Metrology for Molecular Electronics

Duncan Stewart

Hewlett-Packard Labs
Palo Alto, CA  USA
Why study electronic properties of molecules?

A ~1nm a molecule is the smallest thing that will ever have completely engineered electronic and optical properties \((linked\ to\ chemical\ activity)\)

1. New human knowledge
2. New nanoelectronics
3. New nano-enabled sensors and actuators
Metrology for Molecular Electronics

**Electrical:** I-V, C-V, I-V-T, IETS

**Physical:** LB isotherm
C-V electrochemistry
Brewster angle microscopy
Imaging ellipsometry
Static contact angle
IR spectroscopy
AFM
XPS
STM, LEED, AES, UPS, SIMS, HREELS
Metal / molecule / metal devices

Duncan Stewart, Jeanie Lau, Doug Ohlberg, Patricia Beck, Stan Williams
Kent Nielsen, Jan Jeppesen, Fraser Stoddart
First Expt: Al / Al$_2$O$_3$ / monolayer / Ti

Electrical characterization of electrode / monolayer / electrode crossbar devices:
Current-Voltage I-V at 300K

Monolayer molecular film (single species) by Langmuir-Blodgett deposition
Molecular catalogue

**Fast Blue**

**Chlorophyll B**

**Eicosanoic Acid (C_{20})**
Fast Blue & Chlorophyll & Eicosanoic Acid

Fast Blue

Chlorophyll B

Eicosanoic Acid
NIST measurements: $C_{20}$

- Independent confirmation of molecular device behavior.
- C-V curves of moletronic devices

HP data

NIST data

R&D Magazine May 2003

Second Expt: Pt / PtOx / monolayer / Ti

Electrical characterization of Pt / monolayer / Pt crossbar devices: Current-Voltage I-V at Temperatures 300K-2K

40nm - 10 um

Top Electrode (Ti)

Bottom Electrode (Pt)

26-30 Å monolayer
~ 30 Å Pt oxide
Second Expt: Pt / PtOx / monolayer / Ti

C₂₀H₄₀O₂

eicosanoic acid C₂₀

[2] rotaxane
Switching: C\textsubscript{20} and [2] rotaxane

Conclusions: molecule-independent switching

1. Device = Molecules + Electrodes

- need to characterize device system.
Metal / molecule / metal devices

[Diagram showing two configurations of metal/molecule/metal devices with labeled top and bottom electrodes and molecules]
Outline

1. Device = Molecules + Electrodes
2. Bottom interface
3. Top interface
4. Nanoscale electrical switching
Bottom interface:

Surface roughness & monolayer film quality

Jason J Blackstock, Zhiyong Li, Duncan Stewart, Stan Williams, Mark Freeman
Template Stripping

“Backbone” to hold T.S. Metal

Adhesive

Evaporated Metal

Substrate

‘Strip’ away original substrate


AFM of Surfaces

As Deposited Platinum

Template Stripped Platinum

AFM of Surfaces

Template Stripped Gold

Template Stripped Platinum

Peak-to-Valley Roughness

As Deposited

Gold  Platinum

Template Stripped

Gold  Platinum

<100> Prime Silicon Template

Physical Aging

Gold
Freshly Stripped

After ~1 week

Platinum

5 nm
IR spectroscopy of C18 monolayer on Pt

Peak Positions

Peak Position (cm$^{-1}$)

Number of Carbons in Alkane Thiol (N)

As Dep Pt
TS Pt

Liquid
Solid

CH$_2$:CH$_3$ Peak Ratio

![Graph showing the CH$_2$:CH$_3$ peak ratio as a function of the number of carbons in the alkane thiol (N). The graph includes data points for TS Au, TS Pt, and As Dep Pt. The x-axis represents the number of carbons in the alkane thiol, ranging from 6 to 22, and the y-axis represents the peak height ratio (CH$_2$:CH$_3$). The data points are accompanied by error bars, indicating the variability of the measurements. The graph is based on the work of Blackstock et al. (2004).]
Conclusions: template-stripped electrodes

1. Device = Molecules + Electrodes

2. Ultra-flat bottom electrodes dramatically improve monolayer packing density & ordering
   - need nanoscale crystal orientation of TS surface
   - need correlated nanoscale IR
Top Interface:

Deposition of Titanium onto monolayers

Shun-Chi Chang, Zhiyong Li, Jeanie Lau, Brian Larade, Stan Williams
Self-Assembled Monolayers (SAMs) prior to Ti deposition

- Ordered, densely packed SAMs
- Naphthalene groups stand perpendicular to Pt surface
  - Disappearance of absorption 818 & 858 cm\(^{-1}\)
  - (out-of-plane vibration of H on naphthalene)

SAMs after Ti deposition

Conclusions: Titanium deposition

1. Device = Molecules + Electrodes

2. Deposited titanium reacts with top of monolayer, causes disorder, but does not penetrate (macroscopically)

- need nanoscale IR
- need correlated nanoscale physical structure
- need correlated nanoscale electronic transmission
Switching physics:

Nanoscale switching centers via AFM study

Jeanie Lau, Duncan Stewart, Doug Ohlberg, Patricia Beck, Stan Williams, Marc Bockrath
• Apply ~μN force with AFM tip while measuring device conductance
• Simultaneously explores electrical and local mechanical properties
• AFM tip not electrically connected to the device
Molecular junctions in the “off” state exhibited no observable electrical response to local mechanical perturbation by the AFM tip.

A nanoscale conductance peak or "switching center" emerges when the junction turns "on".

Switching “on” a device is always accompanied by the emergence of a new nanoscale pressure-induced conductance peak.

The switching center faded and then vanished upon switching to lower conductance states.

A simple model

- Transport through molecular monolayer via tunneling
- Switching creates nano-asperities
- AFM compression increases tunneling

Applying pressure with the AFM

Elasticity theory (Landau&Lifshitz)

point force applied to semi-infinite plane

\[ u_{zz} \sim \frac{3}{2\pi E} \frac{d^3}{\left(x^2 + y^2 + d^2\right)^{5/2}} F \]

E \sim 80 \text{ GPa} for metals and alkane molecules
d = thickness of top electrode \sim 30 \text{ nm}

- Monolayer compressed \sim 0.2 \text{ Å} for F \sim 1 \mu\text{N}
- Spatial resolution \sim 40 \text{ nm} due to tip radius & thick electrode.

Parametric theory

- Nano-asperity dominates transport

\[ G = G_{\text{off}} + (G_{\text{on}} - G_{\text{off}}) \exp[-\beta \, dz(x, y)] \]

No free parameters: \( G_{\text{off}} \sim 0.1 \mu S, \ G_{\text{on}} \sim 1.3 \mu S, \ \beta \sim 1 \text{Å}^{-1}, \ \delta z (0,0) \sim 0.2 \text{Å} \)

Good agreement between model and data

**switching “on” ↔ growth of asperity**

Conclusions: switching physics

1. Device = Molecules + Electrodes

2. Nanoscale switching centers
   Pt/molecule/Ti electrical switching is directly correlated with the creation and annihilation of nanoscale conductance channels.
   A) Metal filaments  B) Defect chains

- need atomic species and chemical bonding at these (buried) nanoscale conductance channels.
Metrology for Molecular Electronics

Device Behavior

Molecular Design

Controlling the System (electrodes & molecules & contacts & matrix)

ellipsometry, contact angle, AFM, electrochemistry, LB isotherm, IR, XPS, STM, LEED, AES, UPS, SIMS ++ ?
Metrology for Molecular Electronics

= Surface Science ⊗ Chemistry, at nanoscale

Grand challenge: atomically mapped chemical species and bonding at buried organic/inorganic interfaces.
Co-conspirators

QSR
Stan Williams
Xuema Li, Tan Ha, Henri Gamino
Consuelo Olmos, Brian Samuels
Doug Ohlberg - physical chemistry
Shun-Chi Chang - organic synthesis
Gun-Young Jung - polymers & LB
Zhiyong Li - electrochemistry & SAMs
Ted Kamins - materials science & EE
Shashank Sharma - materials science
Yong Chen - materials science
Regina Ragan - materials science
Saif Islam - EE
Duncan Stewart - physics expt
Jeanie Lau - physics expt
Jason Blackstock - physics expt
Alex Bratkovski - physics theory
Brian Larade - physics theory
Phil Kuekes - computer architecture
Greg Snider - computer architecture

HP
Patricia Beck, Dick Baugh, Dick Henze
Manish Sharma, Greg Irby, Pam Long, Margie Flores

NIST
Curt Richter - electrical characterization

UCLA
Prof. Fraser Stoddart - organic chemistry, Jan Jeppesen, Kent Nielsen, Julie Perkins, H-R. Tseng

Caltech
Prof. Jim Heath - physical chemistry
Prof. Pat Collier, Yi Luo, Prof. Marc Bockrath

Stanford
Prof. Curt Frank - LB films, Isaac Lee