SHAPE THE WORLD ATOM BY ATOM

scanning tunneling microscope & its applications
Outline

Introduction

Basic principle of scanning tunneling microscope (STM)

Exciting sciences from STM

- surface structure/morphology
- molecular bonding
- collective electronic behavior
- local electronic properties
- local magnetic properties
- local collective excitations
- surface chemistry
- nanometer scale manipulation
STM: peek in atoms & electron waves

electron density of states
"There's plenty of room at the bottom" — R. Feynman

Quantum Corral

Nanostructure ——— the nature home of quantum phenomena in which electrons express themselves as waves

“Nanotechnology has given us the tools ... to play with the ultimate toy box of nature — atoms and molecules. Every is made from it ... The possibilities to create new things appear limitless.”

— Horst Stormer

Writing with atoms
STM can do more than just peek in on previously hidden nanoscale objects, they can manipulate atoms, fabricate nanostructures and characterize their novel properties. Molecular beam epitaxy is an another game for nano architecture.
Experimental toys at FIU

A: LEED
B: Mini-MBE
C: VT-STM
D: LT-cleaving chamber
E: LMBE chamber
Basic principle of STM

Basic operation modes:
1. Topographic image
   a) constant height: $I = I(x,y)$
   b) constant current: $z = z(x,y)$
2. Spectroscopic mapping
   a) individual spectrum
   b) scanning spectroscopy
   c) $dI/dV$ spectroscopy
   e) $d^2I/dV^2$ spectroscopy
3. Nanoscale manipulation

Disadvantage:
- No insulator (need AFM)
- No chemical sensitivity
- God controls STM tip

Basic principle of STM

A close look of STM

Quantum tunneling

\[ I(d) \propto \exp(-\text{const} \times \sqrt{\Phi d}) \]

- **I**: tunneling current
- **\( \Phi \)**: work function
- **d**: tunneling gap
Basic principle of STM

Tunneling current

\[ I(d) \propto \exp(-\text{const} \times \sqrt{\Phi d}) \]

\( V \ll \Phi \) & constant density of states

\[ I(d) \propto \int_{0}^{eV} \rho_s(r,E) \rho_t(r \pm eV = E) T(E,eV,r) dE \]

\[ \frac{dI}{dV} \propto \rho_s(r,eV) \rho_t(r,0) T(V,r) \]

Probe the electronic density of states is the main objective of STM
Basic principle of STM

Probe empty
density of states

Probe filled
density of states

Positive sample bias

Negative sample bias
The corrugation of electronic density is small for a metal surface.
Structure and morphology

Si(111) surface reconstruction

Filled state image


Empty state image

(b) Side View

Faulted half

Unfaulted half
Si(111): electronic density effect
This reconstruction takes place to make more space for the \( N \) atoms by removing one \( \text{Cr} \) atom per cell from the first layer. This is an adsorbate-induced reconstructions.
Topological orientation of two-dimensional $C_{60}$ domains

Imaged at 5K with -2.0V bias

J. Hou et al. Nature 409, 304 (2001)

two domains with different orientations

molecular states
Molecular dissociation & motion

Single Molecule Dissociation
O₂ on Pt(111)

Apply 0.3 V pulse

http://www.physics.uci.edu/~wilsonho/research.htm
Collective electronic behaviors

Atomic structure of Cu surface

Electron standing waves of Cu surface

Friedel Oscillations

Co/Cu(111)

Quantum corral


PRL 96, 237203 (06)
Collective electronic behaviors

Pt wires on Ge(100)


STS identifies the discrete quantum states and defect effects.
Collective electronic behaviors

Sn atoms on Ge(111) surface

<table>
<thead>
<tr>
<th>EMPTY STATE</th>
<th>FILLED STATE</th>
</tr>
</thead>
</table>

Nature 381, 398 (1996)

Charge density wave

Charge Ordering

Orbital Ordering

Charge Ordering Domains

Science 285, 2107 (1999)
Collective electronic behaviors

Pb on Si(111) surface
Brihuega at al., PRL 94, 046101

Identify the intrinsic character of CDM phase transition \((T_c = 86\, K)\)
Local electronic properties

Identify the d-wave character of electron-pairing in high-$T_c$ superconductors

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

$\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$


http://people.ccmr.cornell.edu/~jcdavis/
Doping induces nanoscale phase separation

Phase inhomogeneity is an alternative balance among several competing states in which many physical interactions are simultaneously active.
Local electronic properties

Static/dynamic spin-charge stripes are the key ingredient in high-TC superconductors

Pan et al., Nature 413, 282

Zhang et al., PRL 96, 066401

(\text{La,Sr})\text{MnO}_3 \, @ \, \sim \, T_c

- Inhomogeneities in density of states
- Altered by external field

Zhang et al., PRL 96, 066401

Fath et al., Science 285, 1540 (1999)
Local electronic properties

Defects are ordered along the crystal axis below $T_c = 220K$
Local electronic properties

Direct Image of \((\sqrt{2} \times \sqrt{2})R45^\circ\) Pattern

New superstructure in which every other atom is bright is observed in defect-ordered state

Cuprate

‘Chekerboard’ electronic crystal

Local magnetic properties

*Tunneling current* depends on spin orientation
- PRL 65 (1990) 247
- Science 292 2053 (2001)
- Science 288 1805 (2000)

http://www.nanoscience.de/group_r/stm-spstm/

Fe islands on W(110)

Cr(100)

Local magnetic properties (Fe islands)

http://www.nanoscience.de/group_r/stm-spstm/
Local collective excitations

http://www.physics.uci.edu/~wilsonho/whoghp.htm
Local collective excitations

Single-molecular vibrational spectroscopy

$h_\omega = 358$ meV is the C-H stretch mode
Local collective excitations

Simultaneous topographic & spectroscopic spatial image $d^2I/dv^2$ at different $v$

Science 280, 1732 (2000)
Surface chemistry

Surface of TiO$_2$(110)

A well-characterized semiconducting oxide surface

600 nm x 600 nm, V = 2V and I = 0.15 nA

50 nm x 50 nm, 1.23V, 0.5 nA
Surface chemistry

Surface O- vacancies and local structures determine the rich catalytic properties of TiO$_2$ surfaces.


STM plays a crucial role in identifying the surface reactivity.
Quantum dot deposition: MBE

Co dots on TiO$_2$(110): Magnetic pearls!

2.5 nm size of dots

- electronic property?
- dot-dot interaction?
- non-RKKY coupling?

Controlled FM semiconductor?
Nanoscale manipulation

Ordered chain structure

\[ V_{\text{tip}} = -0.36 \text{ V} \]
\[ I_t = 0.38 \text{ nA} \]
\[ T = 20^\circ \text{C} \]

- Intra-chain spacing \( \sim 2.5 \text{ Å} \)
- Inter-chain spacing \( \sim 3.3 \text{ Å} \)

The compact structure indicates a strong strain effect induced by the substrate

Quasi-hexagonal close packing

(a)

(b)
The compact structure is due to the mismatch of lattice constants between the substrate and overlayer.
Nanoscale manipulation

Intrinsic polymer structure

A "twisted"-like chain structure was observed!

\[ V_{\text{tip}} = -0.10 \text{ V} \]
\[ I_{t} = 0.21 \text{ nA} \]
\[ T = 20^\circ\text{C} \]

Twisted!
\( \rho(4x1) \) superlattice

Quasi- "\( \beta \)" phase?

A "twisted"-like chain structure was observed!
Can we manipulate these surface dipoles?
A nanoscale domain reversal with apparent lattice shift is created by tip field.

V_{tip} = \pm 0.57 \text{ V} \\
I_t = 0.60 \text{ nA} \\
T = 20^\circ \text{C}

- Shift when scanning across chains
- No shift when scanning along chains
- Shift with 
  \[ 0.1 \text{V} \leq V_{bias} \leq 1.0 \text{ V} \]
  \[ E_{cr} \approx 0.2 - 0.4 \text{ GV m}^{-1} \]
Nanoscale manipulation

Local field induces dipole rotation about the chain axis
Nanoscale manipulation

Flip-reversal

Local lattice distortion

Cant-reversal

The local bond twist causes the lattice shift during flipping
Nanoscale manipulation

Vertical Transport Property:

- Average I(V) Curves
  - Less metallic than that in HOPG
  - Asymmetric I(V)
  - Asymmetric vertical conductance (6 times difference)
  - Showing “ON” and ‘OFF” state by flipping

Local conductance shows excellent “switch” behavior
Understand fundamental physics and materials functionalities.
Sky is the limit!

Thank you!