Molecular Electronics- Past, Present & Future

I. Goals of molecular electronics
   - miniaturization → processing speed
   - “bottom up” massively parallel assembly
   - designer molecules
   - single-molecule studies

II. History & Recent Events
III. Survey of (our) Current Strategies
IV. Summary of Challenges
V. Education
“I don’t know how to do this on a small scale in a practical way, but I do know that computing machines are very large... Why can't we make them very small... For instance, the wires should be 10 or 100 atoms in diameter, and the circuits should be a few thousand angstroms across.”
- Feynman, *There’s Plenty of Room at the Bottom*, 1959.

“The size scale of molecules is between 1 and 100 nm, a scale that permits functional nanostructures with accompanying advantages in cost, efficiency, and power dissipation.” - Heath & Ratner, 2003.
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I. Goals
II. History & Recent Events
   - the Schönen and not so schönen
   - break junctions
   - crossbars
   - nanotubes and nanowires
   - ‘nanowell’ measurements on SAMs

III. Survey of (our) Current Strategies
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Ambipolar Pentacene Field-Effect Transistors and Inverters

J. H. Schön,* S. Berg, Ch. Kloc, B. Batlogg

A Superconducting Field-Effect Switch

J. H. Schön,¹ Ch. Kloc,¹ R. C. Haddon,² B. Batlogg¹

![Graphs and diagrams showing the behavior of ambipolar pentacene FETs and superconducting field-effect switches.](image-url)
Retraction


Absence of Strong Gate Effects in Electrical Measurements on Phenylene-Based Conjugated Molecules

Absence of Strong Gate Effects in Electrical Measurements on Phenylene-Based Conjugated Molecules

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Yield (%)</th>
<th>Total # of fabricated samples</th>
<th>Gate dependent samples</th>
<th>Liquid growth</th>
<th>Gas phase SAM growth</th>
<th>characteristics</th>
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<tbody>
<tr>
<td>1</td>
<td>7.8</td>
<td>256</td>
<td>2</td>
<td>Y</td>
<td>Y</td>
<td>Asymmetric $I-V$</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>216</td>
<td>0</td>
<td>Y</td>
<td>Y</td>
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<tr>
<td>3</td>
<td>16</td>
<td>236</td>
<td>0</td>
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<td>Y</td>
<td>NDC</td>
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<td>0</td>
<td>72</td>
<td>0</td>
<td>Y</td>
<td>N</td>
<td></td>
</tr>
</tbody>
</table>

Summary: no reproducible gate dependence

Absence of Strong Gate Effects in Electrical Measurements on Phenylene-Based Conjugated Molecules

- Electrode edges are not atomically flat!
- Poorly coordinated bonds
- Electrodes screen molecule... very low gate efficiency
Absence of Strong Gate Effects in Electrical Measurements on Phenylene-Based Conjugated Molecules

Electrodes screen molecule...very low gate efficiency

Electrodes edges are not atomically flat!

Poorly coordinated bonds

Other approaches have shows more promise...
Break Junctions – Reed (Yale)

-M. Reed, APL1995.
Break Junctions – molecular bridges

Molecular Crossbars – molecules as nodes in multiplexed circuits

- Heath, UCLA
- Williams, HP
Bistable *rotaxane* crossbars (R.S. Williams, HP)

- resistance at the wire junctions can be reversibly switched
- each cross-point acts as an active memory cell.

Direct Observation of Nanoscale Switching Centers in Metal/Molecule/Metal Structures

Chun Ning Lau,† Duncan R. Stewart,† R. Stanley Williams,*† and Marc Bockrath*†

• bias-driven filament formation & dissolution
• switching behavior due to filaments and not the (insulating) molecular interface
• still some applications...
Other molecular / macromolecular systems:

Nanotubes:

- Electronic structure related to that of graphene.

- Tight-binding: consider only nearest-neighbor wavefunction overlap.

- Let $\gamma_0$ be the overlap integral between the neighboring atoms

$\rightarrow$ 2D dispersion of graphene\(^+\):

$$E(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4 \cos \left( \frac{\sqrt{3}k_x a}{2} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right)}$$

References

\(^+\) P.R. Wallace, Phys. Rev. Lett. 71(9) 622-634, 1947
Highly reproducible results with single-walled carbon nanotubes:

SWNT as molecular interconnects:

- Cylindrical boundary conditions define a tube:
  \[ C = na_1 + ma_2 \]

- Chiral indices \((n,m)\) determine the band structure\(^\ddagger\):
  \[ |n-m| = 0,3,6,... \text{, metallic;} \]
  \[ \text{otherwise semiconducting.} \]

(valid for all but the smallest diameter nanotubes)

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- \textbf{Chirality distribution}

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- **Chirality distribution**
- Rational synthesis of \(C_{60}\) – will we have monodisperse SWNT?

Reference

Nanotube-based FETs

- Channel = semiconducting nanotube
- FETs can also be gated by a local wire or by a liquid
- Smallest tubeFET ~100 nm (gap between source and drain)
- Top-down FET logic gates have been made
FET

SET

Double kink

channel

island

source electrode

drain electrode

nanotube molecule

silicon oxide

silicon gate

S

D

G

S

D

G
Nanowires
Lieber (Harvard)

- Science 2001
Molecular Electronics- Past, Present & Future

I. Goals
II. History & Recent Events
III. Survey of Current Strategies (here at UVA)
   - Nanowells
   - Beyond the 2-terminal / molecular channel paradigm
   - compatibility with Silicon
   - new lithographic tools
   - bioassembly?

IV. Summary of Challenges
V. Education
First Optically Active Molecular Electronic Wires

Yuliang Zhu,† Nadine Gergel,‡ Nabanita Majumdar,‡ Lloyd R. Harriott,‡
John C. Bean,‡ and Lin Pu*,†

Nanowell Geometry

- Organic Letters, 2005
“Surfet” Strategy (with Bean, Ghosh, Harriott, Pu)

- Covalent molecular adsorbates as resonant scattering centers on the channel
- Carriers squeezed into 2DEG-like state at the surface by the backgate
- Several ultraflat/clean surfaces readily available (strong contrast to Au!)
- Device architecture compatible with semiconductor roadmap
- Many directions for physics: Fano, Kondo, RTS, …
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Tunable Fano device (prototype adsorbate modulated transistor)

- Inspired by early Raman work of Cardona on doped semiconductors
- Fano interference between a continuum and a discrete transition, e.g. electronic continuum interferes with Raman-active phonon
- Characteristic asymmetric lineshape seen in Raman spectrum:
Tunable Fano device (prototype adsorbate modulated transistor)

• Resonance / antiresonance behavior depends on strength of the interaction between electronic continuum and discrete phonon states

• Fano lineshape:

\[ I(\omega) = \frac{(q + \epsilon)^2}{1 + \epsilon^2} \]

\[ \epsilon = (\omega - \omega_0) / \Gamma \]

in which \( \Gamma = \) width parameter

\( q = \) asymmetry parameter (\( q \rightarrow \infty \) produces Lorentzian)
Tunable Fano device

Buried oxide / Silicon on insulator (SOI) Si(100) wafer

Doped Si(100) device layer

Doped “handle”
Tunable Fano device

Si(100)

Annealing - dopants diffuse to surface
Tunable Fano device

Open questions: range of tunability; transport signature
Next: molecular adsorbates as surface dopants

Device building in progress (Jack Chan)
Electron Phonon Interaction in Nanotube-channel FETs

Raman Stokes and anti-Stokes processes:
Raman studies on individual nanotube-channel FETs

The DOS contains van Hove singularities and gaps dependent on the tube diameter:

\[ E_{11}^m = \frac{6a\gamma_0}{d} \]

\[ E_{11}^s = \frac{2a\gamma_0}{d} \]

**JDOS:** \[ g(E) = \text{Re} \left( \sum_i \frac{a_{c-c}E}{d\gamma_0 \sqrt{(E - E_{ii} - i\Gamma_j)(E + E_{ii} + i\Gamma_j)}} \right) \]

**References**

Electron Phonon Interaction in Nanotube-channel FETs

- single-channel measurements possible because of resonance conditions
- current-driven phonons
- work in progress: tube devices by CVD, lithography, Stokes/anti-Stokes measurements
Raman mapping of the nanotube channel

40X Scope Image
UNC Sample 1
Area C

Far-field Raman Map, 520 cm⁻¹

Far-field Raman Map, 1500-1600 cm⁻¹

Si
Raman Point Spectrum
633 nm excitation
Related studies:
Current work: electron-beam and photolithography

Device fab. collab. @ Delft with Iddo Heller and Jing Kong (MIT)
New lithographic Tools: Near field ultraviolet photolithography

- $\lambda_{\text{max}} \sim 210 \text{ nm}$
- 5th harmonic from Nd:YAG – 213 nm
- $\sim 0.5 \text{ mW average power possible at } 20 \text{ Hz}$
Standard Photolithography processes with a mask
(very) Brief Summary of Near-field techniques


Very small transmission expected:

\[ T \propto \left( \frac{d}{\lambda} \right)^4 \]

• E. A. Ash and G. Nicholls, University College, London (1972): near field imaging with microwaves through apertures 1/60 of the wavelength.


“unusual optical properties are due to the coupling of light with plasmons—electronic excitations—on the surface of the periodically patterned metal film...”

→ Many orders of magnitude higher than expected
Interaction of photon with surface plasmon
New lithographic Tools: Near field ultraviolet photolithography

- akin to contact print photolithography but with direct write, scanning aperture
- transmission enhancement through near-field aperture
- resolution: PMMA can be spun to ~few nm (thinner than photoresist)
New lithographic Tools: Near field ultraviolet photolithography

camera

microscope

piezo stage

Nd:YAG laser

4th / 5th Generator
New lithographic Tools: Near field ultraviolet photolithography

Focused-Ion beam (FIB) fabrication of nanopore arrays on Ag-coated quartz

Fab work: Andrew Spisak
Lithography: Brian Burke
Anticipated benefits:

• direct write capability (maskless photolithography)
• patterning under ambient conditions
• patterning on soft surfaces
• low equipment cost

Questions we are currently working on: resolution limit, write speed
A dreams of the future: conductive wires with Watson-Crick hybridization?

Several DNA analogues such as PNA can be readily sequenced:

**PNA properties**
- Uncharged backbone
- Free terminal NH$_2$ -> easier attachment to SWNT
- Spacing of bases is almost identical to that of dsDNA
- 20-mers are available
- Soluble* in water/DMF and stable in many solvents
- $T_m$ is higher by $\sim1^\circ$C per base pair, on average

**DNA properties**
- Charged backbone
- Near-perfect molecular recognition
- Unstable in many common solvents
- Buffered environment necessary
- Attachment of DNA to SWNT is more difficult

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*Solubility can be sequence dependent

_PNA-DNA Duplex_ (Nielsen and Haaijma, 1997)

**Development of conjugated backbone?**
DNA junction scaffolds designed by sequence and assembled by ligase:

DNA ligase “welds” the pieces together

12 bp sticky ends

Ligase model: Tom Ellenberger, Washington University School of Medicine
~nm position control in DNA, and limitless structural coding...

20 nm spacing

Manuscript in prep.
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- Molecular electronics vs. microelectronics
- the Big Challenge: reproducibility
- link between present and future
- grand architectural vision

V. Education
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- RET
- SMV
- NUE
Nanoscience Undergraduate Experience (NUE)

• NSF funded ($200k), +$50k (College) +$150k (SEAS)

• First course currently in progress

• Current class equipment: 3 STMs, 3 AFMs, 1 UV-vis spectrophotometer, 6 PCs

• Hands-on experience for beginning undergrads

• Sample topics: imaging techniques; quantum size effect in semiconductor nanocrystals; nanotube growth by CVD; lithography…

• Expand experimental & theoretical repertoire for physics undergrads/grads
Current group:

Brian Burke
Jack Chan
Andrew Spisak
Kenny Evans
Quang Vu

Collaborations:

Adam Hall (UNC)
Jing Kong (MIT)
John Bean
Avik Ghosh
Lloyd Harriott
Lin Pu