Surface Tunneling Microscopy and Spectroscopy

1. **Scanning Tunneling Microscopy (STM)**
   - tunneling current
   - instrumentation, imaging modes
   - surface morphology with atomic resolution
   - research examples

2. **Scanning Tunneling Spectroscopy (STS)**
   - local electronic structure
   - single molecule spectroscopy examples

3. **Photo-assisted scanning tunneling microscopy**
   - Thermal effects
   - Surface photovoltage (SPV)
   - Measuring SPV with the STM
   - Spatial variation of the SPV and I-V curves under illumination

References:
1) K.W. Kolasinski, in *Surface Science*, pp.71-81;
Atomic Force Microscopy (AFM)

4. Atomic Force Microscopy
- Understand the basic principles of atomic force microscopy (AFM)
- Three modes
- Understand how AFM can be used in materials science
- Be aware of the issues that can be encountered,
- Related microscopies:
  - MFM
  - NSOM

http://www.ntmdt.com/spm-principles (SPM Principles (NT-MDT) including animations)
http://nanohub.org/resources/520
http://www.doitpoms.ac.uk/tlplib/afm

Scanning Tunneling Microscopy (STM)

STM used for direct determination of images of surface, with atomic resolution. Method is based on electron tunneling between tip and surface
- Was developed by G.Binnig and H. Rohrer (IBM) in early 1980
- Nobel prize in Physics (1986)
- Scanning Tunneling Spectroscopy (W. Ho, Cornell)

STM tip made from Pt-Ir alloy chemical etching) G. Binnig and H. Rohrer

Basics of STM imaging

A sharp conductive tip (W, Pt/Ir) is brought ~ few nm from a conducting surface. Voltage is applied between the tip and the surface.

Get structural information by scanning tip across surface in constant height or constant current modes.

Constant current mode

- current is the feedback parameter
Electron Tunneling Through a barrier

The wave equation is

\[-\frac{h^2}{2m} \frac{d^2 \psi}{dx^2} + U(x)\psi = \varepsilon \psi\]

In the region \(x<0\), before barrier, \(U = 0\), the eigenfunction is a linear combination of plane waves traveling to the right and to the left with energy \(\varepsilon = \frac{h^2 K^2}{2m}\)

\[\psi_1 = Ae^{iKx} + Be^{-iKx}\]

In the region \(0 < x < w\), within the barrier, the solution is

\[\psi_2 = Ce^{i\eta} + De^{-i\eta} = \psi_1(0)e^{-i\eta}; \text{where } U_0 - \varepsilon = \frac{h^2 Q^2}{2m} \text{ and } \eta = \frac{\sqrt{2m(U-E)}}{h}\]

In the region \(x>w\), behind the barrier, the solution is

\[\psi_3 = Fe^{iKx} + Ge^{-iKx}\]

Probability of finding electrons on the other side of the barrier, i.e. tunneling current

\[|\psi_1(0)|^2 e^{-2\sqrt{2m(U-E)}w/h^2}\]

Tunneling current scales exponentially with the barrier width

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Tunneling Current

- Electrons in the sample with energy within \(E_d\) to \(E_d+\text{delta eV}\) tunnel into the tip above its \(E_f\) to \(E_f+\text{delta eV}\)
- This tunneling of electrons will be measured by the circuit connecting the tip and sample and used as the feedback parameter to maintain a constant current (setpoint)
- \(I \propto \exp(-2Kw)\), \(I\) decreases by a factor of 10 when \(w\) is increased by 1 Å
Local density of states (LDOS)

By varying bias, the tunneling current becomes a measure of local density states for electrons.

**GaAs(110)**

- Here are the STM images of GaAs(110)-2x1 surface.
- Images were obtained by applying (a) +1.9V (b) -1.9V to the sample with respect to the tip.
- It was suggested that the filled states are localized on the As atoms, while the empty states are localized on the Ga atoms.

⇒ Image (a) represents the Ga states, while image (b) represents As states.
Instrumentation

- Vibration isolation is critical to achieve atomic resolution

Piezoelectric Scanners

- Scanners are made from a piezoelectric material that expands and contracts proportionally to an applied voltage
- Displacement accurate to ±.05 Å
### Piezoelectric Scanners

- **Piezoelectric effect**: electric field induced displacement of crystalline lattice and vice versa
- **Lead zirconate titanate: PZT**
  - Curie temperature: ~350°C
  - Need to operate $<< T_C$
- **Powders** are fired (1350°C) to form films. After polarization under an electric field (e.g., 60 kV/cm for an hour), they are used as scanner elements.

### Accuracy of STM measurements

- **Basic imaging**: interaction between the probe tip and surface features
- **If tip is contaminated or dull**, and the size of the contaminant is comparable to or larger than the size of the features on the sample surface, artefacts attributable to the contaminant are observed to dominate the image
Tip preparation

- To achieve atomic resolution, an STM probe has to be effectively terminated by a single atom
- **W tip, anodic oxidation in NaOH:** W wire positively biased (relative to a circle of stainless steel wire) is thinned in NaOH through anodic oxidation and it eventually breaks by the weight of the lower part of the wire.
- Annealing treatments are necessary to remove oxide left on the probe
- Scanning on surface, applying high voltage to the tip a single atom protruded on the tip apex

Keep scanning and probably purposely crashing tip to sample surface

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STM image Si(111) (7x7)

- STM image Si(111) (7x7): standard reference surface for probing atoms in real space

See topmost atom layer
(or electron density in the topmost layer)

![STM image Si(111) (7x7)](http://www.omicron.de)

See topmost atom layer
(or electron density in the topmost layer)

DAS model of Si(111) 7x7

- Analyzed by UHV transmission electron diffraction (TED).
- Model: 12 adatoms arranged locally in the $2 \times 2$ structure; a stacking fault layer; a layer with a vacancy at the corner; 9 dimers on the sides of each of the two triangular sub-cells of the $7 \times 7$ unit cell.
- “The model has only 19 dangling bonds, the smallest number among models so far proposed” Surf.Sci.164(1985) 367

Research Examples

- Surface topography
- Surface structure: compare to bulk structure
- Stuff physicists do: semiconductor surface structure, nanotechnology, superconductors, quantum corrals
- Metal-catalyzed reactions
- Single atom lithography
- Electrochemical STM
Surface topography

• Topographic and electronic contrast of the graphene moiré pattern on Ir(111) probed by scanning tunneling microscopy
• Epitaxial graphene on Ir(111) surface

![Image of STM topography](image)

**Figure 1.** (Color online) (a) Constant-current STM topography image of epitaxial graphene on Ir(111) acquired at $V_{bias} = 0.3$ V and set-point current of 0.3 nA. The line indicates the moiré unit cell and the three inequivalent areas within it are denoted by A, B, and C. (b) High-bias STM image taken at 0.45 V/1 nA showing the moiré pattern. (c) Constant-current dI/dV$_{bias}$ and dI/dV maps recorded at a bias of 0.05 V. (d) Constant frequency shift nc-AFM image with $\Delta f = 425$ Hz and $V_{bias} = 0.01$ V. (e) Average current over the tip oscillation cycle measured simultaneously under AFM feedback.

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Coverage-Dependent Self-Assembly

• Rubrene Molecules on Noble Metals

![Image of Rubrene Molecules](image)

**Figure 1.** (a) Chemical structure of rubrene ($C_{22}H_{18}O$). (b) Three-dimensional model for rubrene in the gas phase, showing the twisted tetracene backbone and the four phenyl rings rotated out-of-plane.

**Figure 2.** (b) Overview STM image of rubrene on Au[111] showing the two-dimensional clusters of rubrene formed after deposition onto a sample held at 30 K without subsequent annealing. (b) STM image showing the densely packed disordered arrangement. An individual molecule is outlined.

The chiral properties of the assemblies

- ~0.2ML: formation of chains of pentamers

Extended close-packed surface structures

(a) Overview STM of rubrene on Au(111) with an extended close-packed island (phase w)
(b) STM image of the hexagonal packing, in which only conformers D are present. The color code indicates the molecule chirality: blue = L enantiomer, green = R enantiomer.
(c) L and R enantiomers of conformer D in the close-packed island.
Cysteine adsorbed to a Au(110) surface


Electrochemical STM

- Three-electrode system: STM tip may also become working electrode as well as a tunneling tip
- Need to insulate all but the very end of the STM tip with wax to minimize faradic currents, which can be several orders of magnitude larger than the tunneling current and make atomic resolution unfeasible or even trigger other unwanted electrochemical reactions
Imaging the structure of electrode surface

- STM images of the Au(111) electrode surface (left: unreconstructed surface at positive charge densities)
- STM images of the Au (100) electrode surface (right)
- Au (100) electrode in 0.1 M H2SO4 at -0.25 V vs. SCE, where potential-induced reconstruction proceeds. The initially unreconstructed surface is being gradually transformed into the reconstructed form.
- The zoom shows a section of the surface, 3/4 of which has already been reconstructed; one single reconstruction row on the left hand side is seen to grow from bottom to the top of the image

Time-resolved STM

- STM in standard imaging modes has a significant limitation: poor time resolution (1 image in 1-30s, bandwidth ~ few 10 kHz)
- Swartzentruber, et. al. (PRL 77(1996) 2518) were able to monitor Si dimer motion in the millisecond rage

Si dimer configuration is reflected in the z-feedback position vs time

“B” has higher probability and longer residence time
Open-loop time-resolved STM (feedback loop is off)

Sato and coworkers (J. Electron. Micro. 48 (1999) 1) recorded similar piezo time traces of \( I_t \) in the open-loop configuration of a Ge dimer of the Ge(001) surface (feed-back loop is off)

- Buckled Ge dimer "flip-flop" in time ⇒ "phasons"
- At high T phasons perform a thermally activated random walk

![Image of STM data and data chart]

**Figure 1**
(a) Filled-state room-temperature scanning tunneling microscopy (STM) image of Ge(001). The sample bias \( V_{bias} = -1.5 \) V and the tunneling current \( I_{bias} = 0.4 \) nA. The local \((4 \times 2)\) and \((2 \times 1)\) reconstructions are indicated. The phase boundary between the two domains is indicated by white lines. (b) Schematic representation of a buckled dimer. The tilt angle of the dimer bond is approximately \( 10^\circ \). The filled-state STM image of Ge(001) \( V_{bias} = -1.5 \) V, \( I_{bias} = 0.4 \) nA. The buckling is most pronounced in dimer rows that contain missing dimer defects. Note that this buckling occurs in a symmetric dimer row (right defect) as well as in an asymmetric dimer row (left defect). (c) The defect positions where the current is measured as a function of time are labeled A through F. Data taken from Reference 28.

I-V Mapping

The \( \text{dI/dV} \) signal can provide information about the surface LDOS

![Image of I-V mapping]

**APL 83 (2003) 4610**
I-V Mapping: Pt quantum wires

3. Scanning Tunneling Spectroscopy (STS)

- Inelastic Electron Tunneling Spectroscopy (IETS)

- Tunneling current can excite vibrational modes of a thin layer of molecules in oxide layer that is trapped between two metal electrodes

- Oxide layer $\Rightarrow$ tunnel barrier

- If electrons have sufficient energy to excite vibrational mode, an additional channel for transport opens

- There will be small abrupt increase in $I$, at the onset of excitation

Kink in I-V curve $\Rightarrow$ step in $dI/dV$ curve $\Rightarrow$ peak in $d^2I/dV^2$

- A lock-in amplifier to detect peaks in $d^2I/dV^2$ curve
**Inelastic Electron Tunneling Spectroscopy**

- Adding a small alternating current high-frequency modulation to the sample bias and subsequently monitoring the tunnel current.
- STM junction should be very stable, as the measurements are taken in the open-feedback-loop configuration (very low T, also ~2 meV at 4.2 K)

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Fig. 1: (a) STM image of a CuEtio molecule on the Cu(001) surface at 4.2 K. Absolute energy decreases on the surface with a maximum depth of 0.03 Å. The sample voltage was 100 mV and the tunneling current was 10 nA. The molecule in (d) was transferred to the tip by means of a voltage pulse of 100 mV, 100 nA, 100 s, and the current was monitored. The current-voltage characteristics show a corrugation of 1 Å. The corrugation is evident from the ratio of the tip and the tunneling parameters. Copper atoms.

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**Single molecule vibrational spectroscopy: Cu(II)etioporphyrin-I on Cu(001)**

The four methene bridge C–H bonds in CuEtil are isolated from each other relative to the two C–H bonds in C₆H₆, thus providing an opportunity to probe the coupling between identical oscillators in the molecules.

Vibrational microscopy was used to image the spatial distribution of the inelastic tunneling channels involved in this excitation.

Chem 9764a
STS at elevated T

- IETS of a decanethiol self-assembled monolayer at 77 K
- Two peaks at $\pm 33$ and $\pm 155$ meV are well resolved.
- The first peak is due to the Au-S (29 meV) and/or the C-S stretch mode (38 meV)
- The second peak is probably induced by the C-C stretch mode (131 meV) and/or the CH$_2$ twist and wag modes (155 and 163 meV, respectively).


STM and STS

3. Photo-assisted scanning tunneling microscopy

**Motivation**: combine optically excited vibrational and electronic states with the spatial resolution of the STM

Immediate effects: photo-induced current on semiconductor surface and nanostructuring

Later: STM-induced luminescence on semiconductors, and NSOM

- Thermal effects
- Surface photovoltage (SPV)
- Measuring SPV with the STM

Thermal effects

- Heating accompanies all other possible effects arising from absorption of light.
- In STM the most dramatic consequence of heating is due to thermal expansion of tip and sample affecting the tunneling gap width.
- Not important in the steady state with constant illumination, but in the case of transient or modulated illumination ⇒ changes of the tunneling current occur.
- Monitoring the optical power coupled to the tunneling junction!

- One can monitor photothermally induced modulation of the tunneling current as a function of modulation frequency, laser power, and focus position and interpreted the data in the framework of a simple model, attributing the effect to thermal expansion of the sample.

- Issue: tip thermal expansion is ignored!

Surface photovoltage (SPV)

- Bands in the subsurface region of a p-doped semiconductor having surface states within the band gap.
- The diagram to the left shows the equilibrium situation in the dark, while the right one illustrates the occurrence of a surface photovoltage when the semiconductor is illuminated. (FB is the Schottky barrier height and Vbb denotes the band bending.)
Measuring SPV with the STM

- SPV delivers information about, for instance, surface states and carrier recombination.

![Diagram of optical system](http://www.molec.com/what_is_afm.html)

**Fig. 2.** Diagram of optical system. EOM: electro-optic modulator; FP: photo-detector grism; BS: beamsplitter; IFD: photodiode.

The spatial dependence of the SPV primarily results from the spatial variation of the surface defect states and their local surface recombination rates

PRL 64 (1990) 1054

4. Atomic Force Microscope (AFM)

- A very high-resolution type of scanning probe microscope was invented in 1986 (Binnig, Quate and Gerber)

![3D render of AFM](http://stm2.nrl.navy.mil/how-afm/how-afm.html#imaging%20modes)

Three common types of AFM tip. (a) normal tip (3 μm tall); (b) supertip; (c) Ultralever (also 3 μm tall).

http://www.molec.com/what_is_afm.html
AFM Operation modes

- **Contact mode**
  - repulsive forces $\sim 10^{-9}$ N
  - damage to sample
  - can measure frictional forces

- **Non contact**
  - attractive (van der Waals) forces regime
  - Lower resolution
  - No (lower) damage

- **Tapping (Intermittent contact) mode**
  - cantilever is oscillated at its resonant frequency
  - repulsive force region, but touches the surface only for short periods of time

Contact Mode AFM

- **Tip** is in contact with the surface $\Rightarrow$ the deflection of the cantilever or the movement in the z piezo required to keep the deflection

- Force constants for commercial cantilevers $\sim 0.1$ N/m $\Rightarrow$ a displacement of 1 nm corresponds to a force 0.1 nM

- high resolution, but wears out the tip
- high scan speed
- surface damage, if the surface is soft
- good for nanomechanical testing
- "must" use it if you measure dimension of the surface features
Non-contact Mode AFM

- The cantilever is oscillated slightly above its resonant frequency.
- Oscillations <10nm
- The tip does not touch the sample
- A constant oscillation amplitude is maintained

• resolution is slightly worse
• useful for sensitive (biological soft) samples

Intermittant (Tapping) Mode AFM

- A cantilever with attached tip is oscillated at its resonant frequency and scanned across the sample surface
- A constant oscillation amplitude (and thus a constant tip-sample interaction) are maintained during scanning. Typical amplitudes ~ 20-100 nm
- Forces can be <200 pN
- The amplitude of the oscillations changes when the tip scans over bumps or depressions on a surface

http://www.quesant.com/Library
Approach vs retraction

Applications

• Vacuum, air (water), liquid environment - mimic biological environment
  - Folding of proteins;
  - Imaging of biomolecules
• 3D surface topography
• Force measurements in pico N – nano N range in real solvent environments
  - Binding forces of complimentary DNA strands
  - Frictional Forces studies
• Combined with optical techniques
  - SNOM (shear force microscopy, luminescence mode)
AFM of thin GaN film

- The surface morphology is dominated by terraces and steps
- The step heights are approximately 0.25 nm, corresponding to one layer of gallium and nitrogen atoms
- This illustrates the ability of AFM to measure very small height changes on surfaces

Scanner related artifacts

- Hysteresis

- Scanner creep
Tip Related Artifacts

- http://www.doitpoms.ac.uk/tlplib/afm/tip_related.php

Summary

- STM and AFM may be used to image the micro- and nano-scale morphology of a wide range of samples, including both conductive and insulating materials, and both soft and hard materials.

- Successful imaging requires optimization of the feedback circuit which controls the cantilever height, and an understanding of the artifacts which may arise due to the nature of the instrument and any noise sources in its immediate environment.

- Despite these issues, atomic force microscopy is a powerful tool in the emerging discipline of nanotechnology