Photochemical Material Analysis
(광화학소재분석기술)

:Surface and Thin Film Analysis
(표면 및 박막분석)

4. Scanning Probe Microscopy

Atomic Force Microscopy

Scanning Probe Microscopy

AFM cantilevers and probes

An optical lever-based AFM force sensor requires a cantilever with a probe at its end for operation

Typically these are fabricated using MEMS technology and are considered a disposable component of the AFM

In principle, an AFM probe should last forever; however, in practice the probe tip is often blunted when it touches a surface.

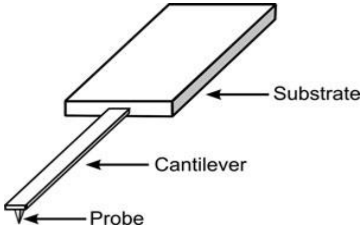

Fig. 2.27. Illustration of an AFM cantilever/probe/substrate created by micromachining of Si or Si_3N_4. All commercially available probes have substrates with the same dimension, for ease of use in different instruments. The probe is sometimes referred to as the tip, and the substrate as the chip. Not to scale

Scanning Probe Microscopy

Probe materials

AFM cantilevers can be fabricated from any material that can be fabricated into a spring-like cantilever

The first AFM cantilevers were fabricated from tungsten wire and had a probe etched in the silicon at the end. Early in the evolution of AFM it was discovered that the best AFM probes could be constructed from MEMs technology. There are two materials commonly used for AFM cantilevers: silicon nitride (Si_3N_4) and silicon (Si).

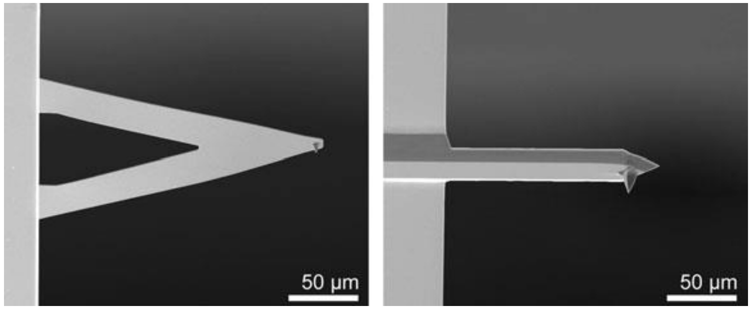

Fig. 2.29. Examples of contact and non-contact probes. Left: a typical v-shaped contact-mode cantilever. The whole probe is made from silicon nitride (Si_3N_4), and has an integrated square pyramidal probe tip. Right: a probe designed for oscillating modes such as non-contact AFM. The cantilever is usually rectangular (or a modified rectangle shape like this one). The whole probe is made from silicon, and is much stiffer and more prone to breaking than the contact probe; however it has a sharper tip.

Contact versus oscillating mode probes

Cantilevers for optical lever-based AFM can be operated in two basic topography modes; contact (static) mode and oscillating modes

- The cantilevers used for contact mode have force constants that are typically much less than 1 N/m and are fabricated from either silicon or silicon nitride
- Oscillating mode cantilevers are usually fabricated from silicon and have force constants that are greater than 10 N/m

There are also a large number of other probes available differentiated by differing tip geometries (for example many examples of probes with 'sharpened' and high-aspect-ratio tips are available), cantilever force constants, and coatings

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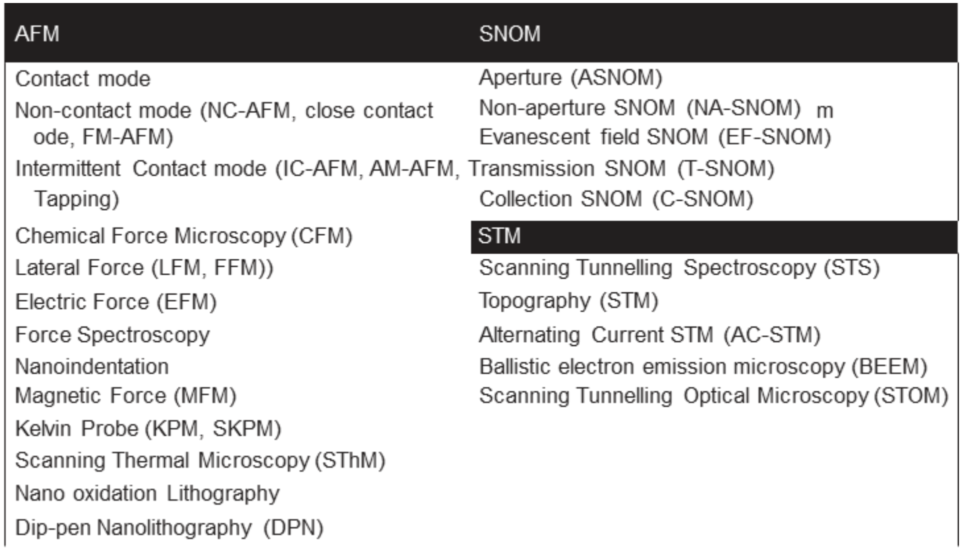
Atomic Force Microscopy

AFM Mode

Topographic modes

The basis of AFM as a microscopic technique is that it measures the topography of the sample



AFM	SNOM
Contact mode	Aperture (ASNOM)
Non-contact mode (NC-AFM, close contact ode, FM-AFM)	Non-aperture SNOM (NA-SNOM) m Evanescent field SNOM (EF-SNOM)
Intermittent Contact mode (IC-AFM, AM-AFM, Tapping)	Transmission SNOM (T-SNOM) Collection SNOM (C-SNOM)
Chemical Force Microscopy (CFM)	**STM**
Lateral Force (LFM, FFM))	Scanning Tunnelling Spectroscopy (STS)
Electric Force (EFM)	Topography (STM)
Force Spectroscopy	Alternating Current STM (AC-STM)
Nanoindentation	Ballistic electron emission microscopy (BEEM)
Magnetic Force (MFM)	Scanning Tunnelling Optical Microscopy (STOM)
Kelvin Probe (KPM, SKPM)	
Scanning Thermal Microscopy (SThM)	
Nano oxidation Lithography	
Dip-pen Nanolithography (DPN)	

Fig. 3.1. Summary of the names of some SPM-based techniques.

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AFM Mode

Topographic modes – contact mode

Contact mode AFM was the first mode developed for AFM. It is the simplest mode conceptually, and was the basis for the development of the later modes

Contact mode is capable of obtaining very high-resolution images. It is also the fastest of all the topographic modes, as the **deflection of the cantilever leads directly to the topography of the sample**, so no summing of oscillation measurements is required which can slow imaging.

In contact-mode AFM, the tip of the probe is always touching the sample. This has the following important implications for contact-mode AFM:

- As a result of the repulsive force between the tip and the sample, the sample may be damaged or otherwise changed by the scanning process.
- Conversely, the tip could also be damaged or changed by the scanning process.
- As the tip and sample are constantly in contact with each other as the tip moves along the sample, in addition to the normal force they apply to each other, lateral forces are experienced by both probe and sample.
- The contact between the tip and the sample means that the nature of the sample surface may affect the results obtained. This means that the technique can be sensitive to the nature of the sample.

Scanning Probe Microscopy

AFM Mode

Topographic modes – contact mode

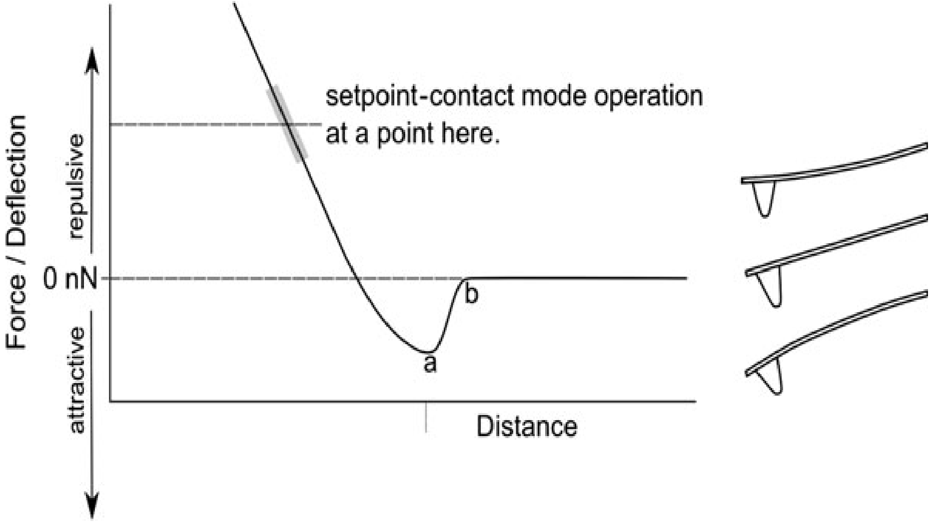

Fig. 3.2. Simplified force–distance curve showing contact (repulsive region) scanning regime. A deflection–distance curve, which is the raw data from which a force–distance curve is measured, has a similar shape. Right: illustration of probe bending in each regime.

Scanning Probe Microscopy

AFM Mode

Topographic modes – Non-contact mode/close-contact mode

Non-contact-mode principles of operation

- Non-contact mode is carried out in amplitude modulation mode, and the error signal may be either the amplitude or phase of oscillation of the tip.
- To avoid the possibility of slipping into the repulsive regime which is likely to damage or contaminate the tip, a high-frequency cantilever is typically used with $ø_0$(resonant frequency) in the range of 300–400 kHz.

Scanning Probe Microscopy

Atomic Force Microscopy

AFM Mode

Non-topographic modes

Force spectroscopy

Force spectroscopy involves maintaining the x-y position of the AFM probe fixed, while ramping it in the z axis, to measure the deflection as the tip approaches and retracts from the sample surface.

Force spectroscopy consists of simply measuring force-distance curves

The great utility of this technique is that the AFM directly measures the force between the contacting atoms or molecules on the end of the probe and sample surface, and as the cantilever may be highly flexible, and deflection sensitivity with optical lever-based instruments is very high, single-molecule interaction studies are possible.

The surfaces probed have been of even wider variety. Again, **for molecule-molecule interactions studies**, often a flat substrate will have the molecules of interest grafted on, but also cell membranes, micro-organisms, whole living cells and a wide variety of solid surfaces including polymers, metals, ceramics and more have been probed

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Atomic Force Microscopy

AFM Mode

Non-topographic modes

Force spectroscopy

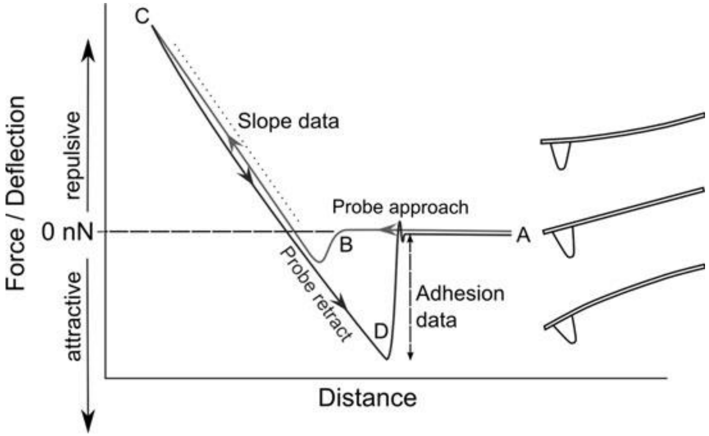

Fig. 3.15. A model force–distance curve. At point A, the probe is far from the surface, at B 'snap-in' occurs as attractive forces pull the probe onto the surface. The force becomes repulsive as the probe continues to be driven towards the sample. At some user-defined point C, the direction of travel reverses. At point D 'pull-off' occurs as the force applied to the cantilever overcomes tip–sample adhesion. Adhesion data is used for force spectroscopy while slope data is used for nanoindentation (Section 3.2.2).

Scanning Probe Microscopy

Atomic Force Microscopy

AFM Mode

Non-topographic modes

Nanoindentation

If instead of measuring the data as the AFM withdraws from the sample surface, we record the data measured as the tip contacts with and presses onto the sample surface, we are carrying out a different experiment, called nanoindentation

- to measure load-displacement curves as a hard indenter (for example diamond) presses into a sample

Typically, such instruments are designed to create a series of indents (holes) in a sample, and allow the measurement of the sizes of the indents (by, e.g. light microscopy), and are sensitive to forces in the micronewton range

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Nanoindentation

Advantages of AFM-based nanoindentation

- High load sensitivity – load sensitivity may be as low as piconewton, although even for soft materials the required sensitivity is not likely to be greater than a nanonewton.
- Inbuilt ability to measure the indents created, at high resolution in x, y and z (see Figure 3.17).
- High positioning resolution – i.e. we can choose small regions of a sample, or perform the experiment on very small samples.

Disadvantages of AFM-based nanoindentation

- Non-perpendicular probe approach – quantitative nanoindentation requires the indenter to approach the sample perpendicularly, which is not the case normally for AFM. This problem can be overcome, with care.
- Non-linear z positioning. Unless the system is equipped with linearization in the z-axis this can cause some serious problems.
- The system must be calibrated to extract real forces.

⟶ useful to look at relative hardness and softness

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Nanoindentation

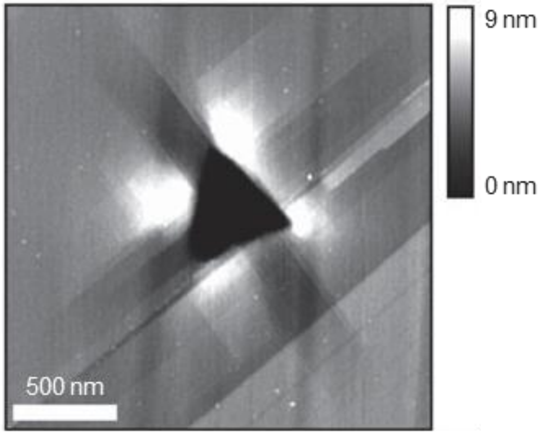

Fig. 3.17. AFM image of an indentation made by a dedicated nanoindenter. The indentation is in a magnesium oxide crystal, and the image shows the indentation (black triangle) pile-up – material pushed out of hole (white features at triangle corners), and also shows long-range dislocations in the crystal structure (diagonal discontinuities)

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Mechanical property imaging - Lateral force microscopy

Compare the left- and right-hand sides of the split photodetector, we obtain the lateral deflection signal. When measuring this signal, the technique is sometimes called **lateral force microscopy, or LFM**

-> this signal contains information about the mechanical interaction of the probe tip with the sample surface

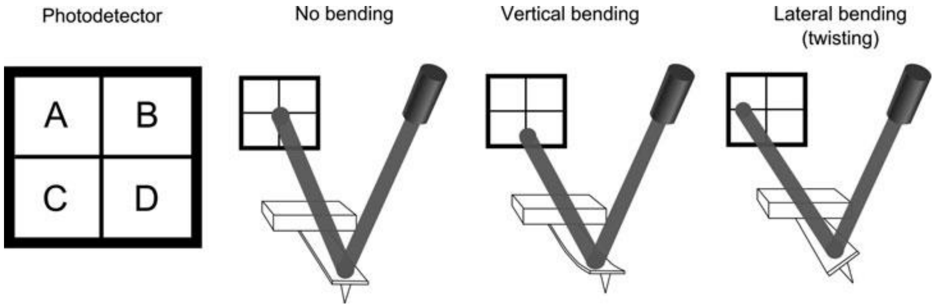

Fig. 3.4. Illustration of how the photodetector detects vertical and horizontal bending of the cantilever.

Scanning Probe Microscopy

Atomic Force Microscopy

AFM Mode

Non-topographic modes

Mechanical property imaging - Lateral force microscopy

The lateral twisting of the cantilever is a measure of the friction encountered by the tip as it scans over the sample. Thus, this signal is sensitive to the nature (shape and frictional properties) of the surface. For this reason, LFM is sometimes also called **friction force microscopy (FFM)**

Even on perfectly flat, homogeneous samples, the two images will be different from each other in the magnitude and possibly sign of the signal. In general, changes of slope will affect forwards and backwards scans oppositely, and changes in friction due to material contrast will give greater or smaller difference between the forward and reverse scans

Scanning Probe Microscopy

Atomic Force Microscopy

AFM Mode

Non-topographic modes

Mechanical property imaging – Lateral force microscopy

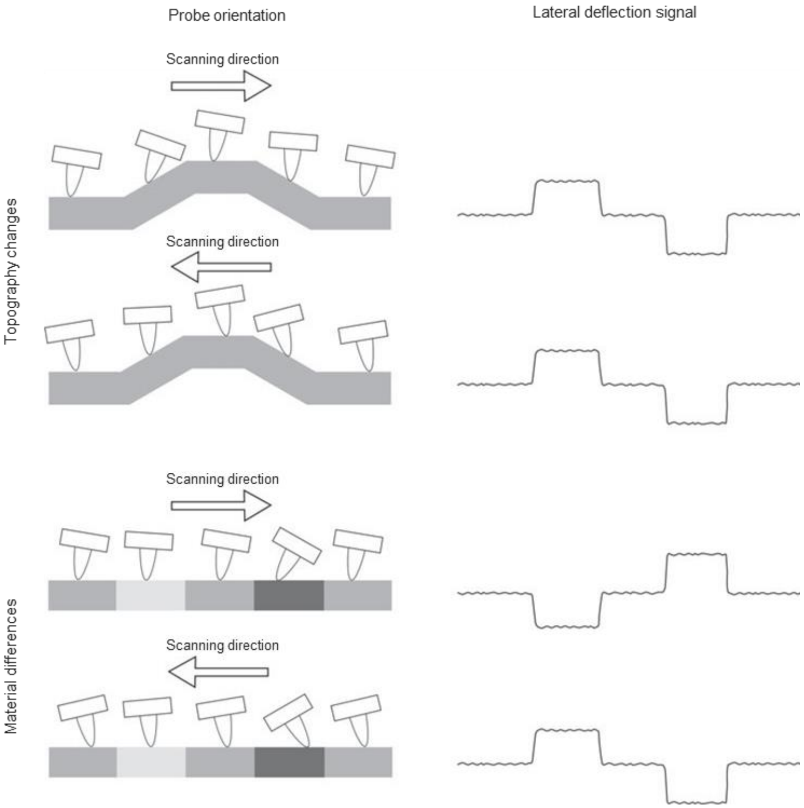

Fig. 3.18. Schematic of lateral force signals recorded on a sample with variations in topography only (top) and in material friction only (bottom). **Darker colours represent material with higher friction**. Note that in the case of topography changes (upper), the difference between the forward and back lateral deflection signals is constant; for material contrast (lower), the difference changes.

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Magnetic force microscopy

The presence and distribution of magnetic fields is measured directly, by using a magnetic probe

- These consist of standard silicon cantilevers with a thin **magnetic coating**. Typical materials used for the coating include ***cobalt, cobalt-nickel and cobalt-chromium***

In 'lifting'-type modes, the topography of the sample is measured first, followed by raising the probe, and scanning again to collect the magnetic data. <u>One method is to collect a normal topography scan, and then change the z set-point to lift the probe from the surface and collect a 'magnetic image'</u>

Scanning Probe Microscopy

Atomic Force Microscopy

AFM Mode

Non-topographic modes

Magnetic force microscopy

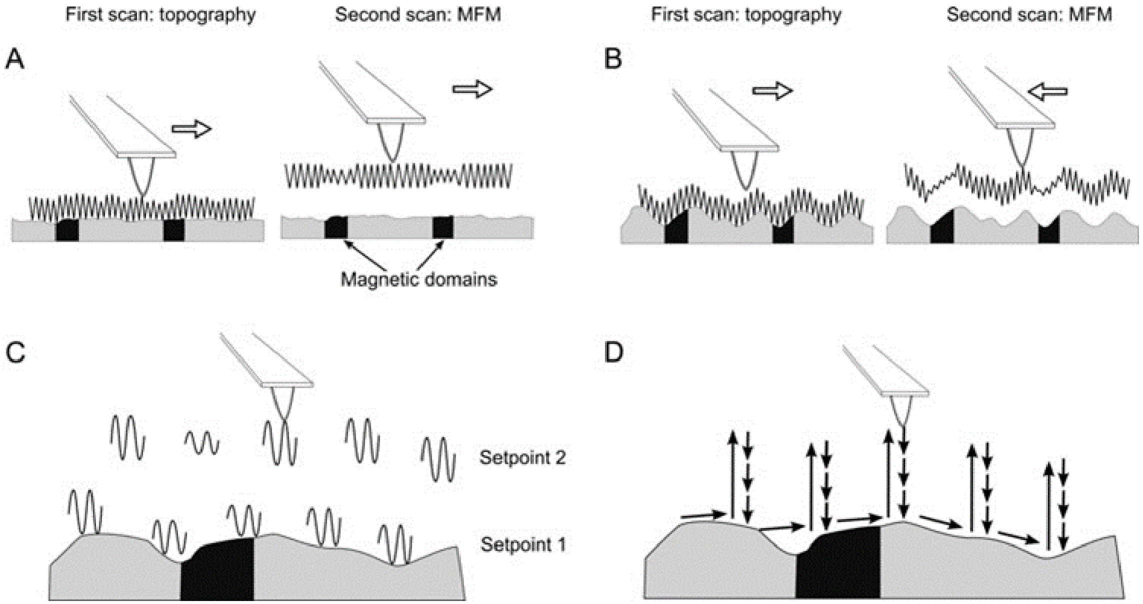

Fig. 3.21. Schematics of various implementations of MFM. A: lifting probe between topography and MFM images. B: Bard method of lifting lever between scan lines. C: *z* set-point oscillation. D: Hosaka method of moving probe close to surface, and recording MFM signal at various points for each height.

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Magnetic force microscopy

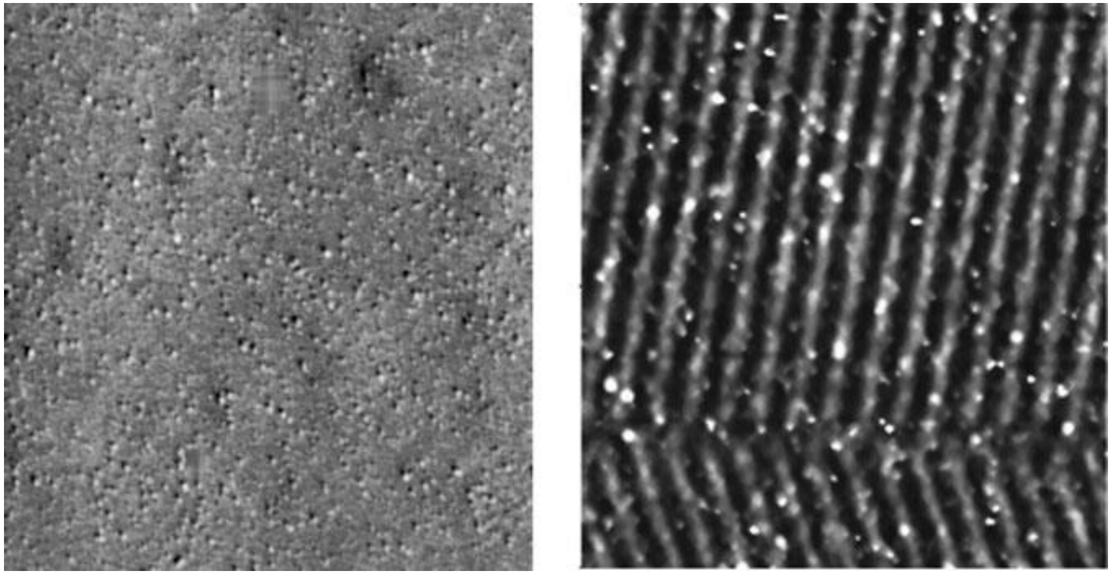

Fig. 3.22. Example MFM images. Left: topography of magnetic tape sample. Right: MFM image of the same region, showing magnetic fields above recorded data bits on the tape. Both are 10 μm × 10 μm images.

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Electric force microscopy and scanning Kelvin probe microscopy

- Electric force microscopy (EFM) refers to a technique analogous to MFM which enables the measurement of electrical fields with the AFM, rather than magnetic fields

- A standard silicon or silicon nitride cantilever may be used for simple EFM imaging, although conductive (metal-coated) tips are required for read/write applications, and more sophisticated electrical modes (see below).

- <u>EFM has been shown to detect trapped charge on surfaces</u>, and in some cases gives clear contrast where none is visible in the topography signal

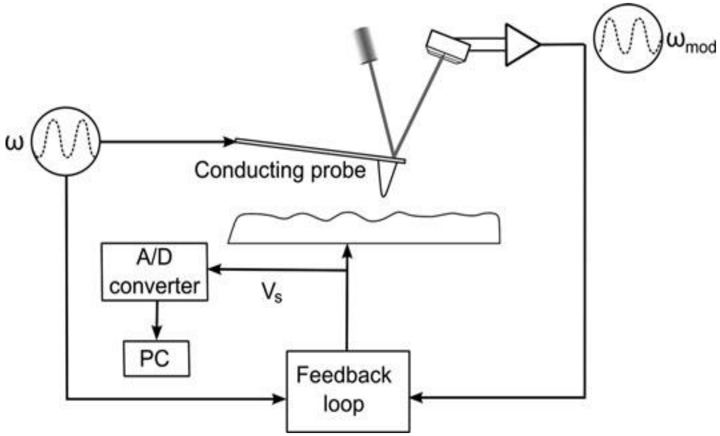

Fig. 3.23. Schematic illustration of instrumental set-up for scanning Kelvin probe microscopy.

Scanning Probe Microscopy

AFM Mode

Non-topographic modes

Electric force microscopy and scanning Kelvin probe microscopy

- More sophisticated technique to measure tip-sample potential is scanning Kelvin probe microscopy (SKPM)

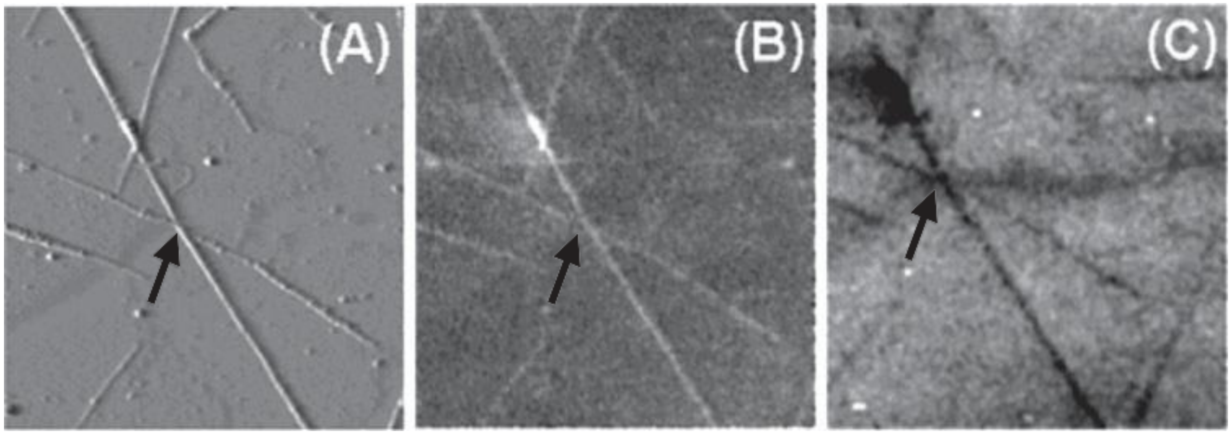

Fig. 3.24. Example of Kelvin probe and electric force microscopy. AFM height image (A, shaded image), Kelvin probe (B), and EFM (C) images of carbon nanotubes on a gold surface. The images are not all in exactly the same place; the red arrow highlights a connection between two nanotubes in each image.

Scanning Probe Microscopy

AFM Mode

Surface modification

As well as measuring sample surfaces, an AFM may be used to manipulate or to modify the surfaces

- local oxidation
- scratching
- dip-pen nanolithography

local oxidation

One of the earliest of the nanolithographic techniques to be demonstrated was local oxidation

- A bias is applied to the tip to cause contact potential difference while scanning the surface, resulting typically in an oxidation of the material at the sample surface.

- These experiments are commonly carried out on silicon and result in features of silicon oxide at the surface

Scanning Probe Microscopy

AFM Mode

Surface modification

Scratching

All that is required is to apply a high normal force to the sample, and use the lithographic controls in the AFM control software to direct the tip in the desired pattern

Dip-pen nanolithography

The great advantage of this technique is that almost any material that can be deposited on a surface can be used and formed into nanometre-scale patterns

- typically water-soluble molecules or very small particles are applied
  - -> The idea is analogous to that of a macroscopic pen

Scanning Probe Microscopy

AFM Mode

Surface modification

Dip-pen nanolithography

The AFM tip is immersed, or dipped into a solution of the molecule to be grafted.
With a hydrophilic tip, and aqueous solution, the AFM probe will become coated in a thin layer of the writing solution.
Then, when the tip is in contact with the substrate, the grafting molecules are applied to the surface via the water capillary layer

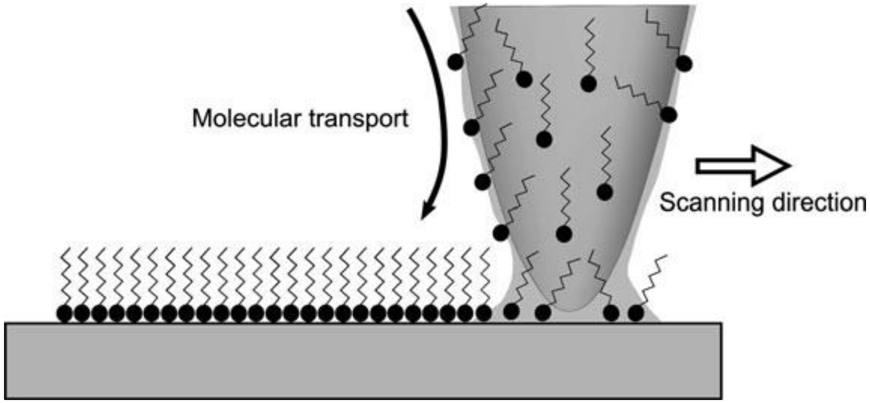

Fig. 3.27. Schematic of dip-pen nanolithography, showing how the water meniscus is used to transport molecules to the surface.

Scanning Probe Microscopy

Atomic Force Microscopy

AFM Mode

Surface modification

AFM based Lithography

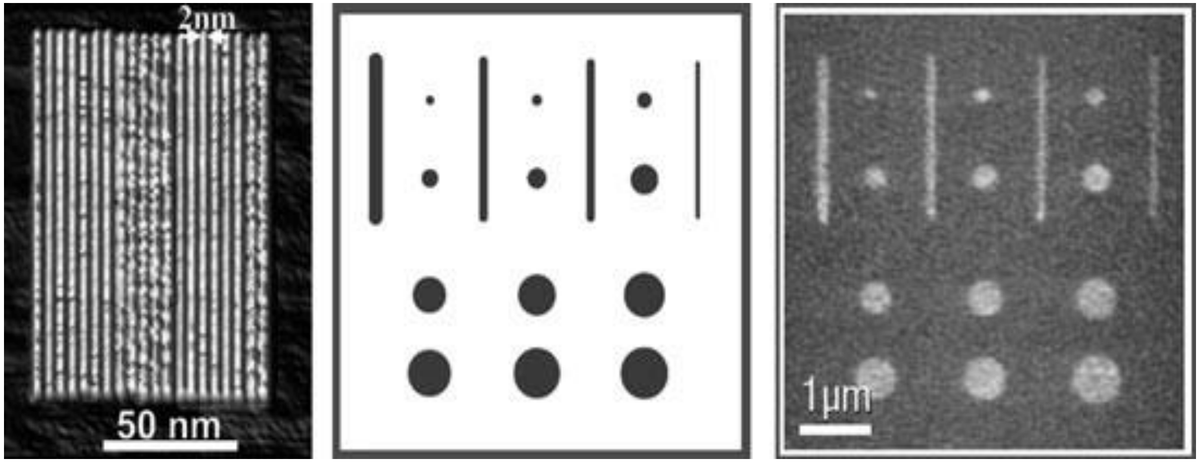

Fig. 3.28. Examples of AFM-based lithography. Left: polymeric patterns on silicon formed by anodic oxidation, showing line widths of approximately 2 nm. Reproduced with permission from [250]. Centre: a bit-map image used as the input for a dip-pen nanolithography (DPN) routine. Right: AFM (lateral force) image of the resulting surface patterns.

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