Scanning probe microscopy characterization techniques

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Scanning Probe Microscopy characterization techniques – n-Mate 2008 Salerno 11/06/2008
Outline

- scanning tunneling microscopy (STM)
- static and dynamic atomic force microscopy (AFM)
- AFM and STM for the local study of field emission current from aligned CNT films
Scanning Probe Microscopy

SPM acronym includes a huge family of microscopes depending on the probe-surface interaction (P) exploited:

- STM (Scanning Tunneling Microscopy, 1981)
- AFM (Atomic Force Microscopy, 1986)
- SCM (Scanning Capacitance Microscopy, 1987)
- SNOM (Scanning Near-Field Optical Microscopy, 1992)
- MFM (Magnetic Force Microscopy, 1992)
- KPM (Kelvin Probe Microscopy, 1987)
- SThM (Scanning Thermal Microscopy, 1986)

Tip radius: 10 - 50 nm
Tip-sample distance $d$: 0.1-10 nm
Control of $d$: 0.01 Å

Most of the figures shown are from the book: V.L. Mironov “Scanning Probe Microscopy”, NT-MDT
scanning tunneling microscopy (STM)

static and dynamic atomic force microscopy (AFM)

AFM and STM for the local study of field emission current from aligned CNT films
The STM: Scanning Tunneling Microscope

The tip-sample tunnel current ($I$) is measured and the amplified difference $\Delta I = I - I_0$ is memorized and used to shift the tip.

The feedback loop system moves the tip to keep $I = I_0$.

Signals applied to tip are used to reconstruct the surface image.

Typical operating parameters:

$V = \pm 2V$, $I = 50 \text{ pA} - 10 \text{ nA}$, $R = 0.01 - 10 \text{ G}$, $d \sim 1 \text{ nm}$, $\phi \sim 5 \text{ eV}$
STM control system

- piezoelectric actuator
- analog part
- digital part
- step motor

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STM: tunnel current

Tunnel current very sensitive to the tip-sample distance \( z \)

\[ \varphi \approx 4\,\text{eV} \Rightarrow \frac{4\pi}{h} \sqrt{2m\varphi^*} \approx 2\,\text{A}^{-1} \]

for \( \Delta z \approx 1\,\text{Å} \), the current density varies by a factor \( \sim 10 \)

Transmission coefficient

\[ D(E) = \left| \frac{A_t}{A_0} \right| = \exp \left( -\frac{4\pi \sqrt{2m\varphi^*}}{h} \Delta z \right) \]

\[ j_T \propto \exp \left( -\frac{4\pi}{h} \sqrt{2m\varphi^*} \Delta z \right) \]
STM scanning modes

Constant tunneling current

Feedback loop on

\[ I_t = \text{const} \]

(a)

Feedback loop off

\[ Z = \text{const} \]

(b)
Probes and Resolution

**Vertical resolution:**
- 1-10 pm (10^{-12} m)

**Lateral resolution:**
- 100 pm (10^{-10} m)

**STM tips:**
- metallic wire
- typical wire diameter: 0.2-0.5mm
- mechanically or chemically etched tip
- typical apex diameter: few nm

**Resolution limitations:**
- vibrations
- temperature
- tip stability
- surface condition

- \(~90\% of the current flows in a channel 0.1nm in diameter\)
- \(\rightarrow\) single atom at apex of broad tip still enables atomic-scale resolution
- but, poor resolution if atom is unstable and jumps around
Tips and thermal drift compensation

Pl-Ir wire cut by scissors and applying a tensile force

Electrochemical etch:

W wire within a ring
With a drop of KOH aqueous solution and current through it

Mechanical vibrations and thermal drift (compensation system)

Fig. 50. Un esempio di struttura per testa di misura STM
1 – base; 2 – piezo-scanner tubolare;
3 – piezo-tubo per compensare la deriva termica esso fa parte di un motore piezo inerziale; 4 – punta; 5 – campione;
6 – cilindro portacampioni
STM images

STM images of carbon nanotubes (Omicron)

Graphite surface image (Salerno SPM Lab, constant height)
STM: workfunction mapping

\[ U(t) = U_0 + U_m \sin \omega t \]
\[ \Delta Z(t) = \Delta Z_0 + \Delta Z_m \sin \omega t \]
\[ \frac{\Delta Z_m}{U_m} = K \quad \text{piezoelectric coefficient} \]

\[ I(t) = I_0 \left( V \right) \exp \left[ - \frac{2}{h} \sqrt{2m\varphi^*} \left( \Delta Z_0 + \Delta Z_m \sin \omega t \right) \right] \]

by series expansion

\[ I_\omega = I_0 \frac{2KU_m}{h} \sqrt{2m\varphi^*}(x, y) \]

Excitation outside the bandwidth of the FS

Lock-in system and \( I(n\omega) \)

\[ I(\omega) \rightarrow \sqrt{\varphi^*}(x,y) \quad \text{workfunction map} \]
STM: local I-V characteristics

- Choose a point
- Turn off the feedback loop and the bias
- Apply a voltage ramp to get several I-V curves to average and obtain a local I-V characteristic

\[ j_t = j_0(V) \exp \left( -\frac{4\pi}{\hbar} \sqrt{\frac{2m\phi}{\Delta Z}} \right) \]
The normalized conductance \( \frac{\partial I}{\partial V} / (I/V) \)

is a measurement of the local density of states LDOS: \( \rho_S(E) \)

Electronic density of states

\[ dI = A \frac{D(E) \rho_T(E) f_T(E) \rho_S(E) \left[1 - f_S(E)\right]}{\partial E} dE \]

assuming \( \rho_T(E) \) constant near the Fermi level

\[ I(V) = B \int_0^{eV} \rho_S(E) dE \]

hence

\[ \rho_S(eV) \propto \frac{\partial I}{\partial V} \]
Van Hove singularities clearly visible in tunneling spectra.

Source:
Odom T. W. Et al.
STM spectroscopy: supercond. sample

At low temperature electrons make Cooper pairs and condensates on energetic levels below the conduction band, with a forbidden energy gap $\Delta$. 

\[ E_{FP} \rightarrow E_{FS} \]

\[ \frac{\partial I}{\partial V} \]

$\Delta/e$
scanning tunneling microscopy (STM)

static and dynamic atomic force microscopy (AFM)

AFM and STM for the local study of field emission current from aligned CNT films
The AFM: Atomic Force Microscope

- Based on ultrasmall forces (~1 nN) between a tip surface and a sample surface
- This force is measured through the deflections of an elastic cantilever
- Suitable for conducting and insulating samples
- Lower resolution than STM
Cantilever deflection and signal on photodiodes

Fotocurrent variations are considered
\[ \Delta I_n = I_n - I_{n0} \]

Surface and frictional forces
- topographic images
- frictional data

Normal component of the force
\[ F_Z \propto \Delta I_Z = (\Delta I_1 + \Delta I_2) - (\Delta I_3 + \Delta I_4) \]

Lateral component of the force
\[ F_L \propto \Delta I_L = (\Delta I_1 + \Delta I_4) - (\Delta I_2 + \Delta I_3) \]
AFM feedback loop and control system

- $\Delta I_z$ used as signal in the AFM feedback loop

- The feedback system (FS) keeps $\Delta I_z$ constant by means of the piezoelectric actuator, which controls the tip-sample distance and keeps the deflection

$$\Delta Z = \Delta Z_0$$

- The voltage applied to the piezoactuator is memorized and used to obtain a topographic image of the sample surface
AFM operating modes

- **Static AFM**
  - contact mode:
    - Constant force
    - Constant height

- **Dynamic AFM**
  - non contact mode
    - amplitude mode - AM
    - frequency mode - FM
  - tapping mode (phase mode)
  - etc.
Static AFM: contact mode

Constant force

\[ F_z = \text{const} \]

Scanning with feedback loop on

Z

repulsion

Constant height

\[ Z_{av} = \text{const} \]

scanning with feedback loop off

ΔZ

• Repulsive forces are measured.
• Damages of the tip and/or the sample surface.
• Low elastic constant k.
**Static AFM: resolution and artifacts**

- **Resolution**: 1-10 nm

- **Sampling** (number of pixels/line)
  - Ex: 500 measurement points on a 100µm line: 1 pixel=0.2µm

- **Piezoelectric Scanner**
  - Ex: 100µm scanner, ΔVmax ±200V; 16-bit electronics → steps ~ 1.5 nm

- **Tip curvature radius**: 5-50 nm

*When the height is small (assuming a tip with spherical apex)*

![Diagram](image)

\[ W = w + 2 \sqrt{h(2R-h)} \]

\[ W = 2 \sqrt{2Rh} \]
AFM contact mode: images

Au(111) polycrystalline

DNA Molecules, 700nm scan.

Cromosoms

Polysaccharides 0.8 µm scan
Dynamic AFM: probe and resonance

Silicon

\[ F = k \Delta z \]

- \( k \) = elastic constant
- \( 10^{-3} – 10 \text{ N/m} \)

Resonance frequency

\[ \omega_0 = \sqrt{k/m} \]

Resonance frequency with dissipation

\[ \omega_{rd} = \omega_0^2 \left( 1 - \frac{1}{2Q^2} \right) \]

\[ Q = \frac{m\omega_0}{\gamma} \]
Dynamic AFM: non contact mode

attractive force

A~1 nm
d ~5-10 nm

\[
\Delta \omega = \omega_{rd} \left(1 - \sqrt{1 - \frac{F'_{Z}}{m \omega_{rd}}} \right)
\]

\[
\Delta \varphi \equiv \frac{\pi}{2} - \varphi(\omega_{s}) = \frac{Q F_{Z}}{k}
\]

Scanning is done by keeping
• amplitude constant (AM)
• frequency shift constant (FM)

the van der Waals force induces a shift on the resonance frequency and phase and a change of the oscillation amplitude which depend on the force gradient \( F'_{Z} = \frac{\partial F_{Z}}{\partial Z} \)

Very good for soft samples!

Tip-sample force

\( U = U_{0} \cos \omega t \) piezo excitation
\( \omega_{s} = \sqrt{k/m} \)
\( Q = \omega_{q} m / \gamma \) \( \gamma \) damping factor
\( \omega'_{rd} = \omega_{h} \left(1 - \frac{1}{2Q^{2}}\right) \) resonance frequency

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Dynamic AFM: tapping (semicontact) mode

While approaching the sample surface there are **variations in the oscillation amplitude**, which are recorded and used for imaging.

Exploits both **attractive and repulsive forces**

Oscillation amplitude 10-100 nm
Excitation close to tip resonance frequency

Overcome the surface tension of the adsorbed water layer
Static vs dynamic mode

Epitaxial Si film

Static mode
- limited resolution
- surface / tip damage
- low k probes $\leq 10 \text{ nN}$
- Measurement of the force

Dynamic mode (tapping)
- atomic resolution
- limited surface / tip damage
- various k probes
- measurement of the force gradient $dF/dZ$
EFM: Electric Force Microscopy

\[ U = U_0 + U, \sin \omega t - \varphi(x, y) \]
\[ E = \frac{1}{2} CU^2 \]
\[ \vec{F} = -\text{grad} \ U \]

In particular:

- \( F_z(\omega = 0) = -\left\{ \frac{1}{2} \left[ \left( U_0 - \varphi(x, y) \right) + \frac{1}{2} U_i^2 \right] \right\} \frac{\partial C}{\partial z} \)
- \( F_z(\omega) = -\left[ (U_0 - \varphi(x, y))U_i \sin \omega t \right] \frac{\partial C}{\partial z} \) component at \( \omega \) frequency
- \( F_z(2\omega) = -\left[ \frac{1}{4} U_i^2 \cos 2\omega t \right] \frac{\partial C}{\partial z} \) component at \( 2\omega \) frequency

\[ F_z(\omega) \rightarrow \text{image of } \varphi(x, y) \quad (\text{kelvin probe microscopy}) \]

\[ F_z(2\omega) \rightarrow \text{image of } \frac{\partial C}{\partial Z}(x, y) \]

Surface potential \( \varphi(x, y) \) of azobenzene film

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MFM: magnetic force microscopy

Ferromagnetic film

Tip trajectory during the first scan

Tip trajectory during the second scan

DC or AC mode for second scan

Amplitude and phase variations due to force gradient variations

Phase contrast MFM
scanning tunneling microscopy (STM)

static and dynamic atomic force microscopy (AFM)

AFM and STM for the local study of field emission current from aligned CNT films
Field Emission experimental setup

- **Vacuum:** $\sim 10^{-8}$ mbar
- **Voltage range:** (-210, +210) V
- **Tip-CNT distance:** 0 - 2 µm

Field on a flat metallic surface, below the tip:

$$F = \frac{V}{kd}$$

$V$ = applied potential
$d$ = tip-CNT distance, $k = 1.6$ correction factor
Substrate:
Si(100) p-type (boron)
$8 \times 10^{14} \div 1 \times 10^{15}$ at./cm$^3$, $\rho = 1 \div 40$ Ωcm
Film of Nickel (30 Å)

Catalytic CVD at 700 °C : $C_2H_2 : NH_3$ in the ratio 1:5

Height: ~ 15 µm
Vertical alignment due to crowding effect
(neighboring tubes supporting each other)

Multi-walled carbon nanotubes
- Outer diameter: 15 – 30 nm
- Inner diameter: 5 – 10 nm
- Average # of walls: 10 – 15
Electric field applied to the CNT surface

Simulation:
- emission from circles with $r \leq d$
- FN formula as for parallel plate setup with
  $$E_s = \gamma \frac{V}{d} \frac{1}{k_{eff}} \quad r_{eff} \approx \frac{2}{3} d \quad k_{eff} \approx 1.6$$
- FN formula for the FE current
  $$I = S \cdot a \frac{E_s^2}{\Phi} \exp\left(-b \frac{\Phi^{3/2}}{E_s}\right) \quad \text{with} \quad S = \pi r_{eff}^2$$
Field emission

Extraction of electrons from a conducting surface

\[ F \sim \text{kV/\mu m} \]

but with sharp tips:

\[ F = \frac{V}{d} \sim \frac{V}{\mu m} \]

Enhancement factor \( \gamma \)

\[ F_s = \gamma \frac{V}{d} \]

Fowler-Nordheim theory:

For triangular surface barrier

\[ I = c_1 \frac{F_s^2}{\phi} \exp \left\{ - c_2 \left( \frac{\phi}{F_s} \right)^{3/2} \right\} \]

\( \phi = \) work function in eV \( \approx 5 \) eV

\[ F_s = \gamma \frac{V}{d} \] electric field at tip apex

\[ \ln \left( \frac{I}{V^2} \right) = A - \frac{c_2 \phi^{3/2} d}{\gamma} \left( \frac{1}{V} \right) \]
Cold cathodes

**Displays**

Field enhancement factor $\gamma$
10 times higher than commercial Mo, PolySi tips

**Lamps**

**X-ray tubes**

**CNT FE triode amplifier**
Field emission measurements

$I = c_1 (V - RI)^2 \exp\left(-\frac{c_2}{V - RI}\right)$

10⁻⁸ mbar, room temperature

Series resistance:
- AFM output circuit
- internal resistance of CNT (defects and heating)
- interfaces
- contacts

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Field emission measurements

Field emission from

- AFM tip: -140 V
- CNT: 120 V
- $\gamma_{\text{AFM tip}} < \gamma_{\text{CNT}} \approx 24$

FN model good fit for data.

Low vacuum: $10^{-3}$ mbar
Room temperature

F \approx 160 \text{ V/\textmu m}

$2 - 6 \times 10^3 \text{ Acm}^{-2}$

SMU sensitivity limit

10 nm

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Field emission figures of merit

- Turn-on field: \( \sim 15 \text{ V/µm} \)
  - Screening effect due to high density
  \[
  E_{\text{turn-on}} = \frac{1}{k_{\text{eff}}} \frac{\partial V_{\text{turn-on}}}{\partial d}
  \]

- \( 60 \leq \gamma \leq 120 \) for \( d = 1 \text{ µm} \)
  - Obtained from the slope of FN plot:
  \[
  \gamma = \frac{b \cdot \Phi^{3/2} \cdot d \cdot k_{\text{eff}}}{m}
  \]

- \( 6 \times 10^{-3} \text{ mbar, room temperature} \)
Electrical conditioning

Field Emission for $V>85$ V
Electrical stress (first sweep)
- Destruction of thinner and longer CNT
- Desorption of adsorbates
- Catalist particulates
- Topology changes

FN plot

Sweep 1

Simulation
Time stability

**Saturation regime**
- Stability 20%
- \(d = 1 \mu m, V = 190 V\)
- \(I_{mean} = 1.05 \times 10^{-6} A\)
- \(\sigma = 0.21 \times 10^{-5} A\)

**Non saturation regime**
- Stability 10%
- \(d = 1 \mu m, V = 100 V\)
- \(I_{mean} = 1.37 \times 10^{-7} A\)
- \(\sigma = 0.14 \times 10^{-7} A\)
Carbon nanotubes peeling off

For small distances (d ≤ 350 nm)

High stress applied to CNT during voltage sweep

- Tensile force on single nanotube ~ nN
- Nanotubes can be peeled off and shorten the AFM to the substrate

Patterning in the CNT Film

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Field emission maps

White peaks correspond to high field emission regions

Technique very useful patterned samples
STM and field emission maps

Apply an oscillation $\omega$ to the sample holder:

$$d = d_0 + \delta \sin(\omega t) \quad \rightarrow \quad I = I_0 + I_\delta \sin(\omega t)$$

Current at frequency $\omega$, $I_\delta$, used for FE map

$$I_\delta \approx I_0 \delta \left( \frac{2 - b \Phi^{\frac{3}{2}} k}{d \gamma V} \right) = -\frac{b I_0 \delta k \Phi^{\frac{3}{2}}}{V} \cdot \frac{\Phi^{\frac{3}{2}}}{\gamma}$$

$\omega$ is higher than frequency response of the feedback loop.

Feedback loop keeps $I_0$ constant and adjusts $d_0$ according to the surface topography + FE properties.

The measurement of the $\omega$ component of the current gives only FE information.
Conclusions

- SPM techniques very useful for surface topography and for electrical local properties

- Different techniques have been reviewed
  STM, AFM, EFM, MFM

- Extension of the technique to measure local FE and to obtain FE maps (FEM)

Thank you for the attention!