Probing Molecular Electronics with Scanning Probe Microscopy

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Outline

• Motivation
• Background
• Construction
• SPM Techniques
An Ideal Experiment for Probing Molecular Conduction

Real Experimental Strategies for Probing Molecular Conduction

The Origin of Scanning Probe Microscopy

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*

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The Scanning Tunneling Microscope

- STM invented by Gerd Binnig and Heinrich Rohrer in 1982
- Led to Nobel Prize in Physics, 1986

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*
Si(111)-7×7: “Stairway to Heaven”

320 Å × 360 Å  Step height ~ 12 Å

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*

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Scanning Tunneling Microscope Schematic

Fig. 1.1. Schematic diagram of the scanning tunneling microscope.

C. Julian Chen, Introduction to Scanning Tunneling Microscopy
One-Dimensional Tunnel Junction

Fig. 1.4. A one-dimensional metal–vacuum–metal tunneling junction. The sample, left, and the tip, right, are modeled as semi-infinite pieces of free-electron metal.

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*
Tunneling Current – Approach #1

Assume metal-vacuum-metal junction, solve Schrödinger Equation:

\[ I \propto V \rho_s e^{-2kW} \]

where \( k = \frac{\sqrt{2m\phi}}{\hbar} = 0.51\sqrt{\phi(eV)} \text{ Å}^{-1} \)

- \( I \) = tunneling current
- \( \rho_s \) = local density of states of sample
- \( V \) = tip-sample voltage
- \( W \) = width of barrier

Typically, \( \phi \sim 4 \text{ eV} \rightarrow k \sim 1 \text{ Å}^{-1} \)

\[ \rightarrow \text{Current decays by } e^2 \sim 7.4 \text{ times per Å} \]
Bardeen Tunneling Theory

Fig. 1.20. The Bardeen approach to tunneling theory. Instead of solving the Schrödinger equation for the coupled system, a, Bardeen (1960) makes clever use of perturbation theory. Starting with two free subsystems, b and c, the tunneling current is calculated through the overlap of the wavefunctions of free systems using the Fermi golden rule.

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*
Tunneling Current – Approach #2

Consider overlap of wavefunctions from either side of barrier:

Using Fermi’s Golden Rule (assuming kT << energy resolution of the measurement),

$$I \propto \int_{0}^{eV} \rho_{s}(E_{F} - eV + \varepsilon) \rho_{t}(E_{F} + \varepsilon) d\varepsilon$$

For a free electron metal tip, $\rho_{t}$ is constant:

$$\frac{dI}{dV} \propto \rho_{s}(E_{F} - eV) \rightarrow \text{STM Spectroscopy}$$
Atomic Force Microscopy

- Invented at Stanford by Binnig and Quate in 1986
- Bring tip-mounted micromachined cantilever into contact or close proximity of the surface
- “Atomic forces” deflect cantilever and is detected with laser deflection into a position sensitive photodiode
- Cantilever deflection is control signal for the feedback loop
- AFM can be done on “any surface” (i.e., conductive, insulating, semiconducting, biological, etc.) in “any environment” (i.e., air, vacuum, liquid, etc.)
Atomic Force Microscope Cantilevers

Fig. 15.3. Microcantilever for atomic-force microscopy. (a) A glass substrate with four cantilevers. (b) One of the cantilevers. (c) Close-up view of the tip. (After Albrecht et al. 1990.)

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*
Force Detection with Optical Beam Deflection

![Diagram of force detection with optical beam deflection]

Fig. 15.7. Detection of cantilever deflection by optical beam deflection. A light beam, typically from a solid-state laser, is reflected by the top surface of the cantilever. The cantilever is vacuum deposited with gold, which reflects red light almost perfectly. The deflection of the mechanical cantilever deflects the optical beam, thus changing the proportion of light falling on the two halves of the split photodiode. The difference of the signals from the two halves of the photodiode is detected. (Reproduced from Meyer and Amer, 1988, with permission.)

C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*
Fluid Cell for Atomic Force Microscopy

Fig. 15.10. Fluid cell for AFM study of electrochemistry. (Reproduced from Manne et al., 1991, with permission.)

C. Julian Chen, Introduction to Scanning Tunneling Microscopy
Example UHV STM Design

• Homebuilt STM in the Hersam lab at Northwestern University
• STM is a modified Lyding scanner
Scanner Construction: Piezotubes

Outer tube:
- 0.650” OD
- 0.570” ID
- 0.750” Long

Inner tube:
- 0.375” OD
- 0.315” ID
- 0.750” Long
Scanner Construction: Base Plug

Front View

Rear View
Scanner Construction: Piezotubes Soldered into Base Plug
Scanner Construction:
Course Translation Platform
Scanner Construction: Course Translation Platform Soldered onto Outer Piezotube
Scanner Construction:
End Cap Positioned onto Inner Piezotube
Scanner Construction:
Tip Contact Assembly
Scanner Construction: Full Tip Assembly
Scanner Construction: Adjusting Clamping Force on Sapphire Washer and Soldering into Inner Piezotube End Cap
Scanner Complete
Cryogenic Variable Temperature UHV STM

(a)
- Outer Thermal Shield
- Inner Thermal Shield
- Heat Sinking Electrical Feedthroughs
- Heat Sinking Isolated Coaxial Feedthroughs
- Front Access Doors
- Sample Dosing Holes and Outer Shield Shutters
- Sapphire Windows and Outer Shield Shutters
- Stage Clamping Screw and Outer Shield Access Door

(b)
- Cryostat Cold Finger
- Heater Tapes
- STM Stage Mirror
- STM Stage Support Posts for Tip/Sample Exchange
- STM Scanner
- Neodymium Magnets

27.5 cm
Vibration Isolation
Detail of Roof Plate
Detail of STM Stage
Thermal Shields with Back Panel Removed
Stage Locking Screw for Cooldown and Cover
Rear Door and Shutter Action
Front Doors Open for STM Access
Sample and Probe Mounted for Scanning
Mirror Allows for Top-Down View of Tip-Sample Junction
STM Suspended for Scanning
UHV Chamber and Liquid Helium Dewar
Scanning Tunneling Microscopy Nanofabrication

Many nanofabrication schemes have been developed with STM (spatial resolution down to the single atom level):

(1) Initially demonstrated by Eigler in 1989 ("IBM" written with atoms at cryogenic temperatures)

(2) Room temperature atom removal from Si(111) by Avouris

(3) Field evaporation of gold

(4) Electron stimulated desorption of hydrogen from Si(100)
Tunable Bond Formation with STM

FIGURE 2. (A) In the imaging mode the tip is stabilized far enough above the surface so that the interaction between the tip and the adatom is negligible. (B) In the manipulation mode the tip is brought close enough to the adatom to drag the adatom along the surface. The force exerted on the adatom by the tip is due to the partially formed chemical bond between the tip and the adatom.

G. Timp, *Nanotechnology*, Chapter 11
Sliding Adatoms with STM

**Figure 3.** Schematic of the sliding process. The tip is placed above the adatom and then lowered to an empirically determined height at which the attractive interaction between the tip and the adatom is sufficient to pull the adatom along the surface. Once the adatom is moved to its final location, the tip is raised back to the height used for imaging, effectively terminating the tip-adatom interaction.

G. Timp, *Nanotechnology*, Chapter 11
The First Atom Moved with STM

Xenon on platinum ➔ requires a defect to prevent tip-induced motion under normal scanning conditions

G. Timp, *Nanotechnology*, Chapter 11
STM Manipulation of Xenon on Nickel

FIGURE 5. A row of seven xenon atoms constructed with the STM. The xenon atoms are spaced apart every other atom of the underlying nickel surface. The xenon atom cannot be packed together any tighter and remain in a single row. From building structures like this we learn about the strength of the xenon-xenon interaction relative to the strength of the in-plane interaction between the xenon atoms and the underlying nickel atoms.

G. Timp, *Nanotechnology*, Chapter 11
Nanograffiti

Kanji for atom:

Xenon atoms on Nickel (110)  Fe atoms on Cu(111)

Quantum Corrals

Fe atoms on Cu(111)

Quantum Mirage (Kondo Resonance)

Topography:

Co atoms on Cu(111)

$\frac{dI}{dV}$:


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Room Temperature Manipulation of Si(111)

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Field Evaporation of Gold

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Hydrogen Passivated Si(100)

- $550 \times 550 \text{ Å}$ filled states
- $50 \times 50 \text{ Å}$ empty states
- $T = 650 \text{ K}$
- $100 \times 100 \text{ Å}$ filled states

Si(100)-2×1:H

- $100 \times 100 \text{ Å}$
- $T = 400 \text{ K}$
- Si(100)-3×1:H
STM Nanolithography on Si(100)-2×1:H

A relatively stable and unreactive surface is produced by hydrogen passivating the Si(100)-2×1 surface in ultra-high vacuum (UHV).

Highly reactive “dangling bonds” are created by using the STM as a highly localized electron beam.

The linewidth and desorption yield are a function of the incident electron energy, the current density, and the total electron dose.

• Selective chemistry can be accomplished on patterned areas.


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Hydrogen Desorption Mechanisms

Si-H(D) $\sigma \rightarrow \sigma^*$ Transition

Heating & Cooling Compete

Vibrational Up Pumping due to Current
Cooling due to Phonon Coupling

Excitation Energy (eV)

Si-H Bonding Distance (Å)
Selective Molecular Adsorption of Norbornadiene on Silicon

Feedback Controlled Lithography

Self-Directed Growth of Styrene Chains from Individual Dangling Bonds

Heteromolecular Nanostructures via Multi-Step FCL
Degenerately Doped Si(100) Surfaces

TEMPO on the Si(100)-2×1 Surface


TEMPO:
(2,2,6,6-tetramethyl-1-piperidinyloxy)

DFT Optimized Geometry (Hyper Chem Release 7)

Individual TEMPO molecules are probed with the STM

- NDR events are only observed at negative sample bias.
- Shoulder is only observed at positive sample bias.
- NDR bias values depend sensitively on tip-sample spacing.
- NDR is observed in both bias sweep directions.
I-V Curve for TEMPO on p⁺-Si(100)


Equilibrium  Shoulder  NDR

- Qualitatively similar behavior to TEMPO on n⁺-Si(100) except opposite polarity.
- Orbital energy shift may be due to charge transfer with the substrate.
STM Spectroscopy: CuPc and Au Nanoelectrodes on NiAl(110)

C$_2$H$_2$ on Cu(100)

Inelastic Electron Tunneling Spectroscopy

Spatial Maps of $d^2I/dV^2$

- $d^2I/dV^2$ @ 358 mV
- $d^2I/dV^2$ @ 266 mV
- $d^2I/dV^2$ @ 311 mV

Contact Mode AFM Potentiometry

Experimental setup:

Requirements of AFM tip:
- Conductive tip with small $R_c$ (kΩ range).
- Low $R_c$ must be sustained after extensive scanning in contact mode.

Conductive diamond coated Si tips provide $R_c = 5$ kΩ with low wear at a repulsive force of 0.54 µN.

Resolution requirements:

To analyze nanowire failure,
- Spatial resolution < 10 nm
- Voltage sensitivity < 100 µV
Noncontact vs. Contact AFM Potentiometry

Noncontact mode:
- Image size = (1000 nm)$^2$
- $0$ V
- $-2$ V
- $-15$ mV
- $-50$ mV

Contact mode:
- Image size = (500 nm)$^2$
- $0$ V
- $-120$ mV$_{p-p}$
- $f = 6.8$ mHz
- $-90$ mV

- Noncontact mode AFM potentiometry possesses $\sim 50$ mV potential sensitivity and $\sim 50$ nm spatial resolution.
- Contact mode AFM potentiometry possesses $\sim 1$ µV potential sensitivity, $\sim 5$ nm spatial resolution, and $\sim 0.01$ ms time response.
AFM Potentiometry of Nanowire Failure

Evolution of nanowire failure:

Contact mode AFM potentiometry images: Wire width = 60 nm
(Breakdown current density = $3.75 \times 10^{12}$ A/m$^2$).

Atomic Force Electroluminescence Microscopy

AFEM on Micron Scale OLED Pixels

- Spatial and temporal variations in current flow and electroluminescence can be directly probed.