SPM Technologies: Past, Present and Future

Qing Tu, MSE & NUANCE Center
– Overview of AFM history

– Basic Modes

– Advanced Modes
A Revolution in the Nanoworld: Scanning Tunnelling Microscope

Nobel Prize 1986

G. Binnig

H. Rohrer
A Brief Moment in the History of STM
Oberlech July 1985
A Giant Step for Nanoscience and Technology
Miedema, Baratoff, Quate, Salvan, Feenstra, Kaiser, Welland, Hoesler, Berghaus, Baro, Marti, Vieira,
Stoll, Dürig, Muralt, Behm, Hansma, Celotta

Back row:
Garcia, Neddermeyer, Van Kempen, Ringger, Pohl, Abraham, Chiang, Demuth, Humbert, Gimzewski,
Salemink, Lang, Golovchenko, Güntherodt, Miranda, Fink, Gomez

Middle row:
Büttiker, Pethica, Baldeschwieler, Rohrer, Wilson, Elrod, Müller, Binnig, Gerber
You are familiar with needlepoint. By placing small stitches on a surface, you can make designs.

This stick figure is made by placing carbon monoxide molecules onto a surface using a Scanning Tunneling Microscope. Each piece was made with a carbon monoxide molecule, with atoms only 0.07 nanometers across.

The “drawing” seems childish until you realize how small the carbon dioxide molecules are.
Science Museum London

„The Making of the Modern World“

Original AFM
Atomic Force Microscope

- Instead of using light or electrons to probe the sample, the AFM uses a tip suspended above the surface.
- The attractions or repulsions between the tip and the surface cause the tip to deflect.
- A laser senses the deflection.
- Scanning the tip across the surface generates the image.

a. Nonconducting Surface – No bias voltage.
b. Sensing tip is cantilever force sensor.
c. Relies on “van der Waals” forces between atoms and molecules
**Contact Mode**
- Tip angstroms from surface (repelled)
- Constant force
- Highest resolution
- May damage surface

**Non-Contact Mode**
- Tip hundreds of angstroms from surface (attracted)
- Variable force measured
- Lowest resolution
- Non-destructive

**Tapping Mode**
- Intermittent tip contact
- Variable force measured
- Improved resolution
- Non-destructive
High bandwidth enables exceptional force control and high scan rates with closed-loop accuracy to surpass efficiency of any other commercial AFM system.

20Hz Tapping Mode scan rates provide excellent quality images, matching that typically seen at 1Hz and maintaining good quality even at scan rates >100Hz.

Higher speed ScanAsyst delivers superb quality images at 6Hz and a surveying capability up to a 32Hz scan rate.

*One scan. All the details.*

20μm, 16M pixel

7.5μm

2μm

*8 minutes with Dimension FastScan AFM*
ADVANCES in SPM: Quantitative Nanomechanics

Height 100 nm
Deformation 25 nm
Modulus 10 MPa
Adhesion 5 nN

Stiffness: DMT model
\[ F_{\text{tip}} = \frac{4}{3} E^n \sqrt{Rd^3} + F_{\text{adh}} \]
ADVANCES in SPM: Quantitative Nanomechanics

- 2D Ruddlesdon-Popper HOIPs: \((C_mH_{2m+1}NH_3)_2(CH_3NH_3)_{n-1}Pb_nI_{3n+1}\)

Here \(m = 4\), \(n = 3\)

Tu et al., ACS Nano, 2018, 12(10), 10347 – 10354
ADVANCES in SPM: Quantitative Nanomechanics

\[ F = \sigma_0^{2D} \pi \delta + E^{2D} \frac{q^3 \delta^3}{r^2} \]

\[ \sigma_m = \frac{1}{h} \sqrt{\frac{F_{\text{max}} E^{2D}}{4\pi r_{\text{tip}}}} \]

Tu et al., ACS Nano, 2018, 12(10), 10347 – 10354
ADVANCES in SPM: Quantitative Nanomechanics

Tu et al., ACS Nano, 2018, 12(10), 10347 – 10354
– Measure OPV conductivity under illumination

– Unravel conduction mechanisms

– Combine with PeakForce TUNA & 1ppm environmental control
Life Science Imaging System

- **Uncompromised Performance**
  - High-resolution imaging capability
  - PicoForce-quality force measurements
  - Supports standard light microscopes for uncompromised optical performance

- **Most Complete Integration of AFM and Light Microscopy**
  - MIRO software allows optical images to guide AFM imaging and force measurements
  - Create correlated AFM and optical datasets with flexible offline analysis features
  - MIRO makes the AFM a natural extension of the optical microscope

- **Easiest to Use and Most Productive Life Science AFM**
  - ScanAsyst automatically optimizes imaging parameters for expert-quality results
  - Probe exchange and laser alignment is made easy with EasyAlign™ accessory
  - “Experiment Selector” automatically configures the software for common modes

- **Simple, Effective Solutions for Biological Samples**
  - Easy mounting for common sample types, including slides, cover slips, and petri dishes
  - Micro-volume perfusion accessory is ideal for applications that utilize expensive reagents
  - Petri dish perfusion accessory with heating capability allows long-duration live cell studies

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MIRO software enables the AFM to be used as a natural extension of the light microscope

- Optical images are directly imported and registered to AFM calibration
- Images can be used to guide AFM imaging and force measurements
- Images can be overlaid and adjusted for presentation

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AFM image overlaid on fluorescence image

Fluorescence intensity corresponds to expression level of a tagged protein on the cell membranes

AFM binding measurements made with a functionalized probe correlate strongly with the fluorescence results
AFM deflection images of live EC prior to any simulation (A); in response to 54 min after treatment with 20 mM imatinib (B) followed by 36 min treatment with 1 mM S1P (C). The mechanical measurements were carried out by acquiring arrays of $32 \times 32$ loading-unloading curves in the force-volume map. The time-lapse elastic modulus maps prior to any simulation (D); in response to 54 min after treatment with 20 mM imatinib (E); followed by 36 min after treatment with 1 mM S1P (F). Each pixel indicates the localized subcellular elastic modulus.

*Nature Scientific Report 8 (1) 1002 (2018),*  
1. Introduce ultrasonic (RF) vibration to sample in contact AFM
2. Cantilever essentially rigid (inertially damped): \( f_{\text{sample}} \gg f_{\text{cantilever}} \)
3. Ultrasonic cantilever oscillation amplitude proportional to sample elasticity
Elastic Mapping (Depth)

Note structure within polymer trench wall
Width of high modulus region ~ 120 nm
Near-Field SPM Platform:

- Excellent Lateral Resolution

Ultrasound source:

- Non-destructive and Depth-Sensitive

Holography Paradigm:

- Sensitive to “Phase” Perturbations
Direct Application in Failure Analysis

- Scanning Near Field Ultrasound Holography in Semiconductors
  - Nanoscale Imaging of embedded features/defects
  - Quantitative modulus imaging of metal-low K dielectrics
  - Non-invasive monitoring of molecular markers
  - Nanoscale non-invasive 3D tomography
  - Failure analysis and 3D Interconnects
  - Voiding, delamination with nanometer scale resolution

Science 310, 89 (2005)
Ultrasound Bioprobe for Nanomechanical Analysis

Imaging magnetic core nanostructure embedded in refractory silica core shell based molecular

AFM topographical image EC cells altered by addition of thrombin and ultrasound bioprobe phase image demonstrates remarkable contrast from intracellular fibers. Intracellular fibers are predominantly seen in the ultrasound phase image along with stretched gaps and sub-cellular phase contrast on the nuclei region of the cells.

*Science Advances 2017: 3;e1701176*
In conventional thermocouples, the junction is directly in contact with the sample. The size of the junction determines the resolution. In this current innovative design of the Thermal Probe, the resolution is determined by the diameter of the metal 1 nano-rod and not by the size of the junction. Using modern microfabrication techniques, one can easily create nano-rods of less than 20 nm diameter. The smaller size, however, may have impact on the response time of the probe. The nanorod is positioned at the apex of the tip. This brings the nanorod in direct contact with the sample and as a result the thermal sensitivity of the probes is significantly improved. The extended length of the nanorod (length beyond the thermal junction) helps achieving long operational life of the probes.

Surface temperature mapping of a silicon micro heater. Left panel: schematic of the silicon micro-heater showing different degrees of ion implanted areas. Gray is plain silicon, blue is low dose implant and pink is high dose implant overlying plain silicon and low dose areas. Middle panel: topography and Right panel: Temp image. The temperature image captures the point-to-point variations in the surface temperature due to joule heating at the center and diffusion of heat by the underlying silicon.

ACSNano, 2018, 12 (2), pp 1760–1767
a) Schematic illustration of thermal probe interaction with gold nanoparticles (GNP) encapsulated in silica shell. b) Shows AFM topography image and (c) shows a remarkable thermal contrast from embedded GNP in silica. It clearly reveals a high thermal sensitivity, lateral resolution and contrast. The thermal image showing the difference in heat transfer from the tip to the silica shell and silicon substrate. d) Shows the cross-sectional profile where temperature change ($\Delta T$) from 0.8-0.9°C was recorded across the particle

ACS Nano, 2018, 12 (2), pp 1760–1767
(a) Optical and (b) AFM images obtained from a MoS$_2$-WS$_2$ heterostructure. (c) Raman spectra obtained from MoS$_2$ and WS$_2$ regions. (d) Raman map of the MoS$_2$-WS$_2$ heterostructure device. (e) AFM topography image of the same device. (f-h) Temperature rise profiles of the device at different dissipated electrical power at $V_G = +60V$. The heating predominantly takes place on the WS$_2$-metal vertical junction and the lateral interface does not contribute to localization of the heat. The green arrows in (h) shows the position of the formed hot-spots. (i) Temperature line profiles on the dashed red line in (h) at different applied powers.
Soft Nanopatterning

Woodblock Printing (China ~200)
Movable Type (Bi Sheng, ~1041-1048)

Printing Press (Gutenberg, 1439)
μ-Contact Printing (Whitesides, 1993)

Parallel Printing

Serial Writing
Quill Pen (~2000 BC)
Ball-Point (Loud, 1888)

Dip-Pen Nanolithography (DPN) (Mirkin, 1999)

Polymer Pen Lithography (PPL)
Hard Tip, Soft Spring Lithography
Scanning Probe Block Copolymer Lithography

Beam Pen Lithography (BPL) (Science, 2010)

(Science, 2008)

Courtesy: Chad Mirkin
11 Million Polymer Pen Array

Average Feature Size = 42 nm

Courtesy: Chad Mirkin
Piezoelectric Materials
Piezoresponse Force Microscopy
Nano IR System Integrated with AFM and sSNOM (Coming soon!)

Chemical Analysis at nanoscale resolution

Scattering near field optical microscope (sSNOM). This aperture-less system collects scattered energy form the near field resulting in sub-20 nm resolution. In comparison, aperture based traditional NSOM system resolution is limited to 100-150 nm.

- 10’s of nanometer optical and sub-eV spectral resolution
- Near-field spectroscopy (nano-FTIR)
- High speed optical near-field imaging
- Simultaneous optical amplitude (reflection) and phase (absorption) measurements
- VIS-IR-THz spectral range.