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Introduction to Scanning Probe Microscopy

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1 INTRODUCTION

In the early 1980's two IBM scientists, Binnig and Rohrer [1] developed a new technique for studying surface structure - Scanning Tunneling Microscopy (STM), for which they received the Nobel Prize in 1986 [2]. The STM spread fast into scientific labs over the world, because of its simple design, low costs, easiness to handle and the possibility to provide atomically resolved images of the surface of every electronically conducting sample.

This technique gave birth to a whole family of related techniques which, together with STM, may be classified in the general category of Scanning Probe Microscopy (SPM) techniques. The family of scanning probe microscopes uses no lenses, but rather a probe that interacts with the sample surface. The type of interaction measured between the probe tip and the sample surface defines the type of scanning probe microscope being used (see Table1).

The most important SPM technique is Atomic Force Microscopy (AFM) developed by G. Binnig, C.F. Quate and C.H. Gerber in 1986 [3]. The AFM was invented to overcome a limitation of the STM which can only image materials that can conduct a tunneling current. The AFM opened the door to imaging other materials, such as polymers, ceramics, glasses and biological samples that do not conduct a current.

Since their invention, SPMs have rapidly become popular for performing very precise, three-dimensional measurements on the nanometer to micrometer scales. The development of above two techniques has without doubt been the most important event in the material surface science field in recent times, and opened up many new areas of science and engineering at the atomic and molecular level. The exceptional attribute of STM and AFM is that they allow for the observation and imaging of solid surfaces at the atomic scale (see Figure 1).
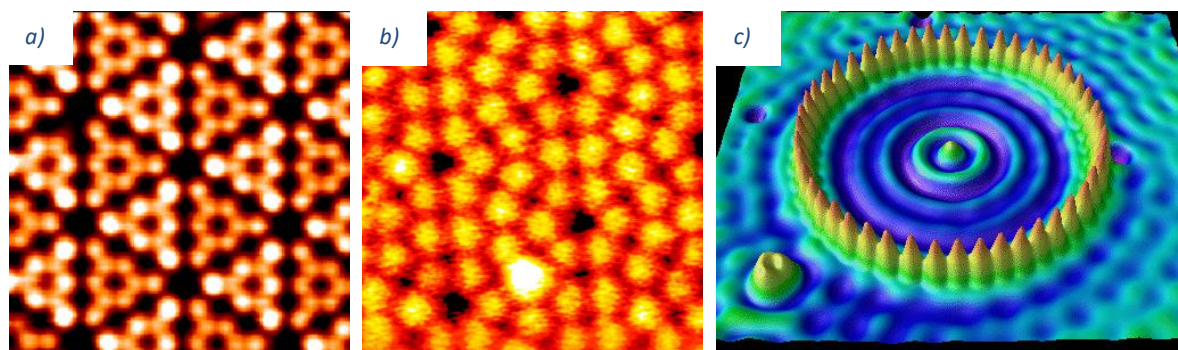

Figure 1: a) Highest resolution experimental result for Si (111)-7x7 [4]; b) Atomic Resolution on Si (111) (7x7) in NC AFM [5]; c) "Quantum corral" - a ring of 48 iron atoms on a copper surface [6]

Invention of AFM was followed by a burst of other SPM techniques which have the purpose to map the distribution of specific surface properties. To the author knowledge it has been more than twenty established types of scanning probe microscopy.

Table 1 lists the most important SPM techniques, along with interaction type and description of their usage. As it can be seen, scanning probe microscopes can measure properties such as surface conductivity, static charge distribution, localized friction, magnetic fields, elastic moduli and others. Scanning probe microscopes are also capable of controllably modifying surfaces at nanometer scales to pattern surfaces (see Figure 1c). As a result of this wide range of imaging possibilities, application of SPMs has been continuously expanding.

Table 1: List of the most used SPM techniques

Abbrev.	Technique	Interaction type	Usage
STM	Scanning Tunneling Microscopy	Tunneling current	3-D topography: size, shape and periodicity of features, surface roughness. Electronic structure, and possible elemental identity
AFM	Atomic Force Microscopy	Interatomic and intermolecular forces	3-D topography: size and shape and periodicity of features, surface roughness.
FMM	Force Modulation Microscopy	Interatomic and intermolecular forces	Hardness and surface elasticity at various locations
LFM	Lateral Force Microscopy	Frictional forces	Differences of adhesiveness and friction at various locations.
MFM	Magnetic Force Microscopy	Magnetic forces	Size and shape of magnetic features. Strength and polarity of magnetic fields at different locations.
SThM	Scanning Thermal Microscopy	Heat transfer	Thermal conductivity differences between surface features.
EFM	Electrostatic Force Microscopy	Electrostatic forces	Electrostatic field gradients on the sample surface.
NSOM	Near-field Scanning Optical Microscopy	Reflection, absorption and Fluorescence of light	Optical properties of surface features

In the following chapter basic principles of the STM, AFM and MFM, which are the most used SPM techniques in metallic glass research, will be introduced. The third chapter presents an overview of mechanical behavior of metallic glasses with an accent on atomic force microscopy.

2 BASIC PRINCIPLES OF SPM TECHNIQUES

All of the techniques are based upon scanning a probe (typically called the tip in STM, since it literally is a sharp metallic tip) just above a surface whilst monitoring some interaction between the probe and the surface. All SPMs contain the components illustrated in Figure 2.
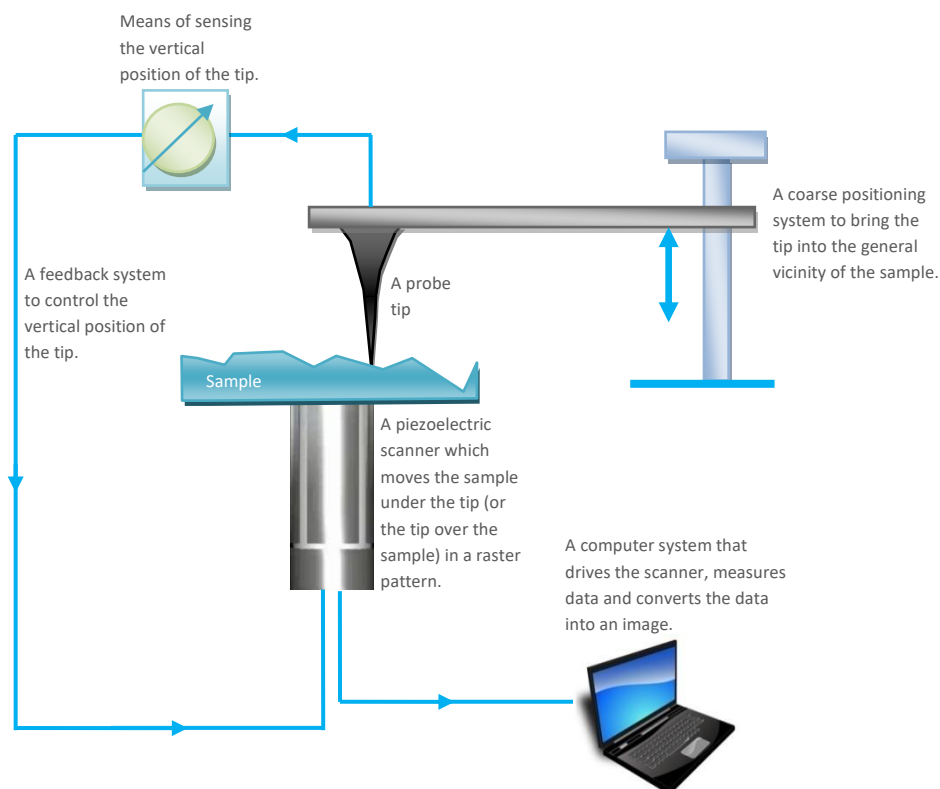

Figure 2: Schematic of a generalized scanning probe microscope [33]

2.1 SCANNING TUNNELING MICROSCOPE

The following is the basic concept of the STM: it has a metal needle that scans a sample by moving back and forth over it, gathering information about the curvature of the surface.

STMs use a sharpened, conducting tip with a bias voltage applied between the tip and the sample. When the tip is brought within about 10Å of the sample, electrons from the sample begin to "tunnel" through the 10Å gap into the tip or vice versa, depending upon the sign of the bias voltage (see the Figure 3). The resulting tunneling current varies with tip-to-sample spacing, and it is the signal used to create an STM image.

The tunneling current is an exponential function of distance; if the separation between the tip and the sample changes by 10% (on the order of 1Å), the tunneling current changes by an order of magnitude. This exponential dependence gives STMs their remarkable sensitivity. STMs can image the surface of the sample with sub-angstrom precision vertically, and atomic resolution laterally.
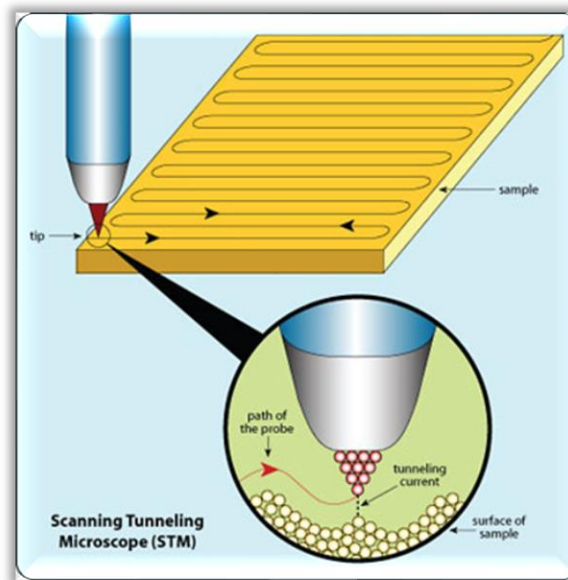

Figure 3: Schematic of tip and sample interaction in scanning tunneling microscope {Document not in library}

STMs can be designed to scan a sample in either of two modes:

- **Constant-height mode:** the tip travels in a horizontal plane above the sample and the tunneling current varies depending on topography and the local surface electronic properties of the sample. The tunneling current measured at each location on the sample surface constitutes the data set, the topographic image.
- **Constant-current mode:** STMs use feedback to keep the tunneling current constant by adjusting the height of the scanner at each measurement point. For example, when the system detects an increase in tunneling current, it adjusts the voltage applied to the piezoelectric scanner to increase the distance between the tip and the sample. In constant-current mode, the motion of the scanner constitutes the data set. If the system keeps the tunneling current constant to within a few percent, the tip-to-sample distance will be constant to within a few hundredths of an angstrom.

Each mode has advantages and disadvantages. Constant-height mode is faster because the system doesn't have to move the scanner up and down, but it provides useful information only for relatively smooth surfaces. Constant-current mode can measure irregular surfaces with high precision, but the measurement takes more time.

As a first approximation, an image of the tunneling current maps the topography of the sample. More accurately, the tunneling current corresponds to the electronic density of states at the surface. STMs actually sense the number of filled or unfilled electron states near the Fermi surface, within an energy range determined by the bias voltage. Rather than measuring physical topography, it measures a surface of constant tunneling probability.

The sensitivity of STMs to local electronic structure can cause trouble in mapping topography. For example, if an area of the sample has oxidized, the tunneling current will drop precipitously when the tip encounters that area. In constant-current mode, the STM will instruct the tip to move closer to maintain the set tunneling current. The result may be that the tip digs a hole in the surface. On the other hand, the sensitivity of STMs to electronic structure can be a tremendous advantage in probing the electronic properties of the sample surface with atomic resolution.

2.2 ATOMIC FORCE MICROSCOPE

The atomic force microscope (AFM) probes the surface of a sample with a sharp tip, a couple of microns long and often less than 100Å in diameter. The tip is located at the free end of a cantilever that is 100 to 200μm long (see Figure 4a). Forces between the tip and the sample surface cause the cantilever to bend, or deflect. A detector measures the cantilever deflection as the tip is scanned over the sample, or the sample is scanned under the tip. The measured cantilever deflections allow a computer to generate a map of surface topography. AFMs can be used to study insulators and semiconductors as well as electrical conductors.
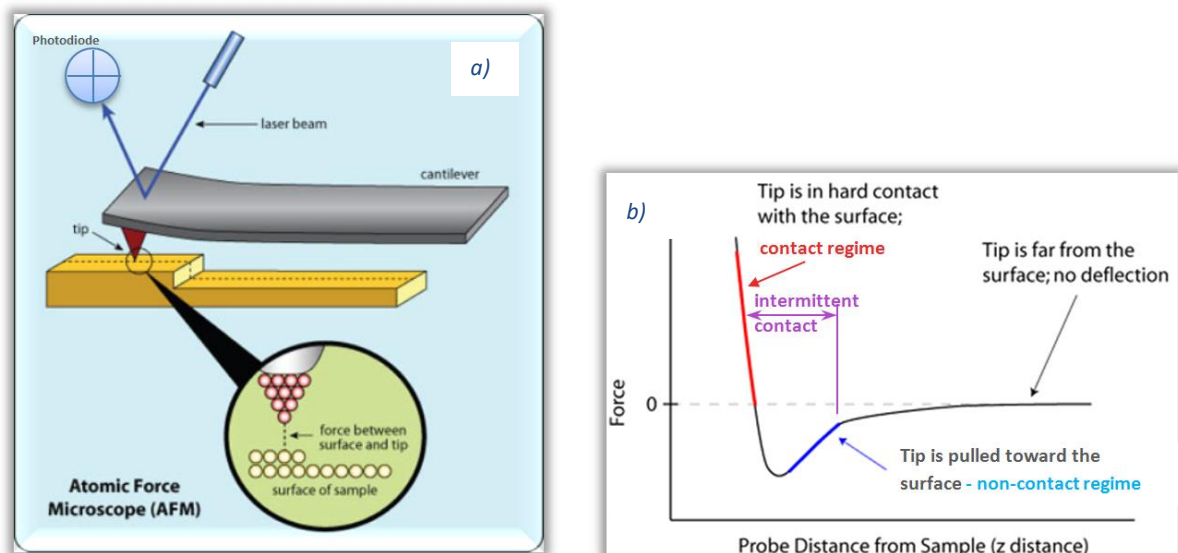

Figure 4: a) Schematic illustration of atomic force microscope {Document not in library}; b) Interatomic force vs. distance curve[33]

Several forces typically contribute to the deflection of an AFM cantilever. The force most commonly associated with atomic force microscopy is an interatomic force called the van der Waals force. The

dependence of the van der Waals force upon the distance between the tip and the sample is shown in Figure 4b.

Two distance regimes are labeled in Figure 4b:

- **Contact regime**: the cantilever is held less than a few angstroms from the sample surface, and the interatomic force between the cantilever and the sample is repulsive.
- **Non-contact regime**: the cantilever is held on the order of tens to hundreds of angstroms from the sample surface, and the interatomic force between the cantilever and sample is attractive (largely a result of the long-range van der Waals interactions).

Figure 5: Working modes of AFM: contact, non-contact and tapping mode, from left to right

2.2.1 CONTACT AFM

In contact-AFM mode, also known as repulsive mode, an AFM tip makes soft "physical contact" with the sample. The tip is attached to the end of a cantilever with a low spring constant, lower than the effective spring constant holding the atoms of the sample together. As the scanner gently traces the tip across the sample (or the sample under the tip), the contact force causes the cantilever to bend to accommodate changes in topography.

The slope of the van der Waals curve is very steep in the repulsive or contact regime (see Figure 4b). As a result, the repulsive van der Waals force balances almost any force that attempts to push the atoms closer together. In AFM this means that when the cantilever pushes the tip against the sample, the cantilever bends rather than forcing the tip atoms closer to the sample atoms. Even if one design a very stiff cantilever to exert large forces on the sample, the interatomic separation between the tip and sample atoms is unlikely to decrease much. Instead, the sample surface is likely to deform.

Most AFMs currently on the market detect the position of the cantilever with optical techniques. In the most common scheme, shown in Figure 4a, a laser beam bounces off the back of the cantilever onto a position-sensitive photodetector (PSPD). As the cantilever bends, the position of the laser beam on the detector shifts. The PSPD itself can measure displacements of light as small as 10Å. The ratio of the path length between the cantilever and the detector to the length of the cantilever itself produces a mechanical amplification. As a result, the system can detect sub-angstrom vertical movement of the cantilever tip.

Other methods of detecting cantilever deflection rely on optical interference, or even a scanning tunneling microscope tip to read the cantilever deflection. One particularly elegant technique is to fabricate the cantilever from a piezoresistive material so that its deflection can be detected electrically.

Once the AFM has detected the cantilever deflection, it can generate the topographic data set by operating in one of two modes:

- **Constant-height mode**: the spatial variation of the cantilever deflection can be used directly to generate the topographic data set because the height of the scanner is fixed as it scans.
- **Constant-force mode**: the deflection of the cantilever can be used as input to a feedback circuit that moves the scanner up and down in z, responding to the topography by keeping the cantilever deflection constant. In this case, the image is generated from the scanner's motion. With the cantilever deflection held constant, the total force applied to the sample is constant.

In constant-force mode, the speed of scanning is limited by the response time of the feedback circuit, but the total force exerted on the sample by the tip is well controlled. Constant-force mode is generally preferred for most applications.

Constant-height mode is often used for taking atomic-scale images of atomically flat surfaces, where the cantilever deflections and thus variations in applied force are small. Constant-height mode is also essential for recording real-time images of changing surfaces, where high scan speed is essential.

2.2.2 Non-contact AFM

Non-contact AFM (NC-AFM) is one of several vibrating cantilever techniques in which an AFM cantilever is vibrated near the surface of a sample. The spacing between the tip and the sample for NC-AFM is on the order of tens to hundreds of angstroms. This spacing is indicated on the van der Waals curve of Figure 4b as the non-contact regime.

NC-AFM is desirable because it provides a means for measuring sample topography with little or no contact between the tip and the sample. Like contact AFM, non-contact AFM can be used to measure the topography of insulators and semiconductors as well as electrical conductors.

The total force between the tip and the sample in the non-contact regime is very low. The low force is advantageous for studying soft or elastic samples. A further advantage is that samples like silicon wafers are not contaminated through contact with the tip.

Because the force between the tip and the sample in the non-contact regime is low, it is more difficult to measure than the force in the contact regime, which can be several orders of magnitude greater. In addition, cantilevers used for NC-AFM must be stiffer than those used for contact AFM because soft cantilevers can be pulled into contact with the sample surface. The small force values in the non-contact regime and the greater stiffness of the cantilevers used for NC-AFM are both factors that make the NC-AFM signal small, and therefore difficult to measure. Thus, a sensitive, AC detection scheme is used for NC-AFM operation.

In non-contact mode, the system vibrates a stiff cantilever near its resonant frequency with amplitude of a few tens to hundreds of angstroms. Then, it detects changes in the resonant frequency or vibration amplitude as the tip comes near the sample surface. Changes in the resonant frequency of the cantilever can be used as a measure of changes in the force gradient, which reflect changes in the tip-to sample spacing, or sample topography. The sensitivity of this detection scheme provides sub-angstrom vertical resolution in the image, as with contact AFM.

In NC-AFM mode, the system monitors the resonant frequency or vibrational amplitude of the cantilever and keeps it constant with the aid of a feedback system that moves the scanner up and down. By keeping the resonant frequency or amplitude constant, the system also keeps the average tip-to-sample distance constant. As with contact AFM (in constant-force mode), the motion of the scanner is used to generate the data set.

NC-AFM does not suffer from the tip or sample degradation effects that are sometimes observed after taking numerous scans with contact AFM. As mentioned above, NC-AFM is also preferable to contact AFM for measuring soft samples. In the case of rigid samples, contact and non-contact images may look the same. However, if a few monolayers of condensed water are lying on the surface of a rigid sample, for instance, the images may look quite different. An AFM operating in contact mode will penetrate the liquid layer to image the underlying surface, whereas in non-contact mode an AFM will image the surface of the liquid layer.

For cases where a sample of low moduli may be damaged by the dragging of an AFM tip across its surface, another mode of AFM operation is available: intermittent-contact mode. Intermittent-contact mode is useful for a variety of applications, and it is described in the following section.

2.2.3 INTERMITTENT-CONTACT AFM (TAPPING MODE)

Intermittent-contact AFM (IC-AFM) is similar to NC-AFM, except that for IC-AFM the vibrating cantilever tip is brought closer to the sample so that at the bottom of its travel it just barely hits (taps) the sample. The IC-AFM operating region is indicated on the force curve in Figure 4b.

As for NC-AFM, for IC-AFM the cantilever's oscillation amplitude changes in response to tip-to-sample spacing. An image representing surface topography is obtained by monitoring these changes. Some samples are best handled using IC-AFM instead of contact or non-contact AFM. IC-AFM is less likely to damage the sample than contact AFM because it eliminates lateral forces (friction or drag) between the tip and the sample. In general, it has been found that IC-AFM is more effective than NC-AFM for imaging larger scan sizes that may include greater variation in sample topography. IC-AFM has become an important AFM technique since it overcomes some of the limitations of both contact and non-contact AFM.

AFM has a number of advantages over other techniques that make it a favorite among leading researchers. It is rather easy to operate and very versatile. It provides easily achievable high-resolution and three-dimensional information in real space with little sample preparation for low-cost. In-situ observations, imaging under vacuum or immersed in a fluid, temperature and environmental controls are all available.

The two main drawbacks of AFM and affiliated techniques are the limited field of view and the possibility of artifacts coming from spurious interactions between the tip and the sample.

Table 2: Comparison of AFM and other Microscopy Techniques

	AFM	TEM	SEM	Optical
Max resolution	Atomic	Atomic	1's nm	100's nm
Typical cost (x $1,000)	100 - 200	500 or higher	200 - 400	10 - 50
Imaging Environment	air, fluid, vacuum, special gas	vacuum	vacuum	air, fluid
In-situ	Yes	No	No	Yes
In fluid	Yes	No	No	Yes

2.3 MAGNETIC FORCE MICROSCOPY

Magnetic force microscopy (MFM) images the spatial variation of magnetic forces on a sample surface. For MFM, the tip is coated with a ferromagnetic thin film. The system operates in non-contact mode, detecting changes in the resonant frequency of the cantilever induced by the magnetic field's dependence on tip-to-sample separation (see Figure 1). MFM can be used to image naturally occurring and deliberately written domain structures in magnetic materials.

During the MFM measurements, there are two forces acting on the tip; magnetic and Van der Waals forces. Hence, an image taken with a magnetic tip contains information about both the topography and the magnetic properties of a surface. The dominating force depends on the distance between the tip and the sample surface, because the interatomic magnetic force persists for greater tip-to-sample separations than the van der Waals force. If the tip is close to the surface, in the region where standard non-contact AFM is operated, the image will be predominantly topographic. As one increases the separation between the tip and the sample, magnetic effects become apparent. Collecting a series of images at different tip heights is one way to separate magnetic from topographic effects.
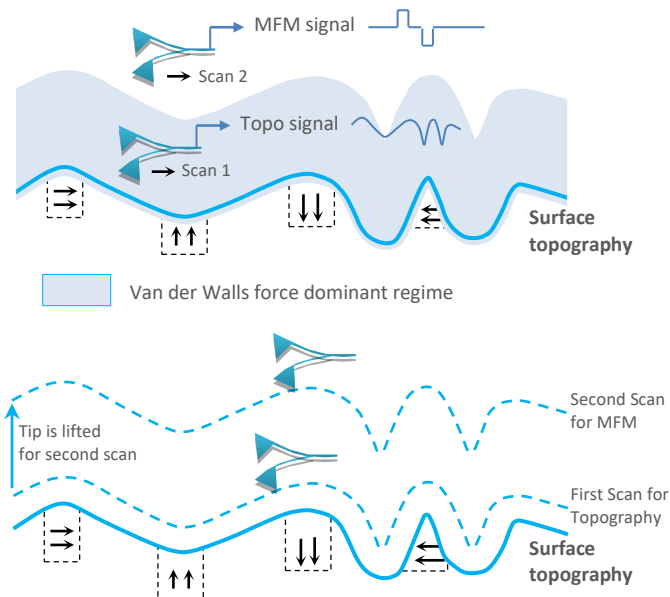

Figure 6: The schematics of (a) Force Range technique and (b) Two Pass technique {Document not in library}

The key to successful MFM imaging lies in separating the magnetic signal from the entire signal. In MFM, this is can be done by two techniques:

- **Force Range technique**: Van der Waals force is a short range force while the magnetic force is a long range force. In the first scan, the tip is scanned in the region where the van der Waals force is dominant for topography image. Then, the set-point is varied to place the tip in the region where the magnetic force is dominant and scanned for MFM image (Figure 6a)
- **Two Pass technique**: Sample is scanned twice to separate the signal (Figure 6b). In the first scan, the tip scans the surface to obtain the topography of the sample. In the second scan, the tip-sample distance is increased and the biased tip is scanned along the topography line obtained from the first scan. The tip is only affected by the magnetic force and MFM image is obtained as a result.

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