.5 A minor case of doubled features caused by a damage tip. The image shows salt crystals embedded in polymer matrix.

In addition, image artifacts can also result when the feedback system is not optimized. The feedback loop consists of a set point value and feedback gains (proportional, integral, and derivative of the error signal). When the feedback gains are too high, the controller will overcompensate and amplify random noise in the system. Sometimes the tip oscillates and creates periodic noise in the images (showing periodic stripes in the image). On the other hand, if the gains are too low, the tip cannot accurately track the features due to the slow response of the feedback loop. Fig. 4.6A-C show some SFM images taken with the gains set just right, too low, and too high.

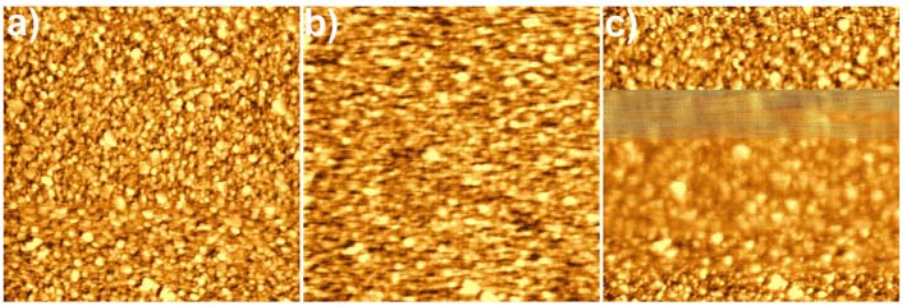

Figure 4.6 Topography of Gold Surface (Scan Size: 1µm*1µm). a) with optimal feedback loop gains, b) with gains set too low, and c) with gains set too high

In contact mode, the set point determines the amount of force applied on the cantilever tip, which also affects the cantilever deflection. You can specify the set point value in nN in the NanoSurf easyScan 2 software. (Note: this value depends on the accuracy of the spring constant assigned to the tip, via Eq 1). In non-contact mode, the set point is specified in a percentage of the amplitude at resonance. Tuning of the NanoSurf cantilevers should be performed far from the surface, i.e. when there are no short- or long-range forces acting on the tip. The SFM controller will bring the tip close to the surface until the vibration amplitude becomes the specified value.

4.3 Dip-Pen Nanolithography (DPN)

In addition to imaging with the SFM, there have been numerous methods developed to use STM and SFM techniques as lithographic tools. STM is capable of actually moving individual atoms, and many interesting examples of STM images can be found online[3].

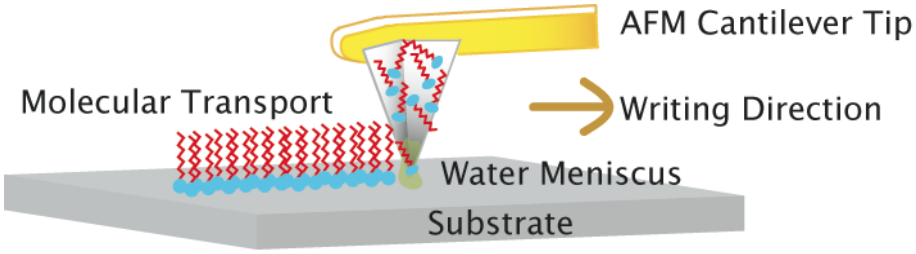

Figure 4.7. Schematics of Dip-Pen Nanolithography

Dip-pen nanolithography (DPN) is a scanning probe-based lithography tool that uses an SFM tip to "write" chemicals onto surfaces. It is a direct-write additive process. It is analogous to a conventional fountain pen, with the SFM tip as the pen and the substrate being the paper (Fig. 4.7). Although there are now more sophisticated systems for delivering chemical "inks" to the tip using microfluidics, etc. (such as built-in ink reservoir or ink wells), the basic DPN approach is still the easiest to implement. To coat the tip with the chemical ink it is simply dipped (using tweezers and a steady hand) into an ink solution. Alkanethiols, DNA, proteins, polymers, etc., have all been used as inks in DPN[4,5]. After the tip is inked, excess solvent is blown off the tip and it is loaded into the SFM. When the tip contacts the substrate the chemical ink flows to the surface and is deposited onto the surface of the substrate. For many inks, such as depositing alkanethiols on gold, the tip can be approximated as a small source delivering a constant flux of molecules to the surface per unit time. Thus, the area of the features increases linearly with the dwell time (the time of contact between the tip and the surface). The diameter of a DPN patterned feature scales approximately to the square root of the contact time:

$$d \approx t^{1/2} \qquad \text{Eq. (2)}$$

where d is the diameter of the patterned dots and t is the dwell time.

DPN is a direct-write technique that does not require a design mask, and it can generate various complex structures on demand using any atomic force microscope. However, like other scanning-probe based lithography tools, DPN is a *serial* process (one feature is created at a time). Nevertheless, it is inexpensive and suitable for rapid prototyping applications. Attempts to improve the serial natural of the DPN technique have resulted in commercially available multiple arrays of DPN probes for mass DPN-patterning[6].

Writing patterns of a thiol (16-mercaptohexadecanoic acid, "MHA") on a gold surface is the most common ink-surface chemistry in DPN. Thiols chemically bond to gold surfaces through their sulfur atom to form a gold-sulfur bond. The chemical reaction is generally accepted to be[7]:

$$R - SH + Au \rightarrow R - S - Au + \frac{1}{2} H_2$$

Long-chain alkanethiols tend to form well-ordered monolayers on gold surfaces, known as self-assembled monolayers, or SAMs. Typically, DPN-generated patterns are characterized with LFM, allowing images of patterned SAMs to be made based on friction contrast (i.e. the lateral defleciton of the lever if moved over the surface), e.g Fig. 4.8 (though with care it is possible to image the SAM pattern based on topography alone; it will be very challenging to image height differences of less than a few nanometers).

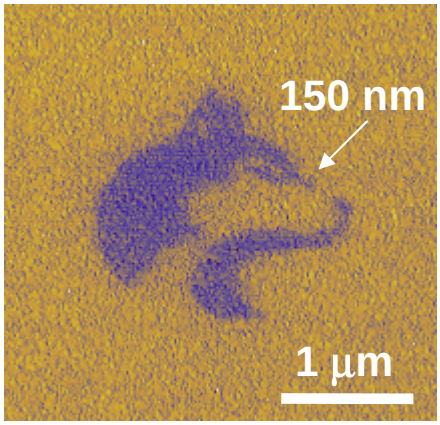

Figure 4.8. Lateral Force Image of DPN-Patterned 16-Mercaptohexadecanoic Acid on Gold

Alternatively, the features can be more easily scanned in the topography mode by using the DPN patterns as etch resists to generate topography on the gold layer after gold etching. A common gold etching solution is a solution of thiourea and ferric nitrate[8]. The amount of etched gold is proportional to the etching time. The bare, unmodified gold (unwritten) regions will etch faster than the regions protected by the alkanethiol SAM, as the SAM prevents the etchant molecules from reaching the gold surface.

References

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