Scanning Probe Microscopy and its Applications

- Scanning-probe-based instrumentation
- AFM-based multi-function modes
- Beyond imaging

Chih-Wen Yang (楊志文)
Surface and NanoScience Laboratory
Institute of Physics, Academia Sinica, Taiwan
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Scanning Probe Microscopy (SPM)

- Scanning Tunneling Microscopy (STM)  

- Near-Field Scanning Optical Microscopy (NSOM)  
  --- D. W. Pohl (1982)

- Atomic Force Microscopy (AFM)  

- Scanning Thermal Microscopy (SThM)  
  --- C. C. Williams, H. Wickramasinghe (1986)

- Magnetic Force Microscopy (MFM)  

- Friction Force Microscopy (FFM or LFM)  
  --- C. M. Mate et al (1987)

- Electrostatic Force Microscopy (EFM)  

- Scanning Capacitance Microscopy (SCM)  

- Force Modulation Microscopy (FMM)  
Key elements of SPM

- Interaction Sensor (figure)
- Nano-scale Positioner (arm)
- Computer & Feedback Controller (brain)
The starting point - STM

F. Giessibl’s Rev. Mod. Phys.


Binnig and Rohrer awarded Nobel Prize in Physics in 1986 for STM

If $|V_t|$ is small compared to workfunction $\Phi$, and tunneling current is given by $I_t(z) = I_0 e^{-2\kappa_t z}$ where $z$ is the gap $I_0$ is a function of the applied voltage and the density of states in the tip and the sample, and $\kappa_t = \sqrt{2m\Phi / \hbar}$

For most metals, $\Phi \sim 4eV$, so that $\kappa_t = 1\text{Å}^{-1}$

Most current carried by “front atom” blunt tips, so atomic resolution possible even with relatively blunt tips

Only electrically conductive samples, restricting its principal use to metals and semi-conductors

**FIG. 1.** Description of the principle operation of an STM as well as that of an AFM. The tip follows contour B, in one case to keep the tunneling current constant (STM) and in the other to maintain constant force between tip and sample (AFM, sample, and tip either insulating or conducting). The STM itself may probe forces when a periodic force on the adatom A varies its position in the gap and modulates the tunneling current in the STM. The force can come from an ac voltage on the tip, or from an externally applied magnetic field for adatoms with a magnetic moment.

**FIG. 2.** Experimental setup. The lever is not to scale in (a). Its dimensions are given in (b). The STM and AFM piezoelectric drives are facing each other, sandwiching the diamond tip that is glued to the lever.

- Binnig invented the AFM in 1986, and while Binnig and Gerber were on a Sabbatical in IBM Almaden they collaborated with Cal Quate (Stanford) to produce the first working prototype in 1986.
Atomic force microscope (AFM)

- Cantilever-tip sense the force interaction
- Beam deflection system detect the change of cantilever beam (PSPD)
- Feedback system monitor the PSPD signal to keep constant tip-sample interaction (constant distance)
- By raster scanning, the surface morphology can be obtained

- Force sensitivity
- Tip-shape effect
Interaction between the probe and sample

Lennard-Jones potential $\phi(r) = - \frac{A}{r^6} + \frac{B}{r^{12}}$

**Short-range:**
1) Bonding
2) Repulsion

**Long-range:**
1) Van der Waal
2) Capillary
3) Magnetic
4) Electrostatic

~50nm
Reaction of the probe to the force
Deflection vs. Distance

Cantilever deflection

Setpoint deflection

Total contact force

Piezo-displacement

1. Cantilever spring force

2. Tip-sample adhesion force

3. Cantilever

4. Setpoint

5. Tip-sample contact
• Detection mechanism of cantilever deflection

Optical method
• Laser interferometry,
• Beam deflection
• Astigmatism

Non-optical method
(STM tip, piezoelectric, piezoresistive…)
Position-sensitive Photo Diode (PSPD)

D ~ 10mm    d ~ 1mm    s ~ 0.01mm
Cantilever beam deflection detection

a) Normal force

A+B = up
C+D = down

a) Lateral force

A+C = left
B+D = right
Piezoelectric effect
Piezo-tube scanner for X-Y-Z precision movement

(a)

(b)
Three scanning modes of AFM

Contact Mode AFM

Semicontact Mode AFM
(Tapping mode)

Non-contact Mode AFM
Two imaging methods in contact mode

- **Constant force method**: By using a feedback loop the tip is vertically adjusted in such a way that the force always stays constant. The tip then follows a contour of a constant contact force during scanning. A kind of a topographic image of the surface is generated by recording the vertical position of the tip.

- **Constant height method**: In this mode the vertical position of the tip is not changed, equivalent to a slow or disabled feedback. The displacement of the tip is measured directly by the laser beam deflection. One of its advantages is that it can be used at high scanning frequencies.
Constant-force scan vs. constant-height scan

Constant-force mode

Constant-height mode
Constant-force scan vs. constant-height scan

**Constant-force**

- **Advantages:**
  - Large vertical range
  - Constant force (can be optimized to the minimum)

- **Disadvantages:**
  - Requires feedback control
  - Slow response

**Constant-height**

- **Advantages:**
  - Simple structure (no feedback control)
  - Fast response

- **Disadvantages:**
  - Limited vertical range (cantilever bending and detector dynamic range)
  - Varied force
Problems with the contact mode

![Diagram of cantilever with tip and fluid layer]

- Electrostatic charge
- Cantilever with tip
- Fluid layer

![Graphs showing cantilever force for different conditions]

- Water
- Air

- Sample Position
- Cantilever Force

100 nN
\[ \omega_1 = \omega_0 \left(1 + \frac{F'}{2c}\right) \]
$$E_{pair}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

Diagram showing:
- Tapping mode
- Contact mode
- Non-contact mode

Contact mode, Non-contact mode, Tapping Mode diagrams with corresponding force graphs.
Tapping mode

Amplitude Detector → High Resolution Oscillator → System Controller

Laser → Photo-detector

Oscillation Piezo (10K – 1MHz)

Sample → Silicon Cantilever with Tip

“Free” amplitude (> 20 nm)

“Tapping” → Fluid layer → Amplitude reduced

Fluid layer
Three Types of Data Collected in Tapping Mode

1) Height Data: z-axis position monitored by input voltage to piezo tube scanner.

2) Phase Data (i): phase of drive signal compared to phase of output signal from photo diode detector.

3) Amplitude Data: output signal measuring RMS value of laser y-axis position on detector.

Piezo driver vibrates cantilever at resonance frequency.

Silicon Cantilever

Sample Surface
AFM image of a fresh Alfalfa root section

Wood pulp fiber
phase image highlights cellulose microfibrils
Phase in tapping-mode depends on:
- drive frequency $f$ (vs. $f_0$)
- drive amplitude $A_0$
- damping ratio $A_{\text{setpoint}}/A_0$
- surface topography
- material properties

There is no simple, general relation between phase in tapping-mode AFM and material properties
Fabrication of AFM probes

Typical Tip Dimension:
150\(\mu\)m x 30\(\mu\)m x 0.5\(\mu\)m

Materials: \(\text{Si}_3\text{N}_4\)

Typical Tip Dimension:
150\(\mu\)m x 30\(\mu\)m x 3\(\mu\)m

Materials: Si
V-shaped

Materials: Si, SiO$_2$, Si$_3$N$_4$
Ideal Tips: hard, small radius of curvature, high aspect ratio

Pyramid Tip

Ultrascharp Tip

Rectangular-shaped

Diamond-coated Tip
Tip of small shear force
(for Contact mode)

Typical Tip Dimension:
150μm x 30μm x 0.5μm

$k \sim 0.1 \text{ N/m}$

Materials: Si$_3$N$_4$
Tip of high resonant frequency
(for Tapping mode)

Typical Tip Dimension:
150μm x 30μm x 3μm

$f_r \sim 100$ kHz

Materials: Si
Criteria for AFM probe

1) Small spring constant \((k)\)
   \[ F = k \Delta z \]
   To detect force of \(~\) nN

2) High resonant frequency \((f_r)\)
   \[ f_r \propto (k / m)^{1/2} \]
   To enable scanning and other operations

3) Highly anisotropic stiffness
   Easy to bent and difficult to twist

4) Sharp protrusion at the apex
   To better define the tip-sample interaction
Convolution Effect

- **AFM image is a convolution** of the surface features and the tip geometry.
- **The spatial resolution is limited by** the sharpness of the probe tip.
- **When the tip is much sharper than the surface features**, it will collect an image reflecting the “true” surface features.
- **When the tip is much larger than the surface features**, using such a tip to scan the surface will result in an image that is merely a reflection of the geometry of the tip apex itself.
AFM artifact

Dirty or Contaminated Tips

Double/multiple tips

Flying Tip

Laser interference

Piezo drift
Boot-shaped tip

 LAS 00 mm
AFM artifact

Double tip
Optical interference artifacts

A. Méndez-Vilas et al. / Ultramicroscopy 92 (2002) 243–250
Scan rate over feedback  Piezo-Scanner drift
AFM versus STM

1. Generally, STM has “better” resolution than AFM.
2. The force-distance dependence in AFM is much more complex when characteristics such as tip shape and contact force are considered.
3. STM is generally applicable only to conducting samples while AFM is applied to both conductors and insulators.
4. AFM offers the advantage that the writing voltage and tip-to-substrate spacing can be controlled independently, whereas with STM the two parameters are integrally linked.
AFM versus EM

1. AFM only reveal the surface and EM can probe the interior structure of the sample with higher resolution.
2. AFM provides direct topographic measurements and EM provides only 2D projection of the sample structure.
3. No charging effect occurs in AFM. So, for insulating samples, no metallic coating is necessary.
AFM versus Optical Microscope

1. AFM has much better resolution than Optical Microscope (OM).
2. AFM provides unambiguous measurement of step heights, independent of reflectivity differences between materials.
3. OM can be applied to much faster dynamic studies with the pump-probe method.
AFM Tip + Carbon Nanotube

AFM Tip

Carbon Nanotube
\( \phi \approx 20\text{nm} \)
\( L \approx 80\text{nm} \)
Image of high aspect ratio
AFM images

CD pits

Integrated circuit

Chromosomes

DVD pits

Bacteria

DNA
AFM-based multi-function modes

Electric probe for EFM

Magnetic probe for MFM

Fiber probe or aperture probe for SNOM

Sample

Scan path

Scan path

Magnetic sample

Excitation light

Near-field

Far-field

Sample
Magnetic Force Microscope, MFM

Topography of hard disk  MFM image

- Scan mode: AC lift-mode
- Sample: hard disk surface
- Scan area: 10μm×10μm

Electrical Force Microscope, EFM

Sample voltage bias applied on one circuit electrode

- Scan mode: AC lift-mode
- Size: 21μm×21μm
1. Cantilever measures surface topography on first (main) scan.

2. Cantilever ascends to lift scan height.

3. Cantilever follows stored surface topography at the lift height above sample while responding to magnetic (electric) influences on second scan (measured by amplitude, phase or frequency detection).

**Lift Mode (MFM & EFM)**

Since magnetic (electrostatic) forces can be either attractive or repulsive, problems with feedback loop stability in the non-contact imaging mode are likely to occur.
Magnetic Force Microscopy (MFM)

\[ F = \nabla (m \cdot H) \]

Tips: silicon probes are magnetically sensitized by sputter coating with a ferromagnetic material.

Resolution: 10 ~ 25 nm.

Applications: hard disks, magnetic thin film materials, micromagnetism.

Bits (50 nm) on a magneto-optical disk
Scan area (5μm x 5μm)
**Electrostatic Force Microscopy (EFM)**

- **Tip:** Si cantilevers with conductive coating.
- The grounded tip first acquires the surface topography using the tapping mode.
- A voltage between the tip and the sample is applied in the second scan (Lift-Mode 50 to 100 nm) to collect electrostatic data. EFM measures electric field gradient and distribution above the sample surface.
- EFM is used to monitor continuity and electric field patterns on samples such as semiconductor devices and composite conductors, as well as for basic research on electric fields on the microscopic scale.
Scanning Surface Potential Microscopy (SSPM)
Kelvin Probe Microscopy (KPM)

As in EFM, this technique is usually implemented in the non-contact mode. In the second scan, the piezo is disengaged and oscillating is applied to the tip.

\[
F(z) = \frac{1}{2} \frac{\partial C(z)}{\partial z} \left[ (V_{dc} - V_{surf})^2 + \frac{1}{2} V_{ac}^2 [1 - \cos (2\omega t)] + 2(V_{dc} - V_{surf})V_{ac}\sin (\omega t) \right]
\]

\[
F_{dc}(z) = \frac{1}{2} \frac{\partial C(z)}{\partial z} \left[ (V_{dc} - V_{surf})^2 + \frac{1}{2} V_{ac}^2 \right]
\]

\[
F_{1\omega}(z) = \frac{\partial C(z)}{\partial z} (V_{dc} - V_{surf})V_{ac}\sin (\omega t)
\]

\[
F_{2\omega}(z) = \frac{1}{4} \frac{\partial C(z)}{\partial z} V_{ac}^2\cos (2\omega t)
\]

1. The lock-in technique allows extraction of the first harmonic signal, \(F_{1\omega}\). A feedback loop is employed to keep it equal to zero (nulling force approach) by adjusting \(V_{dc}\) on the tip. When \(V_{dc} = V_{surf}\), \(F_{1\omega} = 0\). Thus the surface potential is measured.

2. The high spatial and voltage resolution (~ mV) make KPM a prominent tool for the characterization of current devices, especially integrated circuit analysis.

3. This technique is also sensitive to local charge on the surface.
Figure 7.2. a. Topography of Nb-doped 36.8° SrTiO₃ bicrystal in the vicinity of grain boundary (a). b. Surface potential (SSPM) image of the same region. c, EFM (force gradient) images at tip bias $V_{\text{tip}} = 5\text{V}$ and (d) $V_{\text{tip}} = -5\text{V}$. The range is (a) 5 nm, (b) 20 mV and (c, d) 2 Hz.
Friction force microscopy (FFM)

\[ F_L = \alpha (F_N + F_{\text{inter}}) \]

- Lateral force
- Interaction
- Applied normal force
- Dynamic friction coefficient

LFM mode
Lateral Force Microscopy

- LFM is sensitive to friction and chemical forces.
- Image contrast depends on the scanning direction.
- Surface roughness will contribute to the contrast.
Scanning Near-field Optical Microscopy, SNOM
SNOM Probe

- No diffraction limit
- Resolution depends on aperture size
- Shear force detection is used to regulate the tip/sample separation
Imaging modes for NSOM
Topography                       NSOM Image  

Polystyrenes of 100 nm on glass
Quartz Tuning fork
(piezoelectric material)

\[ f_0 = 32.768\text{kHz} \quad \text{L}=3.0\text{mm} \quad \text{T}=330\mu\text{m} \quad \text{W}=120\mu\text{m} \]
Piezo driving signal

Piezo ground

Piezoelectric bimorph

Magnet

Iron disk

To preamplifier

electrode A

electrode B
Vibration modes of Tuning Fork

**Shear force mode (I)**
- Fiber probe
- Bimorph
- Tuning fork

**Shear force mode (II)**
- Fiber probe
- Bimorph
- Tuning fork

**Normal force mode**
- Fiber probe
- Bimorph
- Tuning fork
Beyond imaging

- Force spectroscopy
- Dynamic observation
- Chemical mapping
- Nano-manipulation
- Nano-lithography
Cantilever deflection vs. Distance

Cantilever deflection vs. Distance

Scanner Z-position

Feedback setpoint

Total contact force

Cantilever spring force

Adhesion force
Force curves vs. different surface interaction

(a) Cantilever deflection vs. Scanner Z-position
   - Van der Waals force

(b) Cantilever deflection vs. Scanner Z-position
   - Adhesion force
   - Capillary force

(c) Cantilever deflection vs. Scanner Z-position
   - Long-rang force
   - Elastic force

(d) Cantilever deflection vs. Scanner Z-position
   - Unbinding
Single Molecule Force Spectroscopy

Force measurement of an unfolding complex molecule.

Advanced graphical user interface shows titin muscle molecule force curve.
Interaction measurement by AFM tip

Individual bacteriorhodopsin molecules in water

Science 288, 143(2000)
Force curve vs. pH and solution Concentration

Dependence of double-layer force on the surface charge of a stearic acid sample. Curves are acquired at different pH with a silicon nitride tip (tip radius between 50 and 100 nm). On the x-axis, the sample position in nm. On the y-axis, the force in nN.

Force-displacement approach curves associated with double-layer force between a silicon nitride tip and mica in KC1 solutions of different concentration. The tip radius is estimated between 50 and 100 nm. On the x-axis, the sample position in nm. On the y-axis, the force in nN.

B. Cappella, G. Dietler/Surface Science Reports 34 (1999) 1–104
AFM probe for high speed imaging

株式会社 生体分子計測研究所

RIBM (Research Institute of Biomolecule Metrology)
High-Speed Atomic Force Microscopy

T. Ando, Nanotechnology 23, 062001 (2012)
High-Speed AFM Images of Walking Myosin V

(a) Diagram showing the structure of Myosin V.

(b) and (c) Images showing the walking process at different time intervals.

(d) Diagram showing the interaction of Streptavidin with Myosin V at different stages.

T. Ando, Nanotechnology 23, 062001 (2012)
Manipulation by AFM tip

Chemical Characterization

- Tip functionalization
AFM oxidation lithography

[Image of AFM oxidation lithography patterns and a diagram showing the process of oxidation with water undergoing electrolysis producing hydrogen ions and hydroxide ions.]
Nanolithography with force control

Dynamic plowing

Scratching
In 3D force mapping, a tip was scanned in Z as well as in XY to cover the whole 3D interfacial space.

The sample is modulated in the vertical Z direction with an amplitude of tens to hundreds of nanometers with a sine or triangle wave faster than the bandwidth of the Z distance regulation.

The vertical Z-movement results in cycles of approaching and retracting traces that lead to force–distance curves.

Topography information is obtained from the height correction performed by the feedback loop to keep a constant ‘peak’ of force (constant deflection feedback).

Force–distance curves can determinate surface mechanical information (stiffness, adhesion, deformation or dissipation).

Soft cantilever (k~ 1 N/m) used for this mode.

Multiparametric maps of native purple membrane with PFT mode.

3D-SFM mapping

- In 3D $\triangle f$ mapping, a tip was scanned in $Z$ as well as in $XY$ to cover the whole 3D interfacial space.

- For the scan in $Z$, a small vertical vibration ($< 2$ nm) was modulated with a sine wave faster than the bandwidth of the $Z$ distance regulation.

- The 3D $\triangle f$ image was constructed from either approaching or retracting $Z$ profiles at each $XY$ positions and the 2D height image (constant $\triangle f$ feedback) could be obtained simultaneously.

- Stiff cantilever ($k \sim 40$ N/m) used for this mode.

Typical imaging condition:
- Constant height feedback
- $Z$-Modulation amplitude $< 2$ nm
- $Z$-Modulation frequency $< 200$ Hz
- Line scan rate $= 12.2$ nm/s
- $64 \times 64 \times 256$ pixels for XYZ imaging
Atomic-Scale Distribution of Water Molecules at Mica-Water Interface Visualized with 3D-SFM

- 1D profiles of hydration force
- 2D images of hydration layers
- 3D distribution of water molecules

PRL 104, 016101 (2010), Fukuma et al.
Recent development: AFM-IR system

AFM-IR can perform IR spectroscopic chemical identification with sub-100 nm spatial resolution.

Scheme of the AFM–IR setup. The AFM cantilever ring-down amplitude plotted as a function of laser excitation wavelength produces the IR spectrum.
Operational scheme of PFIR microscopy (PeakForce-IR)

Le Wang et al. Sci Adv 2017;3:e1700255
PFIR imaging of nanophase separation of a PS-b-PMMA block copolymer.

A Topography

B Peak force IR at 1492 cm⁻¹

C Peak force IR at 1725 cm⁻¹

D Peak force IR at 1620 cm⁻¹

E Modulus

F Adhesion

G Peak force infrared spectra

H FTIR reference from bulk

Le Wang et al. Sci Adv 2017;3:e1700255
1. All SPMs are based on the ability to position various types of probes in very close proximity with extremely high precision to the sample under investigation.

2. These probes can detect electrical current, atomic and molecular forces, electrostatic forces, or other types of interactions with the sample.

3. By scanning the probe laterally over the sample surface and performing measurements at different locations, detailed maps of surface topography, mechanical and electronic properties, magnetic or electrostatic forces, optical characteristics, thermal properties, or other properties can be obtained.

4. The spatial resolution is limited by the sharpness of the probe tip, the accuracy with which the probe can be positioned, the condition of the surface under study, and the nature of the force being detected.

5. Multi-parameters mapping based on force-distance curve-based AFM mode can obtain rich and useful information for surface mechanical characterization.