Electron Transport in Strongly Coupled Molecular Electronic Junctions

Richard McCreery, Adam Bergren, Sergio Jimenez
Bryan Szeto, Jie Ru, Andriy Kovalenko, Stan Stoyanov

University of Alberta
National Institute for Nanotechnology
National Institute for Nanotechnology
University of Alberta, Edmonton, Alberta, Canada

Founded 2002
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“Molecular electronics”

Today’s question: How are electrons transported through molecules??

Note:
- molecules become circuit elements
- critical dimension is 1-10 nm
Electrochemical reduction:

- Energy relative to vacuum, eV: -7, -6, -5, -4, 0, +0.5, +1.0
- Distance from electrode:
  - Ionic double layer
  - Molecule in solution
  - Metal electrode

Molecular junction:

- Energy relative to vacuum, eV: -7, -6, -5, -4
- Distance:
  - Two electrodes, no double layer, no solution
  - $E_{\text{fermi}}$
Two common electron transport models:

“off-resonant”
- e.g. tunneling, Schottky, field emission

“resonant”
- LUMO is close (~within kT) to Fermi level
- e.g. “resonant tunneling”, “orbital mediated tunneling”
The scientific question:

How are electrons transported through 1-5 nm thick molecular layers?

Outline:

• fabrication of molecular junctions
• characterization
• electronic properties
• transport mechanism
Things we do differently from everyone else:

- sp² carbon
- very flat (< 0.5 nm rms)
- graphitic carbon substrate (Pyrolyzed Photoresist Film, PPF, essentially metallic, with $\rho = 0.006 \Omega \cdot \text{cm}$)
- covalent C-C surface bond, stable to > 500 °C
- conjugated, partially ordered mono- or multilayer, 1-5 nm thick, $10^8 - 10^{12}$ molecules in parallel
- slow electron beam deposition of Cu top contact, often covalently bonded to molecule

**References**

*Phys. Chem. Chem. Phys.*, 2006, 8, 2572
*J. Chem. Phys.*, 2007, 126, 024704
1 µm

molecular layer (not resolved)

SEM

Si Wafer

5.0kV 4.7mm x25k SE(U) 10/29/2007

1 µm

Cu/Au Top Contact

TEM

EM mount

20 nm

PPF

Thermal SiO2

carbon

metal

polypyrrole
Microfabricated “E-chips”

PPF Echip 4” wafer

PPF Echip

Clip electrode used for electro-chemistry

cut after molecule deposition

PPF leads

Junction

next slide

Bryan Szeto
Jie Ru
Au strip

Junction area:
2.5 x 2.5 µm to 400 x 400 µm

$V_{\text{sense}}$

current amplifier

- $V$

+
Cross section of a PPF/NAB/Cu/Au junction (SEM)
Schematic of junction structure:

molecular layer is really thin compared to metals, does it survive metal deposition??

Cu/Au

PPF

SiN/SiO₂

(molecule layer)

> 100 nm

1-5 nm

Au 30nm

Cu 120nm

SiN 70nm

SiO₂ 50nm

PPF 1µm

to scale:

(molecule layer is really thin compared to metals, does it survive metal deposition??)
“backside” Raman of buried interface:

514.5 nm laser excitation at 45°

Collect Raman scattered light normal to substrate

~4 nm NAB

~10 nm PPF

Quartz substrate (0.13 mm)

(~ 4 nm thick multilayer)
Quartz/PPF/NAB/Cu/Au (after metal deposition)

Quartz/PPF/NAB, no Cu or Au

Raman intensity (30 sec, 19 mW)

NO₂

Adam Bergren
Amr Mahmoud (Monday, 4:20 PM)
FTIR of buried interface:

**NAB on Au/Ti**

![Graph showing -log(R/R₀) vs. wavenumber in cm⁻¹ for NAB on Au/Ti.]

**Au/Ti**

![Graph showing -log(R/R₀) vs. wavenumber in cm⁻¹ for Au/Ti.]

**Ti** is “primer layer” for NAB bonding to Au

**after 100 nm Au deposition:**

![Graph showing -log(R/R₀) vs. wavenumber in cm⁻¹ for Si/Ti(5)/NAB/Au(100).]

**IR transparent Si**

Adam Bergren
Amr Mahmoud (Monday, 4:20 PM)
Electronic behavior:

$V_{\text{sense}}$  
\[ \rightarrow \]  
\[ \rightarrow \]  
\[ \rightarrow \]  
current amplifier  
Labview

carbon/molecule

= fluorene

12 nm

20 nm

1.7 - 2 nm

2 μm

carbon on SiO$_2$

Au

Cu
Start with something familiar:

**PPF/SiO\textsubscript{2}/Cu**

- **PPF/Cu slope = 1.6 \(\Omega\)**
- **breakdown \(\approx 3\) MV/cm**
- **slope = 420,000 \(\Omega\)**

**V, carbon relative to Au**
How about a molecule instead of SiO$_2$?

Nitrobiphenyl multilayer 4.6 nm thick:

NBP film much more conducting than SiO$_2$
Nitrobiphenyl junctions of differing thickness:

7 A/cm²

\( \sim 10^6 \) e⁻/sec/molecule

1.6 nm 2.8 nm 4.6 nm

Typical error bar

rSD 5-15%
yield > 90%

• No obvious shape change from 1.6 to 4.6 nm thickness

• Symmetric with minimal hysteresis

• Repeatable > $10^8$ cycles
\[ \beta = 0.22 \, \text{Å}^{-1} \]

\[ \beta = 0.21 \, \text{Å}^{-1} \]

\( d = \text{thickness, nm} \)

**Literature:**
- alkanes (echem or junctions) 0.8 Å\(^{-1}\)
- aromatic (echem, 1999) 0.22
- conjugated (echem, SAM) 0.3 to 0.6
- polyene* (2005) 0.22
- oligothiophene* (2008) 0.1
- oligoporphyrin* (2008) 0.04
- oligophenyleneimine\(^+\) (2008) 0.3

* single molecule junction
+ ~100 molecule junction

\( \beta \) is smaller for aromatic structures (i.e. conjugated molecules are better “conductors”)
Is this behavior molecular?

- (1.5 nm)
- (2.0 nm)
- (1.4 nm)
- (1.9 nm multilayer)
- (3.7 nm multilayer)

strong effect of structure and thickness on conduction

- no molecule

Various transport mechanisms:

**Weakly Temperature dependent:**

- Coherent tunneling, "superexchange"
- Incoherent, diffusive tunneling
- Field emission (Fowler Nordheim)

**Strongly Temperature dependent ("activated"):**

- Thermionic (Schottky) emission
- Poole-Frenkel effect ("coulombic traps")
- "hopping", including redox exchange (Marcus-Levich)

**Distance dependence:**

- \( \exp(-\beta d) \)
- \( \exp(-\beta'd) \)
- \((V/d) \exp(-a d)\)
- \( \exp(-c d^{1/2}) \)
- \( \exp(-c'd^{1/2}) \)
- \( d^{-1} \)
A good probe of mechanism: Temperature dependence

“activated”

temperature independent

$J, \text{A/cm}^2$

$V$

400 K

325 K

250 K

400 K

325 K

100, 120, 150 K

100, 120, 150 K

$J(0.2 \text{ V})$

$J. \text{Phys. Cond. Matter, 20, 374117 (2008)}$
Arrhenius plots

40 K  20 K  10 K  5 K

\[ \ln j_{0.2} \text{ (A cm}^{-2}\text{)} \]

\[ 1000 \frac{T^{-1}}{(K^{-1})} \]

BP (1.4)

FL (1.8)

NAB (3.3)

AB (3.2)

(1.8 nm)

(3.3 nm)
need to explain:

- apparent ohmic contact
- T-independent, despite:
- 4.5 nm thick (too thick for tunneling)

T = 5 K
(T independent, 5 – 250 K)
All common off-resonance tunneling mechanisms fail:

PPF/NAB (2.6 nm)/Cu

Simmons with image charge

Simmons, $\varphi = 0.85$ eV (i.e. tunneling through a rectangular barrier)

Field emission (Fowler Nordheim)
Tunneling with reduced electron mass (modified Simmons equation):

\[ J = \frac{q}{4\pi^2 \eta d^2} \left\{ \left( \phi - \frac{qV}{2} \right) \times \exp \left[ -\frac{2\sqrt{2m^*}}{\eta} \sqrt{\left( \phi - \frac{qV}{2} \right)d} \right] - \left( \phi + \frac{qV}{2} \right) \times \exp \left[ -\frac{2\sqrt{2m^*}}{\eta} \sqrt{\left( \phi + \frac{qV}{2} \right)d} \right] \right\} \]

\( m^* \) = effective electron mass, where mass of charge carrier = \( m^* \times 9.1 \times 10^{-31} \) kg

Experimental data collected at 5 or 6 K

"off resonant" tunneling just doesn’t work

Simmons, J. G. Journal of Applied Physics (1963), 34, 1793-1803
An alternative approach:

We expect these levels to be broadened, by:

- electronic coupling to substrate
- intermolecular interactions
- variable bonding geometry
- uncertainty (i.e. lifetime) broadening

Some evidence for broadening:

Optical Absorbance

NAB in hexane (X.02)

NAB bonded to carbon

*Experimental, from Kelvin probe

NAB LUMO (-3.0 eV, from DFT)

HOMO (-6.6, DFT)

NO₂

N=N

0.02

0.04

0.06

200 300 400 500 600 700

wavelength, nm

Optical Absorbance

NAB in hexane (X.02)

NAB bonded to carbon

NO₂

N=N

Some evidence for broadening:

- electronic coupling to substrate
- intermolecular interactions
- variable bonding geometry
- uncertainty (i.e. lifetime) broadening

Applied Spectroscopy. 2007, 61, 1246-1253
DFT with periodic boundary conditions for graphene

Stan Stoyanov
Kirill Koshelev
Andriy Kovalenko
NINT
HOMO and LUMO energies vary with torsion angle.
Modeling of both contacts and molecule

C_NAB_Au

C_NAB_Cu

strong interaction of both Cu and graphene with NAB

E, eV

Koshelev

HOMO

LUMO
energy relative to vacuum, eV

-2
-3
-4
-5
-6
-7

Distance

HOMOs

LUMOs

E_{\text{fermi}}

filled states in metal

a range of orbital energies

Zero bias:

positive bias:

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Note that more HOMOs become accessible for higher bias, causing upward curvature.

Once a bias is applied, empty metal orbitals are created, allowing electrons to leave the HOMO. The HOMO fills again from the negative electrode, effectively “hole transport.”

+ bias

HOMO fills again from negative electrode, effectively “hole transport”
more HOMOs becoming accessible with increased bias

sech distribution
$\sigma = 0.31 \text{ eV}$
$E_f - E_{HOMO} = 1.7 \text{ eV}$
$N_{\text{chan}} = 10^5$

gaussian distribution
$\sigma = 0.52 \text{ eV}$
$E_f - E_{HOMO} = 1.7 \text{ eV}$
$N_{\text{chan}} = 10^5$

$\sigma$ = half width of orbital energy distribution
$E_f - E_{HOMO}$ = Fermi level to orbital offset
$N_{\text{chan}}$ = total number of active channels

Sergio Jimenez
Adam Bergren
Main parameters of the model:

- \( E_f - E_{HOMO} \)
- HOMO “linewidth” (\( \sigma \))
- and number of channels (\( N \))
- molecular layer thickness (\( d \))

for the electrochemists: NOT Marcus/Butler-Volmer; similarity due to distribution of orbital energies rather than thermal fluctuations
Important notes:

- broadening caused by coupling and local environment, not thermal fluctuations

- main parameters are distribution width ($\sigma$), energy offset ($E_F - E_{HOMO}$), and thickness

- overlap of metal and molecule orbitals may (and probably does) occur at zero bias

- depending on offset between molecular orbitals and Fermi level, we can greatly vary conductance

The punch line: strong interactions between molecule and contacts result in resonant electron transport rather than classical tunneling
Adam Bergren (NRC)
Sergio Jimenez (visit. prof.)
Andriy Kovalenko
Stan Stoyanov
Kirill Koshelev
Jie Ru (Uof Alberta)
Bryan Szeto

Also:

Rory Chisholm (2:00 PM Monday)
Mark McDermott