Manipulation and spectroscopy of adsorbates by low-temperature scanning tunneling microscopy

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Scanning tunneling microscopy (STM)

- Announced by Gerd Binnig and Heinrich Rohrer, IBM Zürich

- Imaging of surfaces with atomic-scale resolution
  - Nobel price in physics 1986
Atom manipulation by low-temperature STM

- Positioning of single atoms at surfaces with atomic precision

35 Xe atoms on Ni(110)


STM technique

1D tunnel contact

- STM setup
- Contours of electron density

- Topography information
  (constant-current mode)

\[ I(z) \sim e^{-2kz} \]
Tunneling current as a function of the bias $V_0$

\[ I(V_0) \sim \int_{E_F}^{E_F+eV_0} D_S(E) D_T(E-eV_0) M(E,V_0) \, dE \]

- $D_S(E)$: Density of sample states
- $D_T(E)$: Density of tip states
- $M(E,V)$: Transmission rate
Assuming that \( D_T \) and \( M \) are constant:

\[
\begin{align*}
I(V_0) & \sim \int_{E_F}^{E_F+eV_0} D_S(E) D_T(E-eV_0) M(E,V_0) \, dE \\
\Rightarrow \frac{dI(V_0)}{dV} & \sim D_S(E_F+eV_0)
\end{align*}
\]

(at constant tip height)
Probing & moving adatoms on metal surfaces
Lateral manipulation

Adsorbed atom

Pioneered by D. M. Eigler (IBM, Almaden)

...
Assembly of monatomic adatom chains on Cu(111)

- Atom-by-atom assembly of Cu chains along the <110> direction
- Chain atoms occupy nearest-neighbor lattice sites (a\textsubscript{Cu-Cu} = 2.55 Å)
**Cu/Cu(111) chains: unoccupied quantum states**

- **Cu adatom chains:** confined unoccupied quantum states (1D quantum box behavior)

Cu/Cu(111) chains: quantum state densities

- Chain-localized electronic states: One-dimensional quantum confinement
- Squared wave functions with $n$ lobes and $n-1$ nodes (artificial molecules)

Linear Combination of Atomic Orbitals (LCAO)

**Example:** Linear molecule, four identical atoms

s-like AO’s

\[ \Psi = c_1 \phi_1 + c_2 \phi_2 + c_3 \phi_3 + c_4 \phi_4 \]
### Eigenstate energies $E(n,N)$ within LCAO approach

**LCAO scheme:**
Solving the $(N\times N)$ secular determinant for a chain of finite length

$$
\begin{vmatrix}
\alpha - E & \gamma & 0 & 0 & \cdots & 0 \\
\gamma & \alpha - E & \gamma & 0 & \cdots & 0 \\
0 & \gamma & \alpha - E & \gamma & \cdots & 0 \\
0 & 0 & \gamma & \alpha - E & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & 0 & 0 & 0 & \cdots & \alpha - E \\
\end{vmatrix} = 0
$$

**Eigenvalues for an N-atomic chain:**

$$E_n = \alpha + 2 \gamma \cos\left(\frac{n\pi}{N + 1}\right) \quad n = 1, 2, \ldots, N$$

$\alpha$: binding energy \quad $\langle \phi_i | H | \phi_i \rangle$

$\gamma$: hopping integral \quad $\langle \phi_i | H | \phi_j \rangle$

**1D energy band:**

$E(\Gamma) = 1.41 \text{ eV}, \quad m^* = 0.68 \, m_e$

Adsorbates on semiconductor surfaces
**III-V semiconductor – InAs**

- **In:** $4d^{10} 5s^2 5p^1$
- **As:** $3d^{10} 4s^2 4p^3$

InAs(111)A
A: In-terminated

- Zinc blende structure
- $a_0 = 6.06 \text{ Å}$
- Band gap: 0.36 eV
- 3/4 electrons per In dangling bond (DB)

\[\text{top layer In atoms} \quad \text{2nd layer As atoms}\]
III-V semiconductor – InAs

In: $4d^{10} \, 5s^2 \, 5p^1$
As: $3d^{10} \, 4s^2 \, 4p^3$

Zinc blende structure
$a_0= 6.06 \, \text{Å}$
band gap: $0.36 \, \text{eV}$

- 3/4 electrons per In dangling bond (DB)
- surface In vacancies create As DBs each with 5/4 electrons
- (2x2) In vacancy reconstruction: electron transfer from In to As creates fully empty/occupied surface DBs
**InAs(111)A-(2x2) substrate surface**

- In-terminated InAs(111)A: (2x2) reconstruction with In-vacancy structure
- (2x2) reconstruction renders the surface non-reactive: no partially filled dangling bonds
- MBE-grown surface exhibits donor-type In adatoms residing on the In-vacancy sites
Electronic properties of InAs(111)A

- Fermi level pinning in the conduction band due to donor-type In\textsubscript{ad} atoms
- charge accumulation at the surface
- In\textsubscript{ad}: unoccupied atomic orbital-derived state \( \sim 0.7 \) eV above \( E_F \)
Vertical manipulation

Adsorbed atom
Assembling an In adatom chain on InAs(111)A

STM topograph

Vertical manipulation – surface-to-tip transfer

Set point values prior to manipulation: 0.1 nA, 0.5 V

- **Surface-to-tip transfer** *only* at positive sample bias > 0.7 V
- tunneling into the adatom-derived unoccupied state is important for the pick-up process
- transfer via *vibrational excitation* of the adsorbate-surface bond

Vertical manipulation – tip-to-surface transfer

Set point values prior to manipulation: 0.1 nA, 0.5 V

- Jump to contact occurs at a critical tip height (saturation of the tunneling current)
- Critical tip height is bias-independent, transfer attainable also at zero bias
- Tip-to-surface transfer triggered by short-range cohesive forces upon tip-surface contact

Atomic switches
In$_6$ chain on InAs(111)A: a binary switch

- Reversible switching of the tunnel conductance in the chain center
- Bistable regime between about -0.4 V and +0.4 V
- ON and OFF states robust and stable within the switching thresholds
- Switching never observed at the chain ends ➔ energetically unfavorable

J. Yang et al., Nano Lett. 11, 2486 (2011)
Periodic boundary conditions: In$_6$ ring

5 K

40 Å x 40 Å
0.1 nA, 0.3 V
Bistability in vertical atomic height and charge state

- $\text{In}_{\text{surf}}$ next to the chain remains stable at $z=0$ (“normal” $\text{In}_{\text{surf}}$)
- $\text{In}_{\text{surf}}$ between two $\text{In}_{\text{ad}}$ becomes bistable and can assume a popped-up position at 1.47 Å, i.e., almost at the height of the $\text{In}_{\text{ad}}$ atoms themselves (1.7 Å)
**Bistability in vertical atomic height and charge state**

- $\text{In}_{\text{ad}}$ chain on $\text{InAs(111)}\text{A}$

- Total energy *versus* height of $\text{In}_{\text{surf}}$

*Image showing a diagram of $\text{In}_{\text{ad}}$ chain on $\text{InAs(111)}\text{A}$ with $\text{In}_{\text{surf}}$, $\text{As}_{\text{surf}}$, and $\text{In}_{\text{ad}}$ depicted, and a graph showing total energy *versus* height with labeled points at 1.47 Å and -65 meV.*

- $\text{In}_{\text{surf}}$ next to the chain remains stable at $z=0$ (“normal” $\text{In}_{\text{surf}}$)
- $\text{In}_{\text{surf}}$ between two $\text{In}_{\text{ad}}$ becomes bistable and can assume a popped-up position at 1.47 Å, i.e., almost at the height of the $\text{In}_{\text{ad}}$ atoms themselves (1.7 Å)
- Switching process changes the charge state of the nanostructure
Probing the steady state in extended In chains

Steady-state imaging at 0.2 V, subsequent excitation at 0.6 V (multiple switching)

- Number of defects increases with chain length, suggesting a preferred defect density
- Energy of the ON state determined by the balance between
  1. Energy gain associated with a popped-up In\textsubscript{surf} atom, $E_0 = -65$ meV
  2. Energy cost due to Coulomb repulsion between popped-up In\textsubscript{surf} atoms
Pinning switchable molecules to a semiconductor surface
Free-base phthalocyanine ($H_2Pc$)

- Planar geometry with twofold $D_{2h}$ symmetry
- two protons caged by four benzene rings via pyrrole units ➔ tautomerization reaction
**H₂Pc/InAs(111)A – adsorption geometry**

- Molecular rotation slows down with decreasing bias
- Centered above In surface vacancy site ⇒ *Coulomb* interactions important for bonding
- Three equivalent in-plane orientations of the H₂Pc molecule

Constant-current STM images, 50 pA, 28 Å x 28 Å, 5 K
Three-level current switching due to molecule rotation

- Three-level current noise: switching between three different in-plane orientations
- Normalized jump rate \( \frac{I}{\tau e} \): probability per electron to induce a single rotational jump
- Threshold behavior suggests that rotation is induced by inelastic excitation
Assembling an In-H$_2$Pc-In complex

Lateral manipulation

1$^{\text{st}}$ H$_2$Pc repositioned by lateral manipulation (here at a constant current 4 nA, 0.36 V)

2$^{\text{nd}}$ blocking the rotation by pinning a H$_2$Pc between two In$_{\text{ad}}$ atoms (spacing: 17.14 Å)

• two stable conformers showing left- and right-handed appearance → tautomerization?

STM images of the In-H$_2$Pc-In structure, 50 pA

Ch. Nacci et al., ACS Nano 6, 4190 (2012)
In-H$_2$Pc-In: binary current switching

- Binary current switching with an ON-to-OFF ratio ten-to-one
- threshold behavior of the yield suggests that the switching is induced by inelastic excitation ➔ activation of the tautomerization reaction
Theoretical energy landscape for H atom switching

Filled-state simulated STM images clearly reflect the asymmetry created by the two H atoms

energetics of H switching virtually unaffected by the substrate and the pinning In\textsubscript{ad} atoms

Ch. Nacci et al., ACS Nano 6, 4190 (2012)
‘Take-home’ message

- Resolution of and sensitivity to single atoms and molecules at surfaces
- Local spectroscopy probe of the electronic density of states
- Low-temperature STM: Combined approach

Manipulating matter with atomic-scale control

Assembling nanostructures from single atoms/molecules

Atomic-scale characterization

Local electronic structure and elementary excitations
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