ABC’s of Electrochemistry: Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM)

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Presentation Outline

• Background
• AFM Basics
• AFM Operation
  o Non-Contact Mode
  o Contact Mode
• Other Techniques
History

• The Scanning Tunneling Microscope (STM) was invented by G. Binnig and H. Rohrer, for which they were awarded the Nobel Prize in 1984.

• A few years later, the first Atomic Force Microscope (AFM) was developed by G. Binnig, Ch. Gerber, and C. Quate at Stanford University by gluing a tiny shard of diamond onto one end of a tiny strip of gold foil.

• Currently AFM is the most common form of scanning probe microscopy.
Basic Principles of Scanning Probe Microscopy (SPM)

**SPM** – Covers all techniques which scan a sharp-tipped probe over a sample while monitoring response of that probe to a particular surface property.

**Feedback** – Z position controlled to keep particular property constant.

- **STM** – Current
- **AFM** - Deflection
- **AC Mode** – Amplitude

**Operates in:**
- ✓ vacuum
- ✓ gas / ambient
- ✓ liquid
How the AFM Works

- The AFM brings a probe in close proximity to the surface.
- The force is detected by the deflection of a spring, usually a cantilever (diving board).
- Forces between the probe tip and the sample are sensed to control the distance between the tip and sample.
Raster the Tip: Generating an Image

- The tip passes back and forth in a straight line across the sample (think old typewriter or CRT)
- In the typical imaging mode, the tip-sample force is held constant by adjusting the vertical position of the tip (feedback).
- A topographic image is built up by the computer by recording the vertical position as the tip is rastered across the sample
Two Modes

Repulsive Forces (contact)
- At short probe-sample distances, the forces are repulsive

Contact Mode

Attractive Force (non-contact)
- At large probe-sample distances, the forces are attractive

Non-contact Mode

The AFM cantilever can be used to measure both attractive force mode and repulsive forces.
Non-Contact Mode

- Uses attractive forces to interact surface with tip
- Operates within the van der Waal radii of the atoms
- Oscillates cantilever near its resonant frequency (~ 200 kHz) to improve sensitivity
- Advantages over contact: no lateral forces, non-destructive/no contamination to sample, etc.

van der Waals force curve
Contact Mode

- Contact mode operates in the repulsive regime of the van der Waals curve.
- Tip attached to cantilever with low spring constant (lower than effective spring constant binding the atoms of the sample together).
- In ambient conditions there is also a capillary force exerted by the thin water layer present (2-50 nm thick).
Force Measurement

- The cantilever is designed with a very low spring constant (easy to bend) so it is very sensitive to force.
- The laser is focused to reflect off the cantilever and onto the sensor.
- The position of the beam in the sensor measures the deflection of the cantilever and in turn the force between the tip and the sample.
**SPM Probes**: Images produced with scanning probe techniques are convolution of tip and sample geometries.

STM works on forces with much shorter range than AFM, leading to more tip-dependent artifacts.
Data Interpretation: Image Artifacts

Probe Size: Affects measurements of features.

Feature measures larger than it actually is.

Feature measures smaller (& perhaps shallower) than it actually is.
Data Interpretation: Image Artifacts

**Probe Shape:** Most noticeable when imaging samples with steep features.

The image data shows the artifact seen when small particles on a surface are imaged with a blunt AFM tip. Notice the “tenting” around the features on the surface. Sample images tip rather than tip imaging sample.
Multiple tips: Usually appears as all small features in image appearing identical. Sample is imaging tip rather than the other way around.
How good an image would you expect from these probes?
Data Interpretation: Resolution

**Lateral Resolution:**
- Limited by electronics, tip size and number of pixels.

**Vertical Resolution:**
- Less tip dependent except when measuring high aspect ratio holes, trenches or closely packed small particles.
- Ultimately limited by ADC resolution.
  - 16-bit ADC = 65536 bits. 8um range => 8000nm/65536 bits = 0.12nm/bit. Easily seen on atomically smooth surfaces such as gold.
  - Reduce Z range to compensate. 1um range = 0.015nm/bit
Data Interpretation: Resolution

34 x 34 pixels

512 x 512 pixels
Image Rendering

Motivation

- Digitally image a topographical surface
- Determine the roughness of a surface sample or to measure the thickness of a crystal growth layer
- Image non-conducting surfaces such as proteins and DNA
- Study the dynamic behavior of living and fixed cells
Image Rendering

Motivation

• Digitally image a topographical surface
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• **None:** Displays raw (‘as is’) data.

• **Flatten 1\(^{st}\) - 3\(^{rd}\) Order:** Displayed data is corrected line by line for tilt (and bow with 2\(^{nd}\) and 3\(^{rd}\) order selected).

• **Data always stored as ‘raw’**.
Flatten $1^{st}$ Order removes Z offset between scan lines, setting average height of each line to average height of previous line, and also removes slope of each scan line (dotted lines are successive scan lines, orange line the result of flatten routine).

Flatten $2^{nd}$ Order removes the Z offset, slope and the parabola-shaped bow in each scan line.

Flatten $3^{rd}$ Order removes the Z offset, slope and the S-shaped bow in each scan line.
Image Rendering

Raw Data

Length = 45 µm  Pt = 345 nm  Scale = 400 nm
1\textsuperscript{st} Order Flatten – Tilt Removed
Image Rendering

2nd Order Flatten – Tilt and Bow Removed

Length = 45 µm  Pt = 22 nm  Scale = 35.5 nm
3rd Order Flatten – Tilt, Bow and ‘S’ Artifact Removed
But what about those high areas between the pits? They are due to the average height of the scan lines that go through the pits being very different than the average height of the scan lines that don’t go through the pits.

One solution? Calculate the best plane fit to the entire image and subtract that from the raw data.
Image Rendering

- **Intrinsic Piezo Effects**
  - Non-linearity
  - Hysteresis
  - Creep

- **Tip Effects**
  - Probe shape
  - Probe size
  - Multiple/dirty tips
Contact Mode: Force Distance Curves

• Two Main Functions
  o Determine and control scanning force
  o Measure physical properties of sample
Force vs. Distance Spectroscopy

1. Away from Sample, Not Deflected
2. Jump to Surface
3, 4. In Hard Contact with Sample
5. Adheres to Sample
Force vs. Distance Spectroscopy

- Long range forces
- Short range forces, film thickness
- Hardness, Stiffness, Elastic Modulus
- Adhesion effects, tip-sample affinity
• Typical Force vs. Distance plot. Horizontal axis is Z position of piezo. Vertical axis is deflection of cantilever (output of photodetector in volts).
• Use rulers and markers to read data points and differences between two points.
• Menu bar has buttons for changing scale, etc.
Measures Tunneling Current
- Exponentially relation between separation and current.
- At low bias the image reflects the local electronic structure of the sample surface.

Imaging Modes
- Constant Height
- Constant Current

Spectroscopy
- I/V, I/S
**Basic Principles - STM**

**Constant Height**

Feedback off, topography measured by change in current.

Fast but requires flat sample.

**Constant current**

Topography measured by voltage sent to piezo to keep current constant.
Basic Principles - STM

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AC Methods - Acoustic Drive (AAC)

- A piezoelectric transducer shakes the cantilever holder at or near the resonant frequency of the cantilever (100 - 400 kHz typically).

- Interaction with the sample reduces the oscillation amplitude. This reduced amplitude is used as the feedback signal.
Acoustic AC (AAC) Mode: Why Use It?

- Minimal lateral forces to distort sample and degrade resolution.
- Generally less damage to tip and/or sample and higher resolution than contact mode.
- Different information available due to dynamic nature of mode.
- Phase lag of cantilever is sensitive to changes in sample physical properties.
- Higher order responses
AC Methods – Magnetic AC (MAC) Mode

- The cantilever is coated on the top side with a proprietary magnetic film.

- A solenoid applies an oscillating magnetic field which is used to vibrate the cantilever.

- Since only the cantilever is oscillating, fewer resonances are excited.
AAC vs. MAC Mode Drive

**AAC Mode:**
- Drive “transmitted” through nose holder to tip.
- Cantilever chip vibrates along with tip.
- Vibration of nose causes turbulence in solution which may interfere with amplitude vs. frequency response.
- Higher frequencies than MAC Mode.
- Best in air but works in solution.

**MAC Mode:**
- Drives the cantilever “directly”.
- Cantilever chip does not vibrate.
- No vibration of nose or cantilever chip so no problems with interference in solution.
- Limited frequency ranges due to LRC circuit limitations.
- Best in solution but will also work in air.
Topography (left) and Phase (right) images of rubber sample. Bright spots in Phase image show areas of different composition. No indication of these differences in Topography image.
Review

- AFM Operation
  - Non-Contact Mode
  - Contact Mode
- Image Rendering
- Other Techniques
  - STM
  - AAC
  - MAC
Questions

Thank You