Nanoscale Contact Formation Dynamics

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Other Research Activities

NanoMechanical and electromechanical measurements
Why Contacts?

• The success of future nanoscale devices is critically dependent on gaining an atom-level understanding of contact formation
  – How are electronic properties of the molecule/nanomaterial affected by contact?
  – How does the molecule/material respond when contact is established?
  – What role is played by the contact metal?
  – Can we predict the conductance of nanoscale systems?

• How can one go about answering these types of questions?
  – Approach: develop new methodologies based on cryogenic STM
Scanning Tunneling Microscopy

- Overlap of tip and sample wavefunctions
- Applied bias defines the energy window sampled
- Study HOMO and LUMO levels

\[ I_t \propto \rho_s(0, E_F) e^{-\phi^{1/2}Z} \]

LDOS at location \( z \) and energy \( E \)

\[ \rho(z, E) = \frac{1}{E} \sum_{E_n=E-E}^{E} |\psi_n(z)|^2 \]
DOS, Molecular Vibrations, and Barrier-height

\[ I(V) \propto \int_{E_F}^{E_F+eV} \text{DOS}(E) T(E,V) \, dE \]

\[ \frac{dI}{dV} \Rightarrow \text{peaks}^{\text{DOS}} \]

\[ \frac{d^2I}{dV^2} \Rightarrow \frac{d}{dV} (\text{DOS}) + \text{peaks}^{\text{IETS}} \]

\[ I \propto \exp(-A\sqrt{\phi Z}) \Rightarrow \phi \propto \left( -\frac{dI}{dZ} \right)^2 \frac{1}{IA} \]

In principle STM can provide significant insights

Not delivered in practice, poor correlation of properties with contact formation, no ability to account for forces involved
Strategy

• Separate the electronic and mechanical effects:
  – Record detailed changes in the electronic and vibrational properties of molecule as probe approaches to contact
  – Measure forces experienced during contact (new technique, refer to as relaxation spectroscopy)
  – Study contacts with molecules and nanomaterials
Scanning Tunnelling Spectroscopy (STS)

- Modulation
- Lock-In detection

<table>
<thead>
<tr>
<th>Parameters</th>
<th>STM mode</th>
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<tr>
<td>I(V)</td>
<td>Z constant</td>
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<td>dI/dV</td>
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Conventional STS measurements

Basis for force measurements

Only for specific energy window defined by the applied bias
Integrated Substrate* for probe preparation

Substrate developed by CRANN and Intel

Degenerately doped Si substrate

Metal-inking: drawing material from the surface onto the probe apex

Each sample prepared independently

Metal-inking essential to control composition and electrical properties of probe
Guarantees that bias maps onto the energy scale in STS measurements

*co-developed with Intel, processing at Tyndall National Institute
Integrated Substrate for probe preparation

Probe sharpening on Pd surface

Characterize sharpened probe by STS and barrier height measurements on known samples

Single conductance channels evident during probe retraction - study single atom wires
Example A: Si(100) Substrate and Molecule

1,3-cyclohexadiene (1,3-CHD)

After reaction one C=C double bond remains and corresponds to the topographic maximum visible in STM (5 different possible configurations)
1,3-CHD on bare Si(100) surface

[4+2] Products

[2+2] Products

Color Key:  Si  C  C=C  H  Si-C

Product identification based on location of single remaining C=C

Always some noisy sites on surface

Empty state images: tunnelling into $\pi^*$ level of C=C?
Can’t explain origin of STM contrast

- DFT reveals broadened $\pi^*$ state at +3.5eV
- Broadened $\pi^*$ does not extend appreciably below +2 eV

Bias +1.0eV
1,3-CHD reacted Si(100) surface at 5 K

Dimer flipping at 5 K, especially under high bias/current conditions
Contacts: Single Molecule on Si(100)

- Large LDOS feature grows in at 350meV (completely reversible) and anticorrelated with disappearance of C=C vibrations
- Bias window 0 – 200meV LDOS independent of separation (basis for subsequent relaxation and force measurements)
Current during approach to contact

Contact with Pt surface
Current well described by:
\[ I \propto \exp(-A\sqrt{\phi_A} z) \quad (1) \]
Jump to contact & neck formation

Contact with 1,3-CHD molecule
Current not globally described by Eq. (1)
Deviations seen in harmonics
Shaded region: no hysteresis

What is the origin of these deviations from Eq. (1)?
Origin of Relaxation Interaction

\[ \Delta Z_{\text{gap}} = \Delta Z_{\text{piezo}} + \Delta Z_{\text{C=C}} \]

\[ = -\Delta Z_{\text{piezo}} + \frac{F_P}{k_S} \]

\[ = -\Delta Z_{\text{piezo}} + \alpha F_P \]

Current increase during approach deviates from

\[ I \propto \exp(-A\sqrt{\phi_A} z_{\text{piezo}}) \]

Interpreted locally as a change in the apparent barrier height \( \phi_A \)
Qualitative Analysis of Current Hysteresis

Shaded hysteresis-free regions

- Bond compression and relaxation (reversible)
- Approach to bond formation (reversible)

Bond-making and breaking region (dissipative)
Quantitative Analysis

\[ F = 0 \]

\[
\begin{align*}
I &\propto \exp(-A\sqrt{\phi} Z) \\
I' &= \frac{dI}{dZ} \propto -A\sqrt{\phi} I \\
I'' &= \frac{d^2I}{dZ^2} \propto A^2\phi I \\
\left(-\frac{I'}{IA}\right)^2 &\propto \phi_{A_1} \\
\frac{I''}{IA^2} &\propto \phi_{A_2} \\
\left(-\frac{I''}{I'A}\right)^2 &\propto \phi_{A_3}
\end{align*}
\]

Nominally identical

\[ F \neq 0 \]

\[
\begin{align*}
I &\propto \exp[-A\sqrt{\phi}(Z_{\text{piezo}} + Z_0 + \alpha F)] \\
I' &= -A\sqrt{\phi}(1 + \alpha F')I \\
I'' &= \left[A^2\phi(1 + \alpha F') - A\sqrt{\phi} \alpha F''\right]I \\
\left(-\frac{I'}{IA}\right)^2 &\propto \phi(1 + \alpha F')^2 \\
\frac{I''}{IA^2} &\propto \phi(1 + \alpha F')^2 \frac{\sqrt{\phi}}{A} F'' \\
\left(-\frac{I''}{I'A}\right)^2 &\propto \left[\sqrt{\phi}(1 + \alpha F') - \frac{\alpha F''}{A(1 + \alpha F')}\right]^2
\end{align*}
\]

Forces present: harmonics \(dI/dZ\) and \(d^2I/dZ^2\) are related to the local force gradient.
Quantitative Analysis: Interaction Potentials

Invert current and barrier height data to determine forces & potentials

Description of the $\phi$ data requires a barrier term

Questions:
1. Is the well depth meaningful?
2. What is the origin of this barrier?

Use DFT
Emergence of LDOS feature

- Energy window 0-1ev
- Energy window 1-2ev
- Energy window 2-3ev
- Energy window 3-4ev
DOS in the presence of the probe tip

Interaction of probe with C=C bond upon contact yields interface state in 0 – 1eV
Origin of Interface State

15Å separation

4Å separation

15Å separation

Bonding interaction associated with $p\pi \rightarrow d\pi$ charge transfer from C=C to Pt apex atom

Molecule conductance dominated by interface state which is responsible for STM image

∫ LDOS (0-1.5 eV) ~ STM image

Tip above C=C
Origin of Interface State

15Å separation

4Å separation

15Å separation

Tip approach: Interface state

Deformation of molecule

DFT also observes barrier - due to deformation and rehybridisation of the molecule C=C bond

E_p

π* +3.41eV

0.59eV

0.39eV

-1.25eV

+3.10eV
Comprehensive picture of contact bond formation

Track dynamics of contact formation  Precise overlay of potential, electronic and vibrational properties

*NANO LETTERS* 6(9) 2006;  *PRL* 97, 098304, 2006.
Conclusions: Molecular Contacts

- Three types of current-approach curves
  - Smooth exponential increase (tunnelling)
  - Sharps jumps (local atomic motion)
  - Slow, reproducible change in slope (relaxation forces)

- Interface states may provide route to tailor molecule transport properties
- Track actual formation of contacts (chemical bond formation, evolution of vibrations, actual measure of potential)
- Widely applicable; catalysts and studies of general reaction dynamics

Relaxation map of single 1,3 CHD
Example B: Nanoscale contact with Si(100):H

Specific Problem: contact resistance between contact metal and n+ region at source and drain limiting device performance

Approach: study of controlled contact formation at 5K. Measure local forces, electronic density of states and vibrations simultaneously
Pd Nanocontacts on n+ Si(100):H

Control of the electrical contact
$D_{\text{contact}}$ from 2 to 7 nm shift from non-ohmic to ohmic behaviour
No evidence for Schottky barrier

Ohmic behaviour observed even with tunnelling contact – not an E-field point contact effect
Macroscopic Pd:Si(100) Contacts

Annealed sample ~ 6.5W

MS Ohmic contact

MS Schottky contact

Pd melting
Measurements on Carbon Nanotubes

Well defined van Hove singularities
RT study – peak broadening
No contact studies at 5 K yet

Address issue of Pd vs Pt contacts etc
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