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

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9 February 2007

“ 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.

Molecular Electronics- Past, Present & Future

I. Goals
II. History & Recent Events

- the Schőn and not so schőn
- break junctions
- crossbars
- nanotubes and nanowires
- ‘nanowell’ measurements on SAMs

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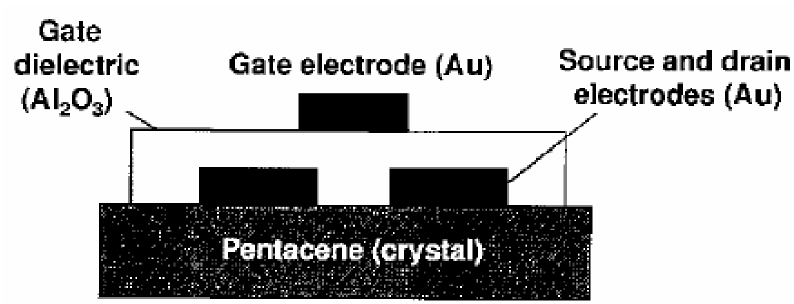
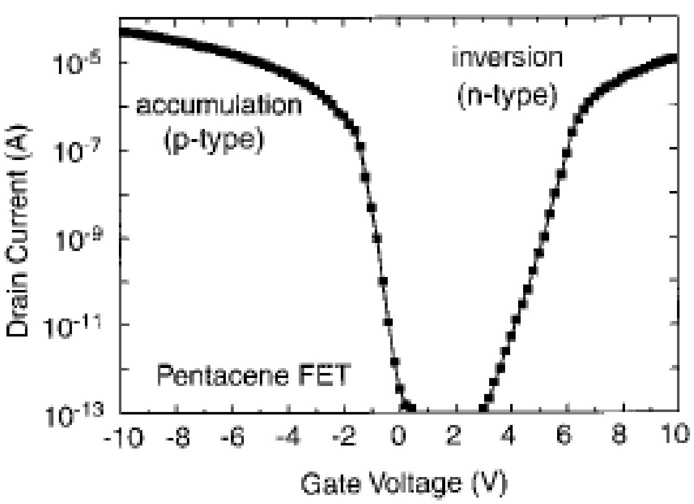
Ambipolar Pentacene Field-Effect Transistors and Inverters

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

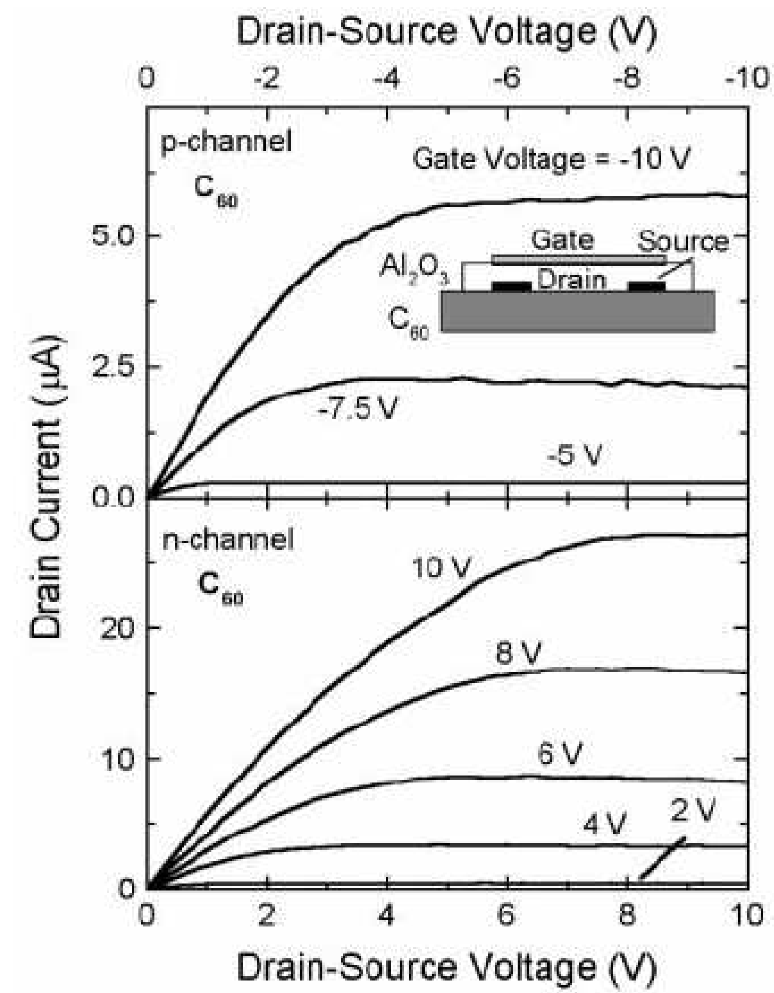




11 FEBRUARY 2000 VOL 287 SCIENCE www.sciencemag.org

A Superconducting Field-Effect Switch

J. H. Schön,[1] Ch. Kloc,[1] R. C. Haddon,[2] B. Batlogg[1]



28 APRIL 2000 VOL 288 SCIENCE www.sciencemag.org

Retraction

1) J. H. Schön, S. Berg, Ch. Kloc, B. Batlogg, Ambipolar pentacene field-effect transistors and inverters, *Science* **287**, 1022 (2000).

2) J. H. Schön, Ch. Kloc, R. C. Haddon, B. Batlogg, A superconducting field-effect switch, *Science* **288**, 656 (2000).

3) J. H. Schön, Ch. Kloc, B. Batlogg, Fractional quantum Hall effect in organic molecular semiconductors, *Science* **288**, 2338 (2000).

4) J. H. Schön, Ch. Kloc, A. Dodabalapur, B. Batlogg, An organic solid state injection laser, *Science* **289**, 599 (2000).

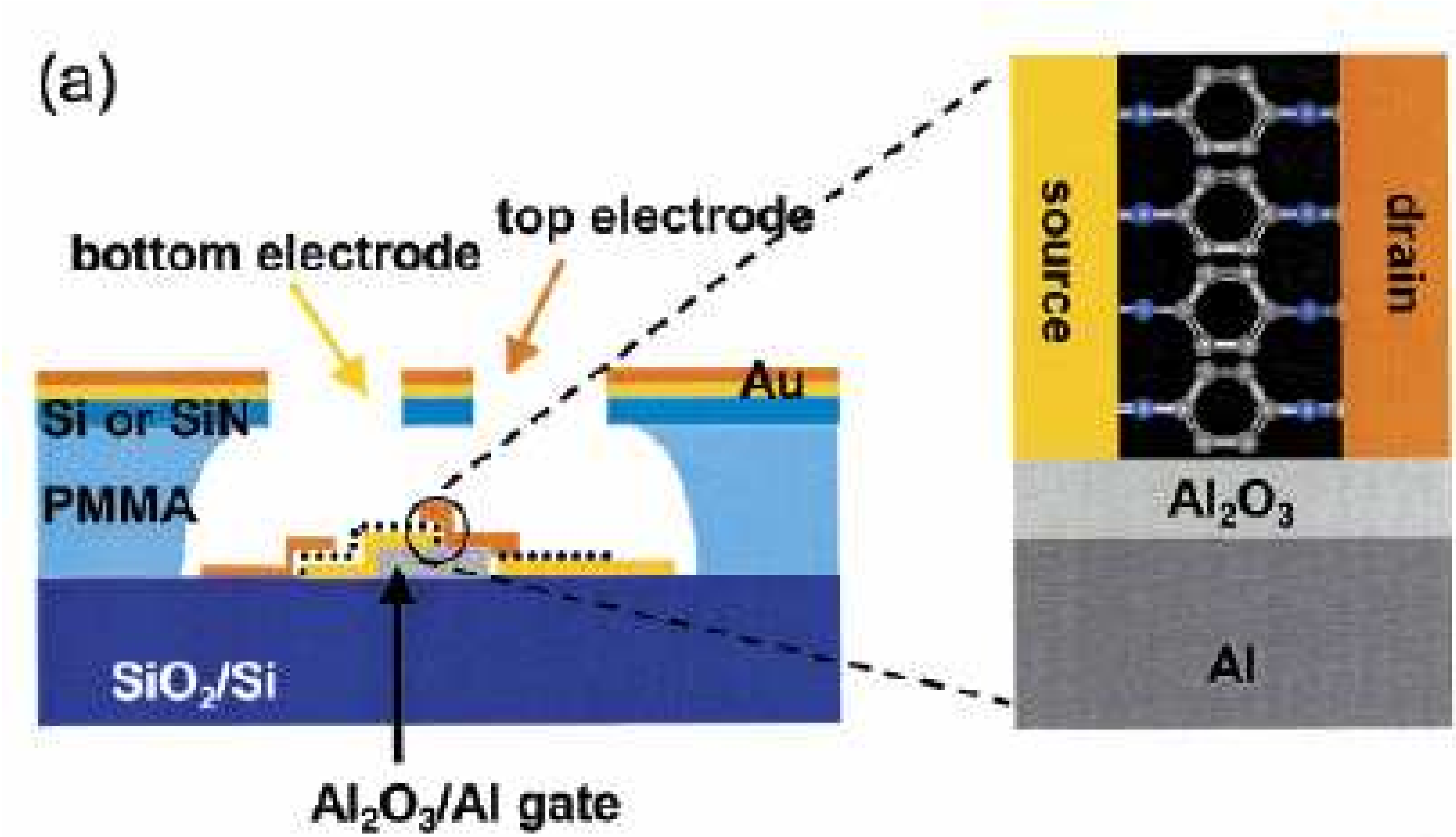
5) J. H. Schön, A. Dodabalapur, Ch. Kloc, B. Batlogg, A light-emitting field-effect transistor, *Science* **290**, 963 (2000).

6) J. H. Schön, Ch. Kloc, H. Y. Hwang, B. Batlogg, Josephson junctions with tunable weak links, *Science* **292**, 252 (2001).

7) J. H. Schön, Ch. Kloc, B. Batlogg, High-temperature superconductivity in lattice-expanded C_{60}, *Science* **293**, 2432 (2001).

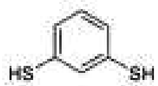
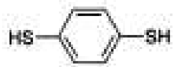
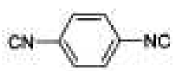
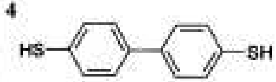
8) J. H. Schön, H. Meng, Z. Bao, Field-effect modulation of the conductance of single molecules, *Science* **294**, 2138 (2001).

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



-Lee, 2003.

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

Molecules	Yield (%)	Total # of fabricated samples	Gate dependent samples	Liquid growth	Gas phase SAM growth	characteristics
1 	7.8	256	2	Y	Y	Asymmetric *I-V*
2 	0	216	0	Y	Y	
3 	16	236	0	Y	Y	NDC
4 	5	108	0	Y	N	NDC
5 	0	72	0	Y	N	

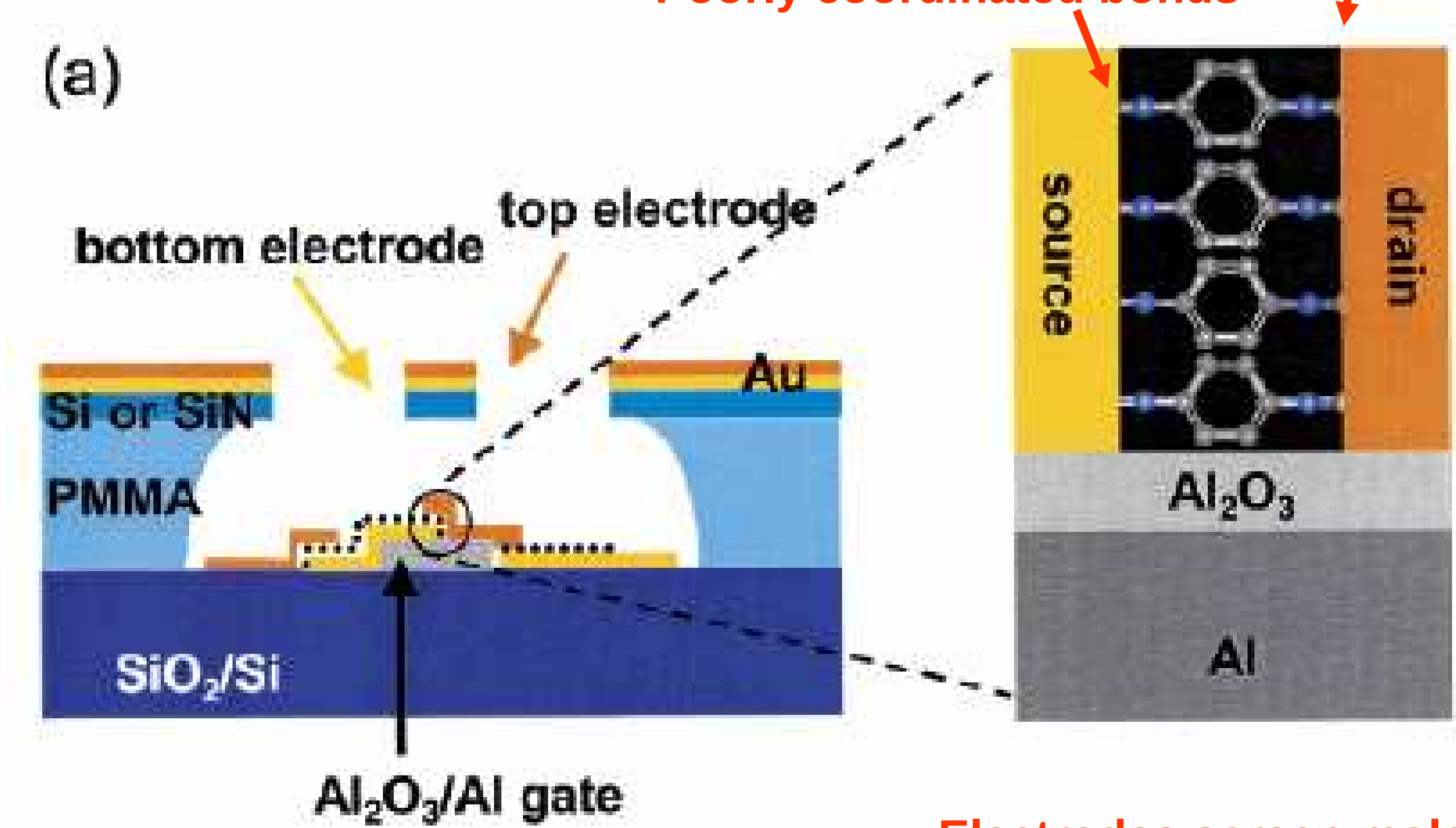
Summary: no reproducible gate dependence

-Lee, 2003.

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

electrodes 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

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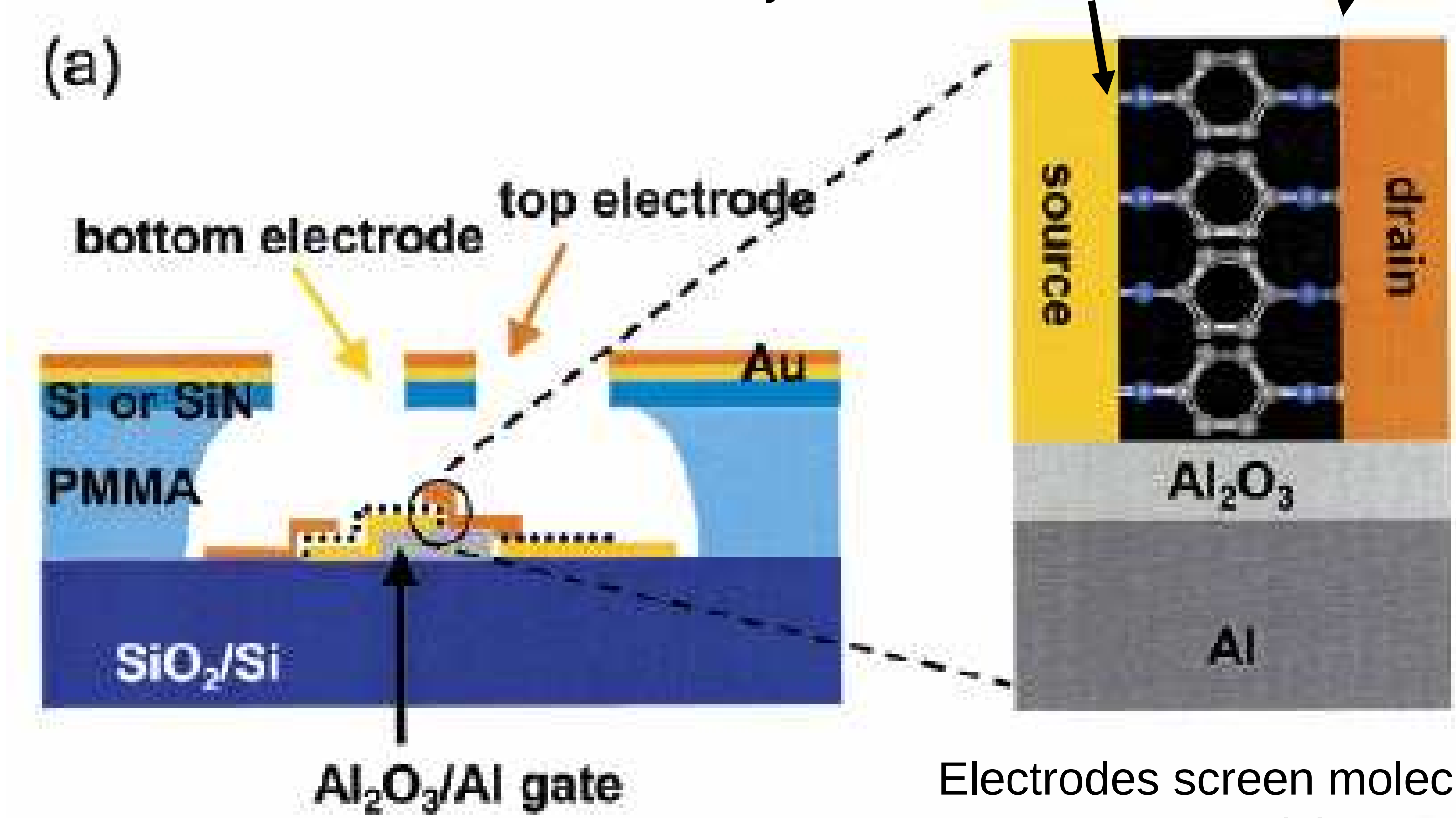
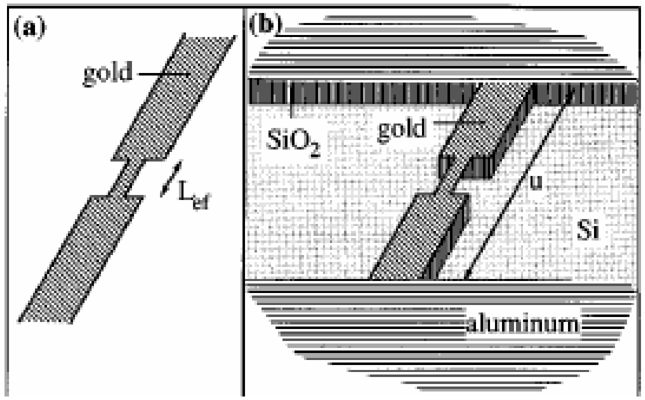
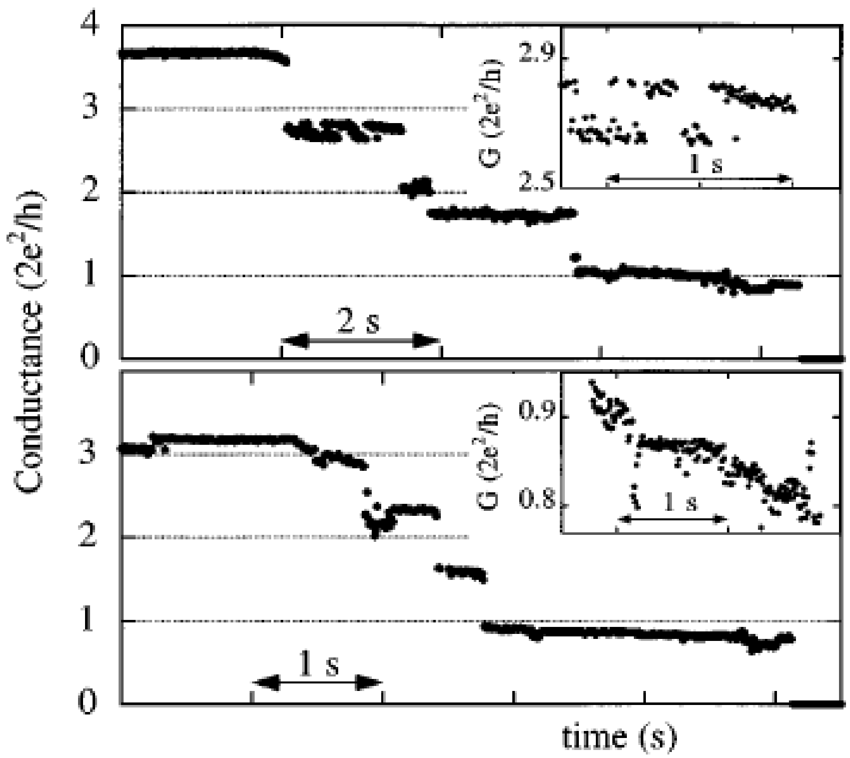


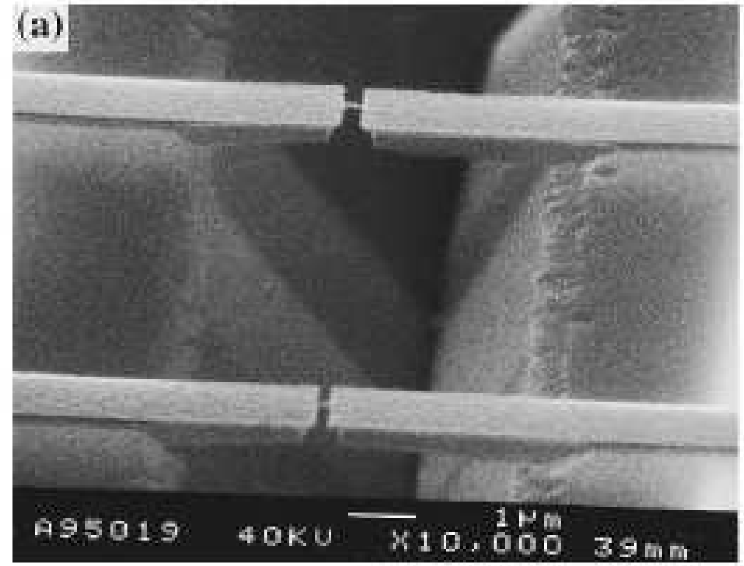
Electrodes screen molecule…
very low gate efficiency

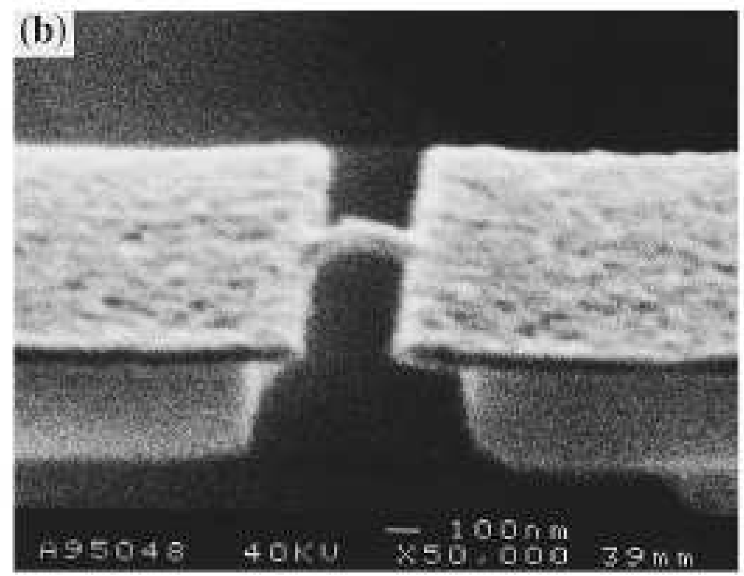
Other approaches have shows more promise…

Break Junctions – Reed (Yale)



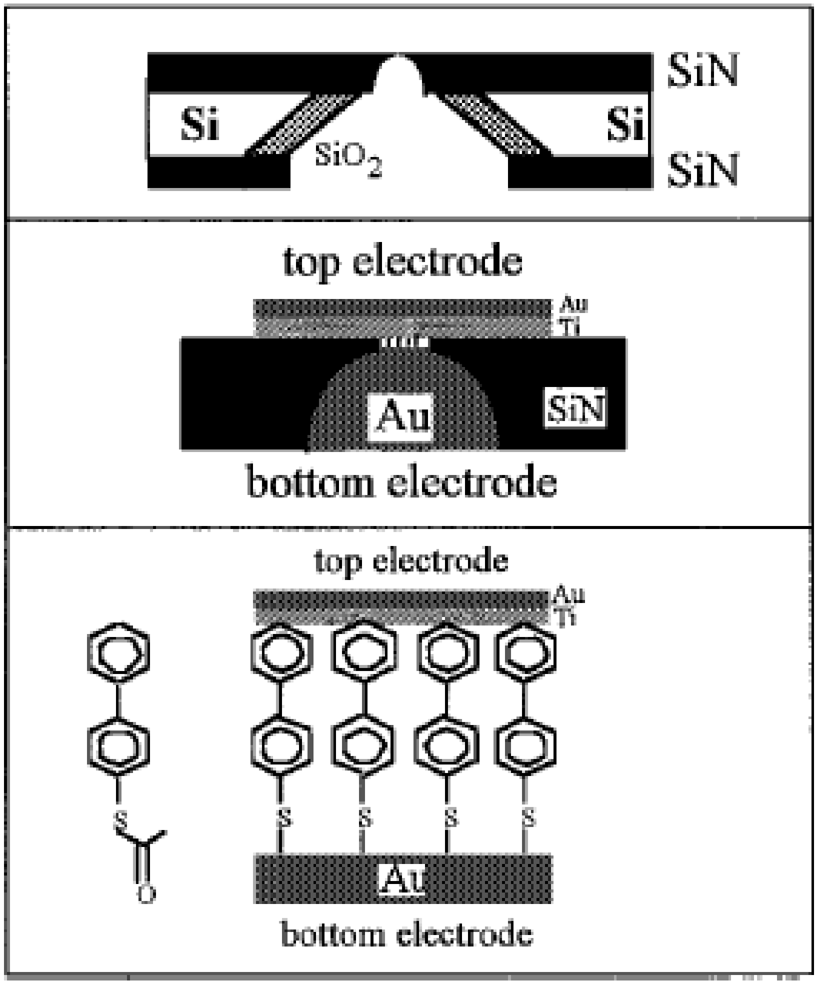


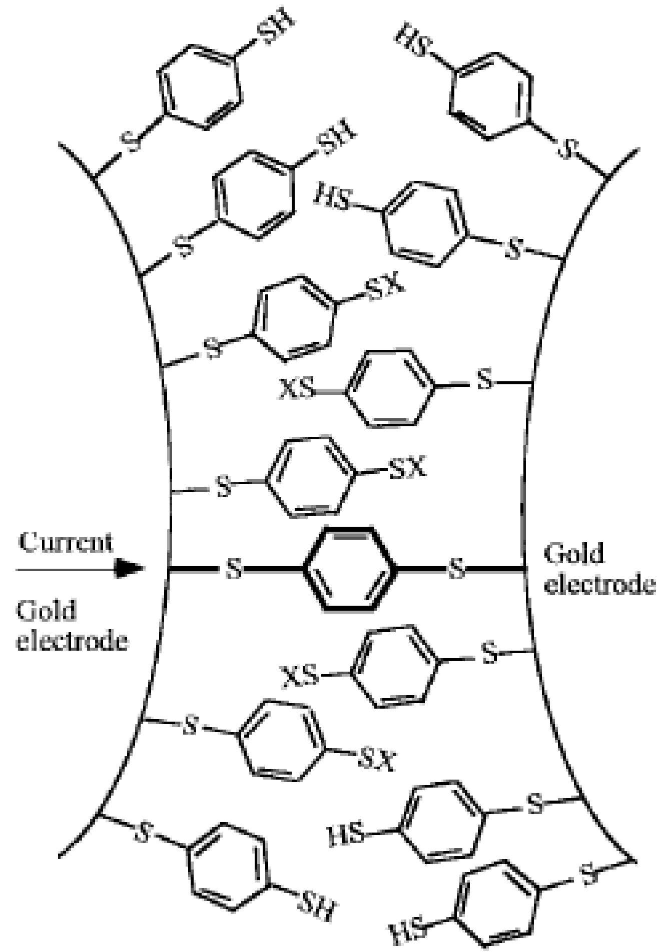




-M. Reed, *APL*1995.

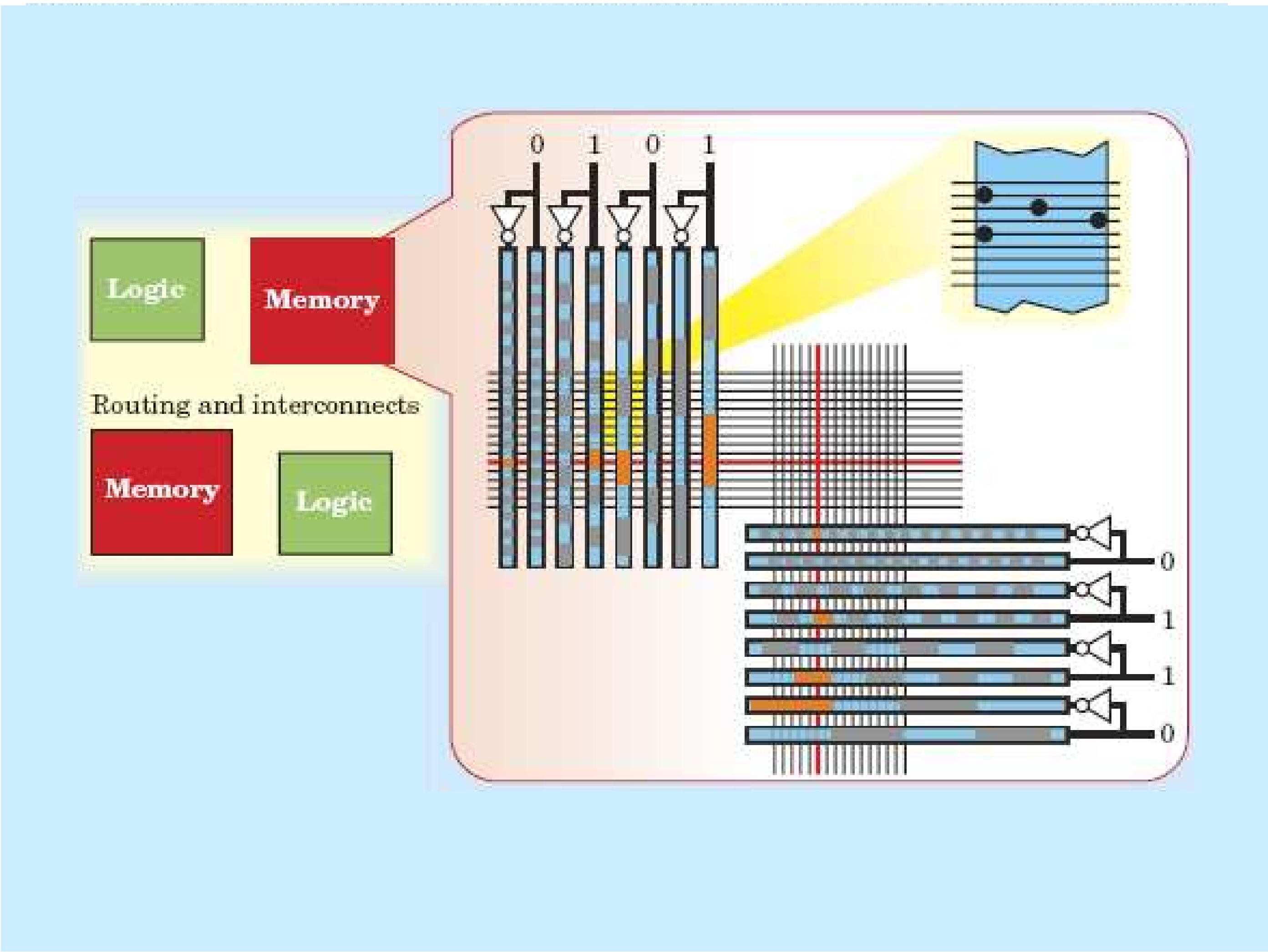
Break Junctions – molecular bridges



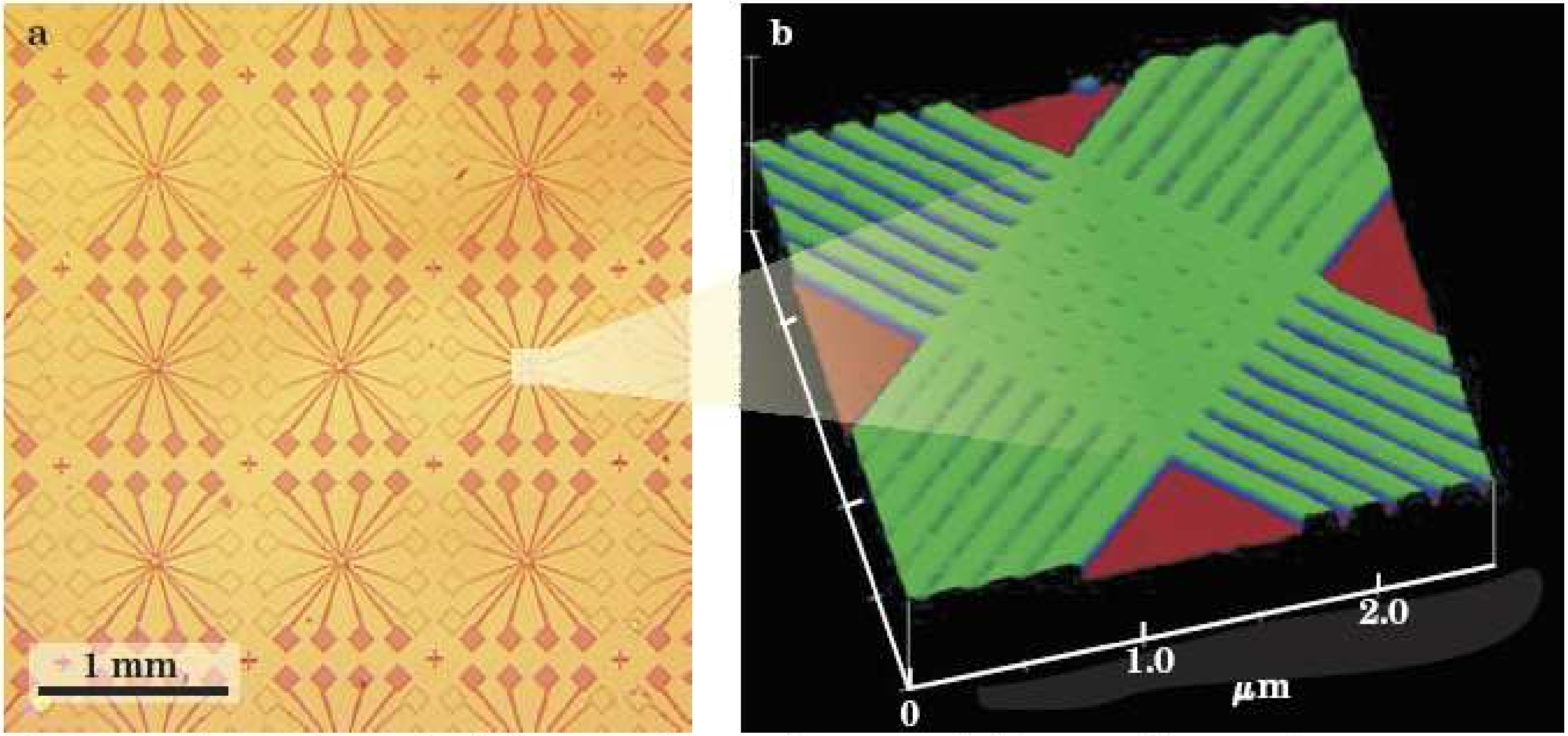


-M. Reed, *Proc. IEEE* 1999.

Molecular Crossbars – molecules as nodes in multiplexed circuits



- Heath, UCLA
- Williams, HP



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

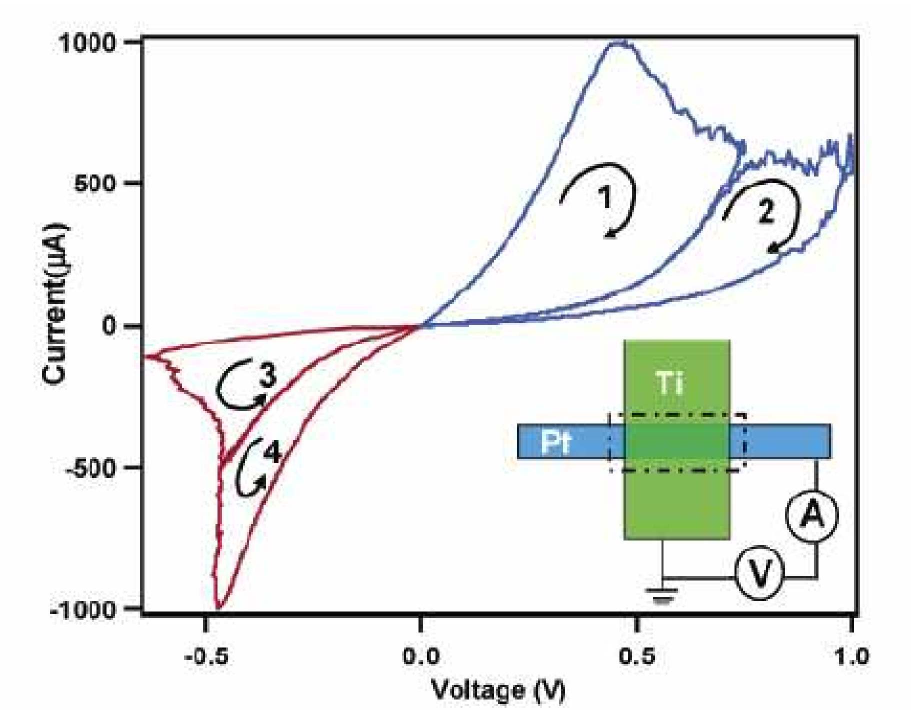
• resistance at the wire junctions can be reversibly switched
• each cross-point acts as an active memory cell.

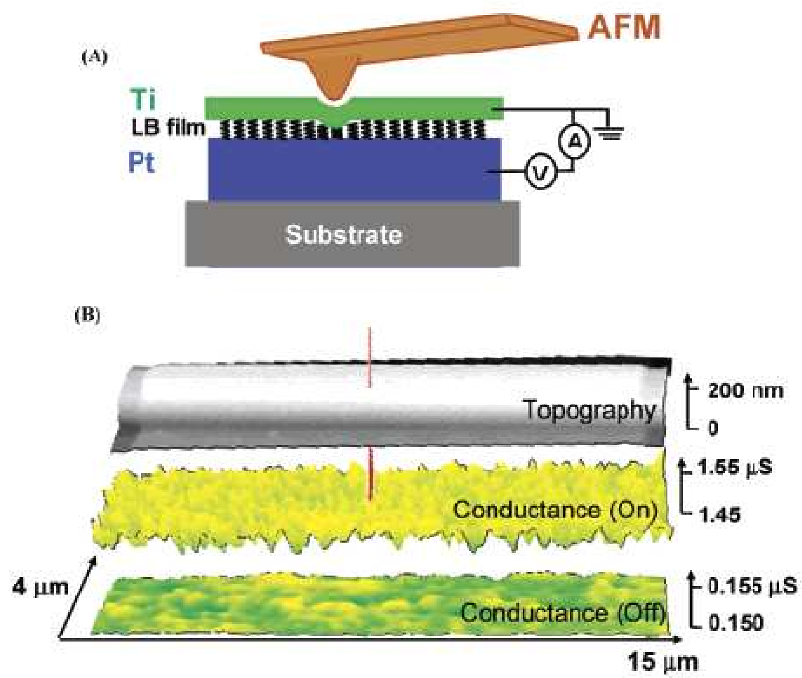
-Heath and Ratner, 2003.

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…



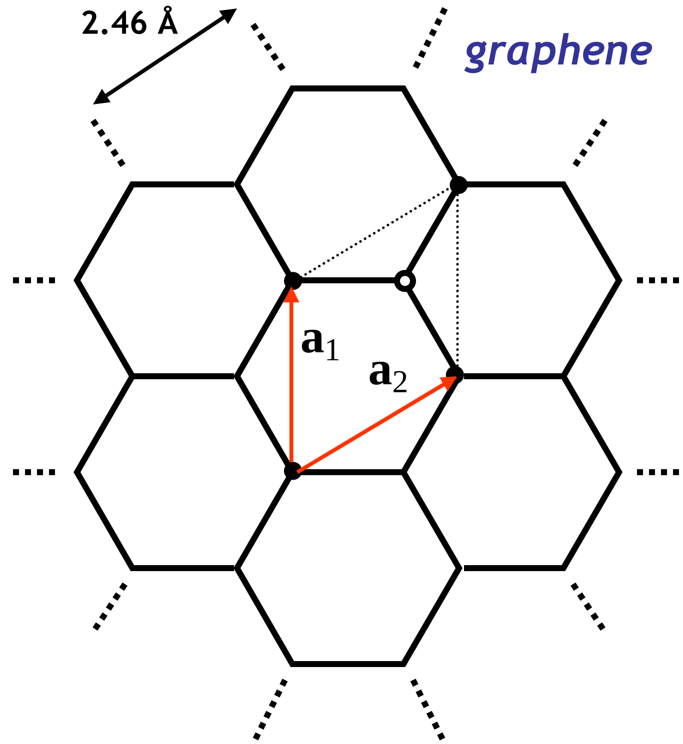


Other molecular / macromolecular systems:

Nanotubes:

- Electronic structure related to that of *graphene*.
- Tight-binding: consider only nearest-neighbor wavefunction overlap.
- Let γ_o 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:

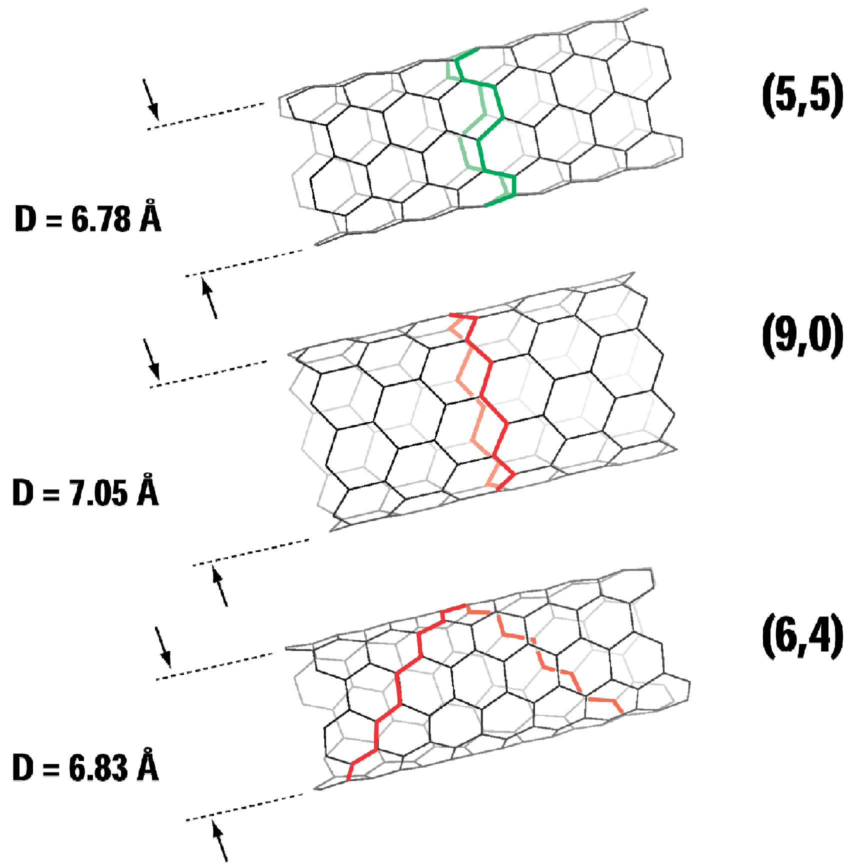
$$\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$$

- Chiral indices (n,m) determine the band structure[‡]:

|n-m| = 0,3,6,... , *metallic*;

otherwise *semiconducting*.

(valid for all but the smallest diameter nanotubes)



Reference

‡ J.W. Mintmire et al., *J. Phys. Chem. Sol.* **54**(12) 1835-1840, 1993.

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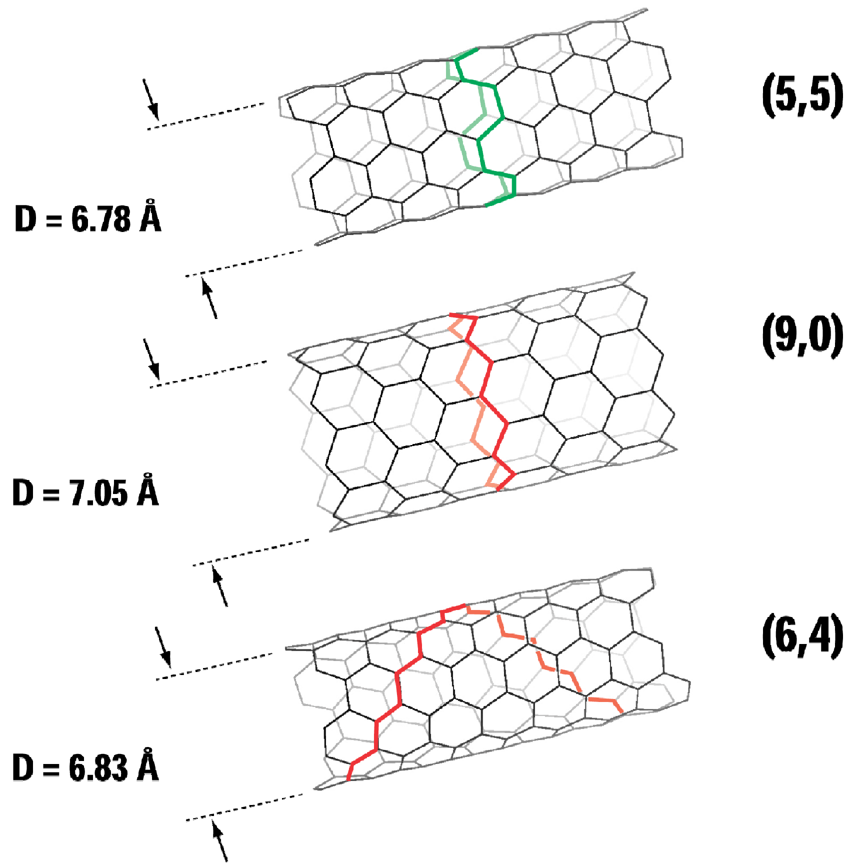

- **Chirality distribution**

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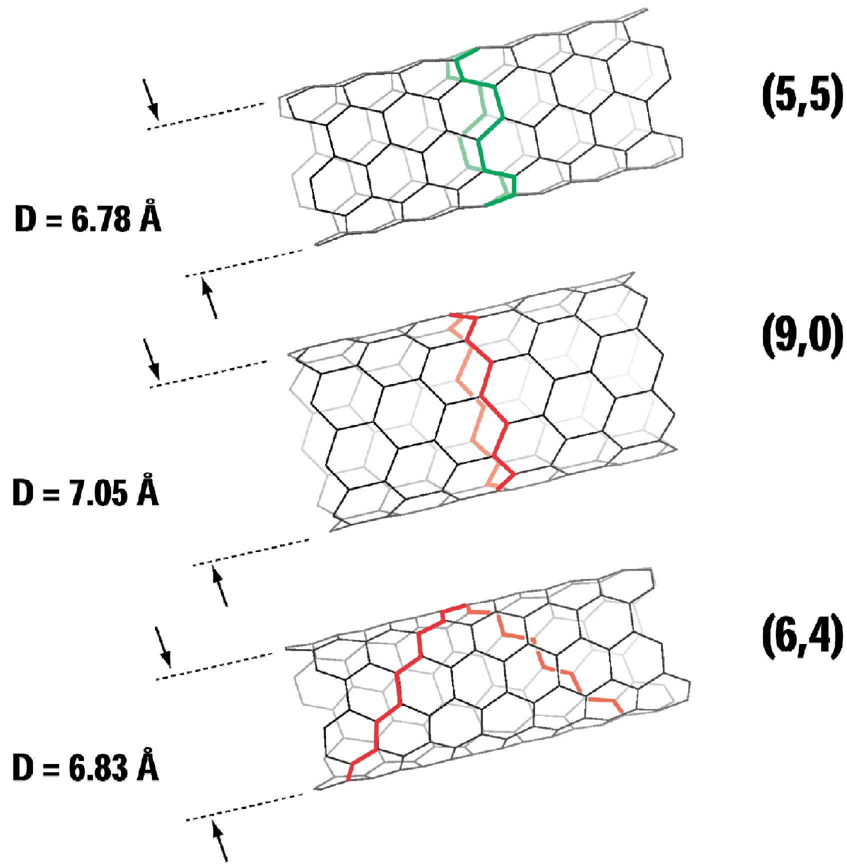
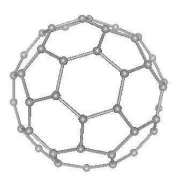


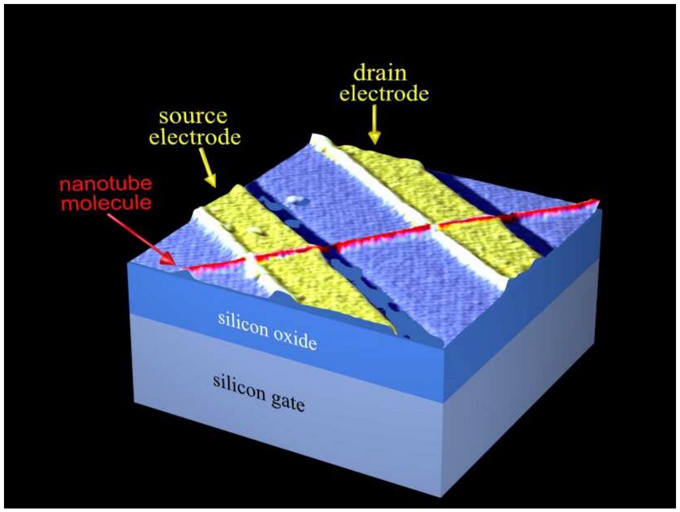


- **Chirality distribution**
- **Rational synthesis of C_{60} – will we have monodisperse SWNT?**

Reference

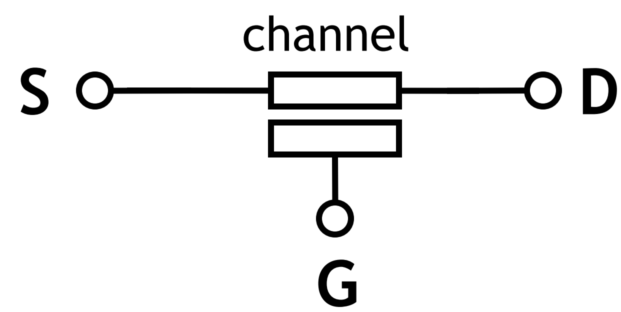
‡ J.W. Mintmire et al., *J. Phys. Chem. Sol.* **54**(12) 1835-1840, 1993.

Nanotube-based FETs

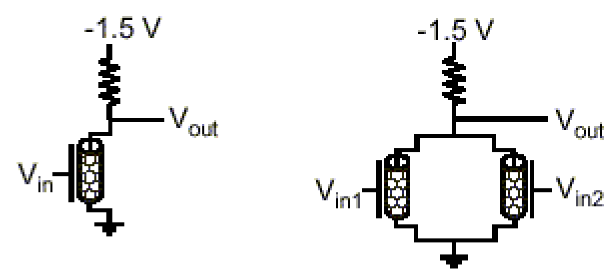


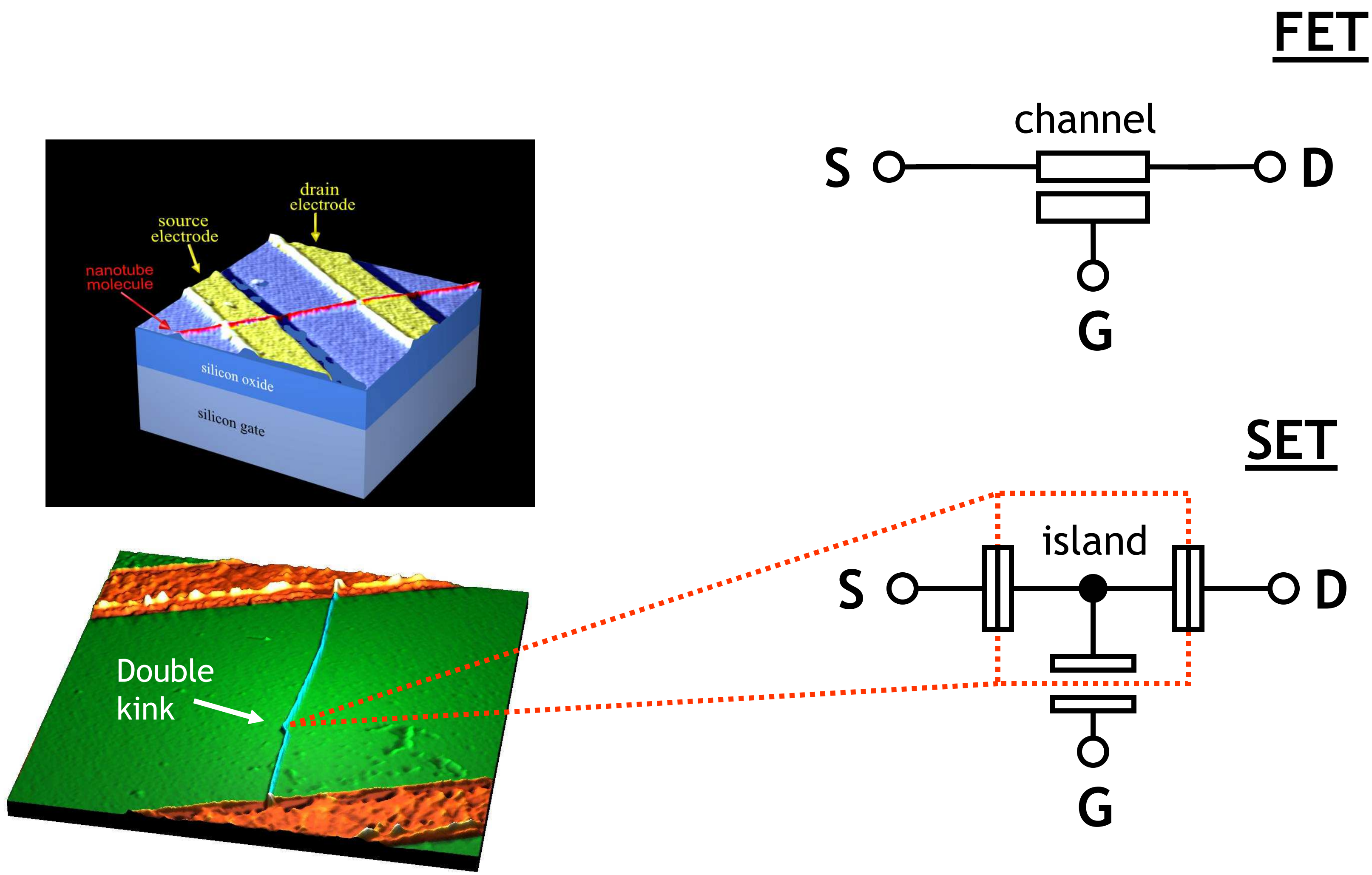
- Channel = semiconducting nanotube
- FETs can also be gated by a local wire or by a liquid
- Smallest tubeFET ~100 nm (gap between source and drain)
- Top-down FET logic gates have been made

FET Structure:

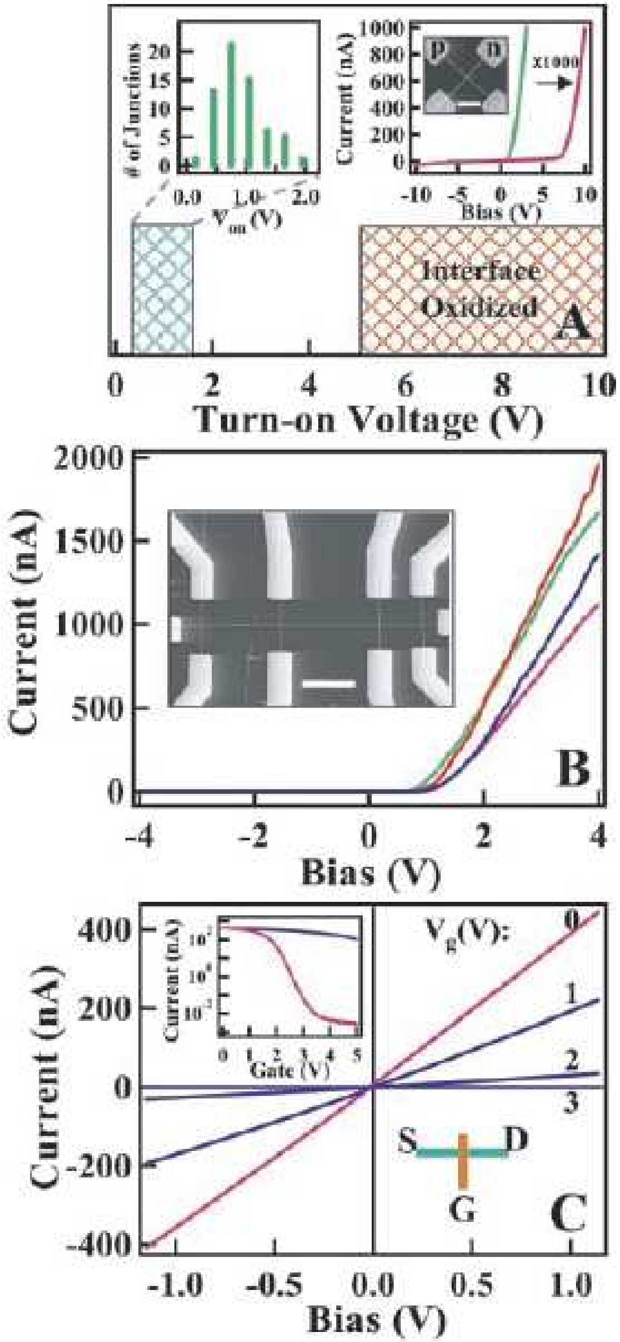


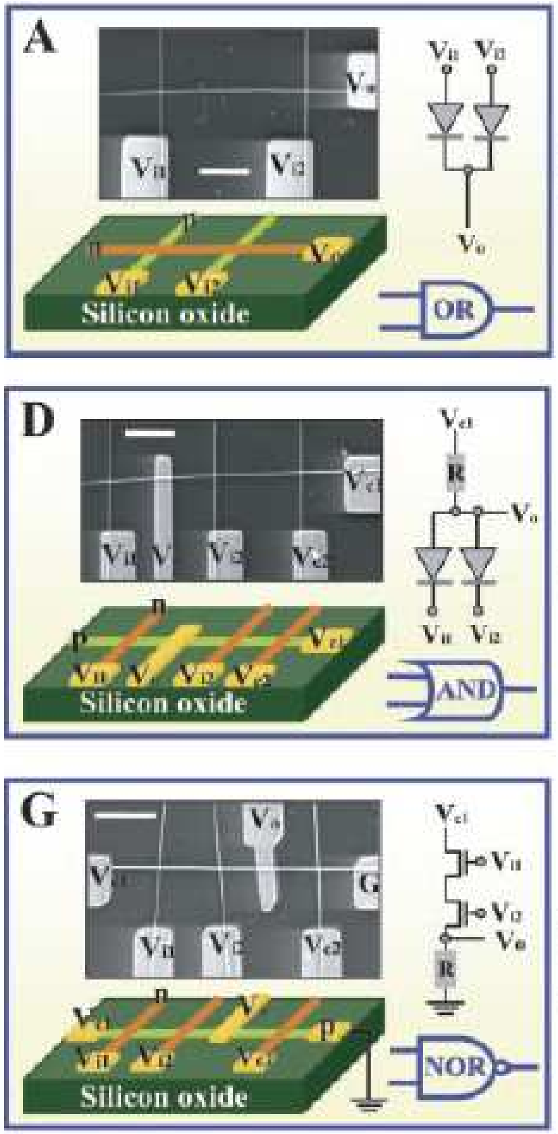
Tube-FET Logic (Bachtold, Delft)




FET
channel
S
D
G
drain electrode
source electrode
nanotube molecule
silicon oxide
silicon gate
SET
island
S
D
G
Double kink

Nanowires
Lieber (Harvard)





- Science 2001

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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
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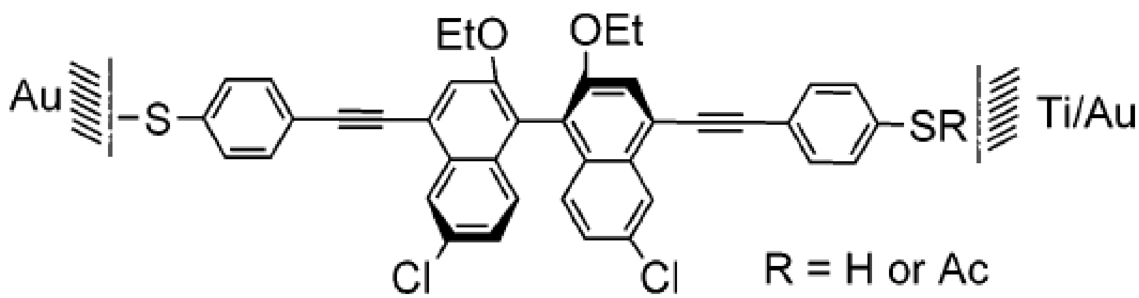
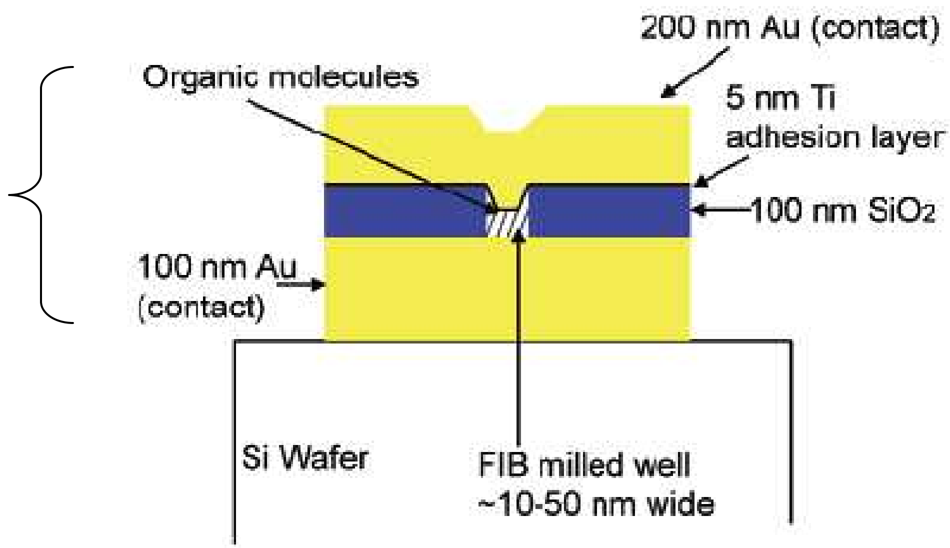
First Optically Active Molecular Electronic Wires

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

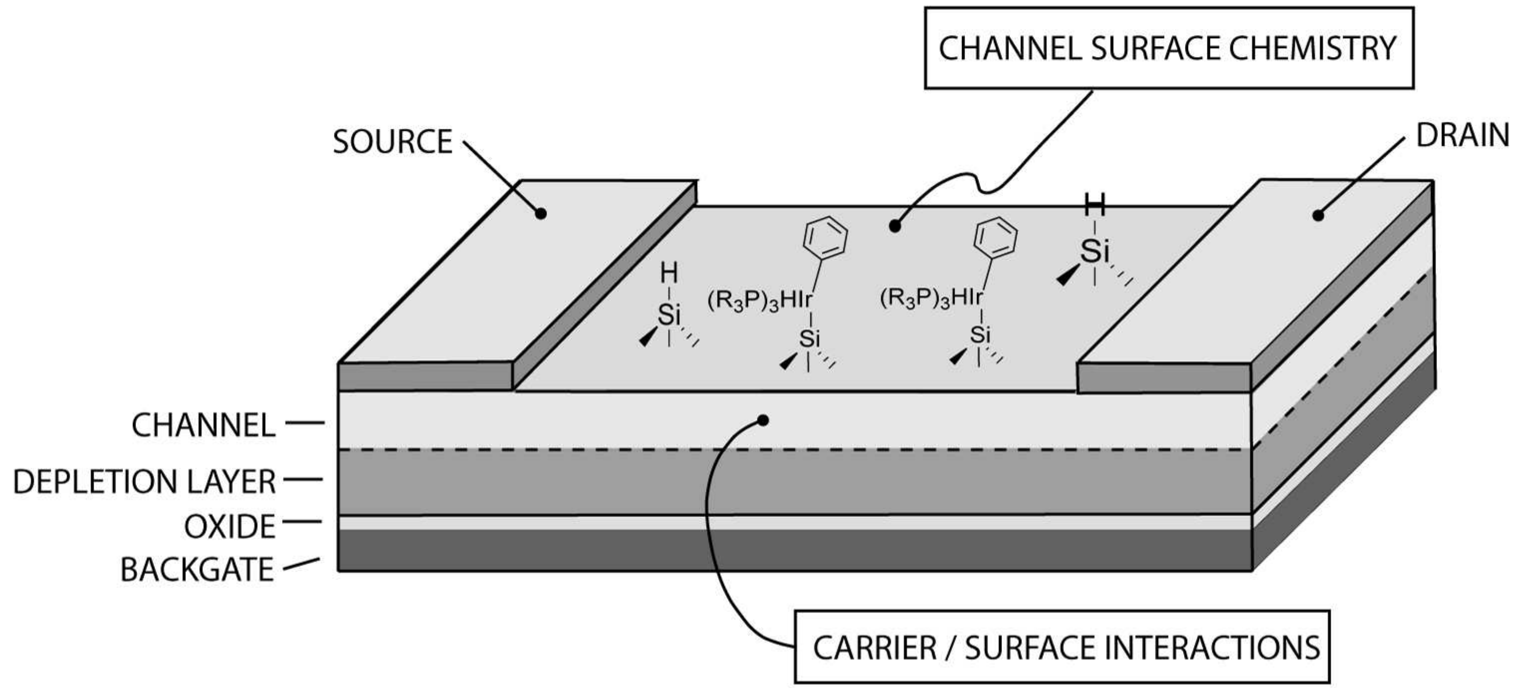


Nanowell Geometry



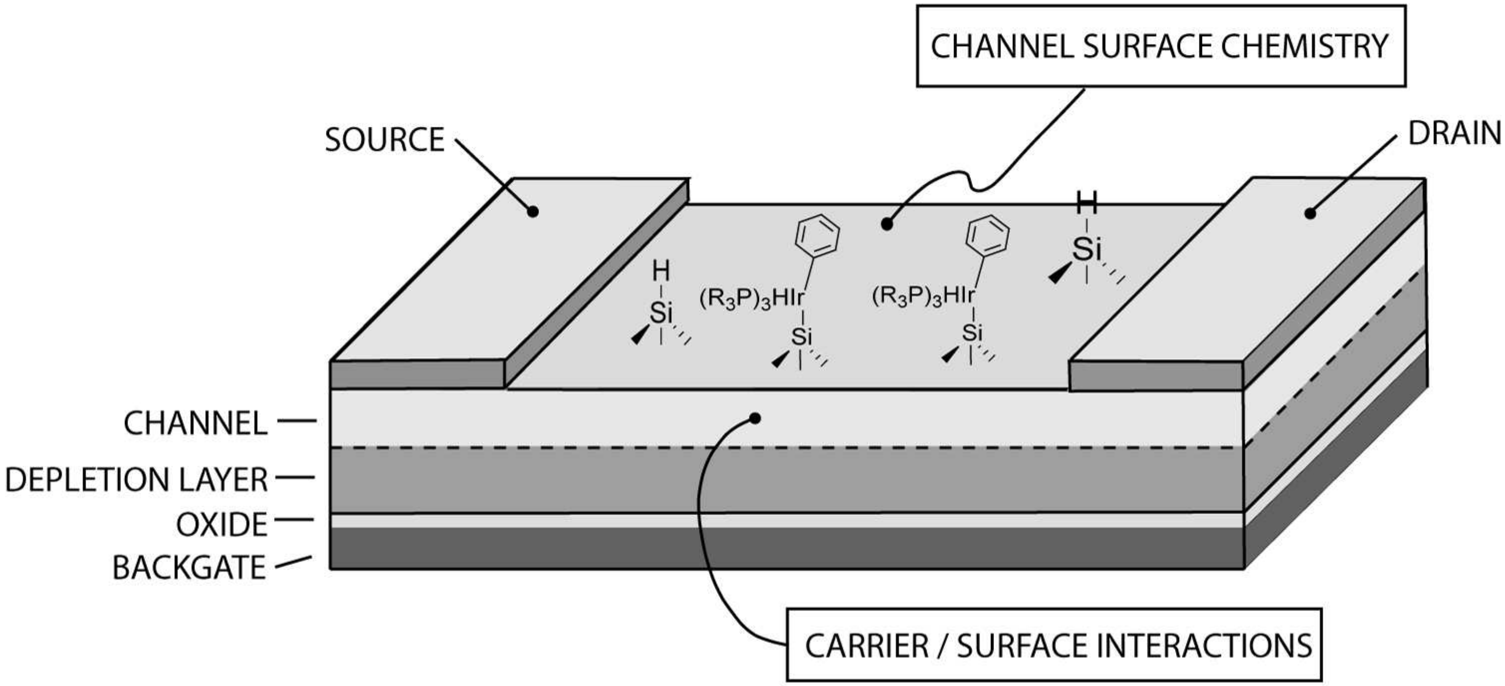
- Organic Letters, 2005

"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, …

“Surfet” Strategy (with Bean, Ghosh, Harriott, Pu)



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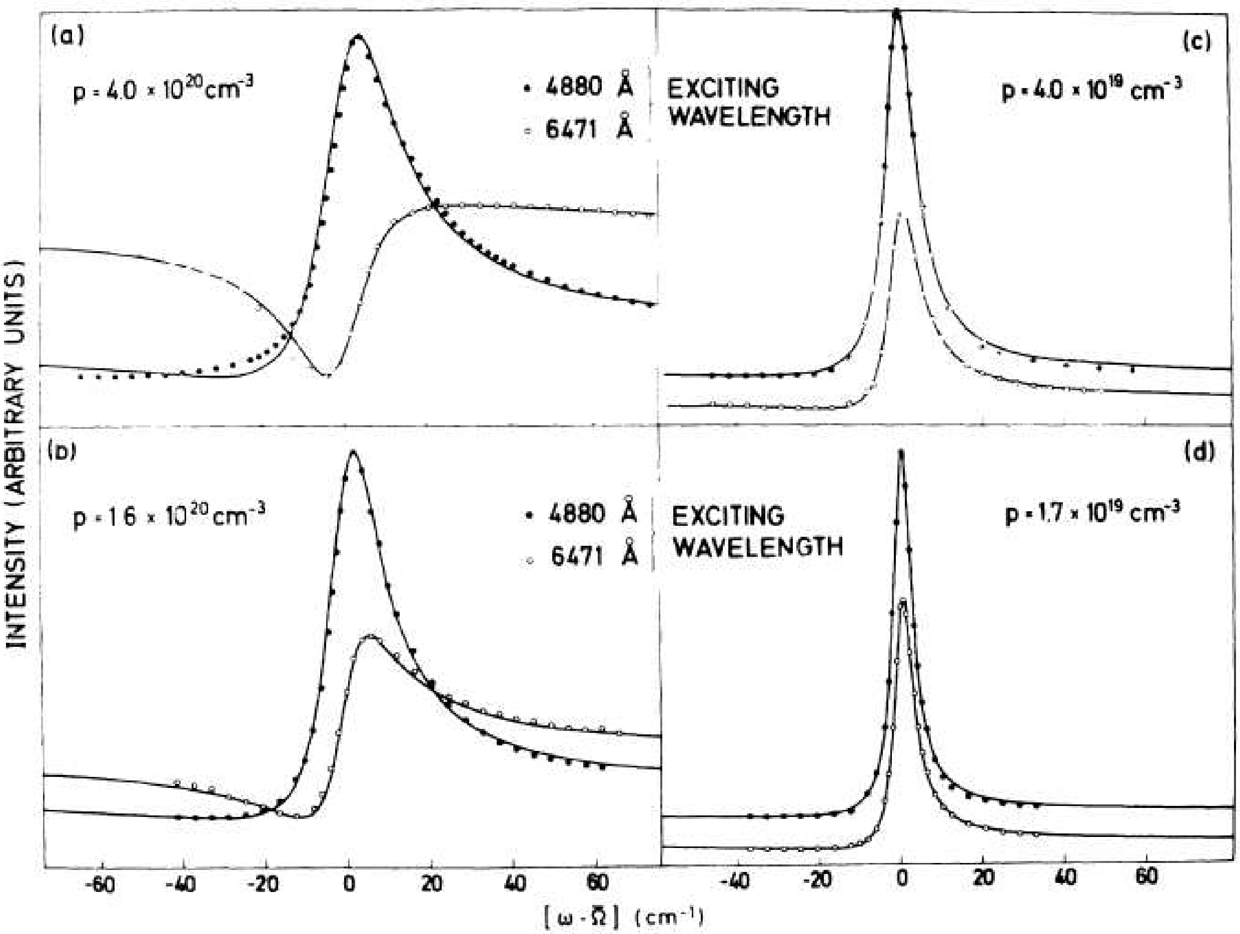
Tunable Fano device (prototype adsorbate modulated transistor)

- 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:



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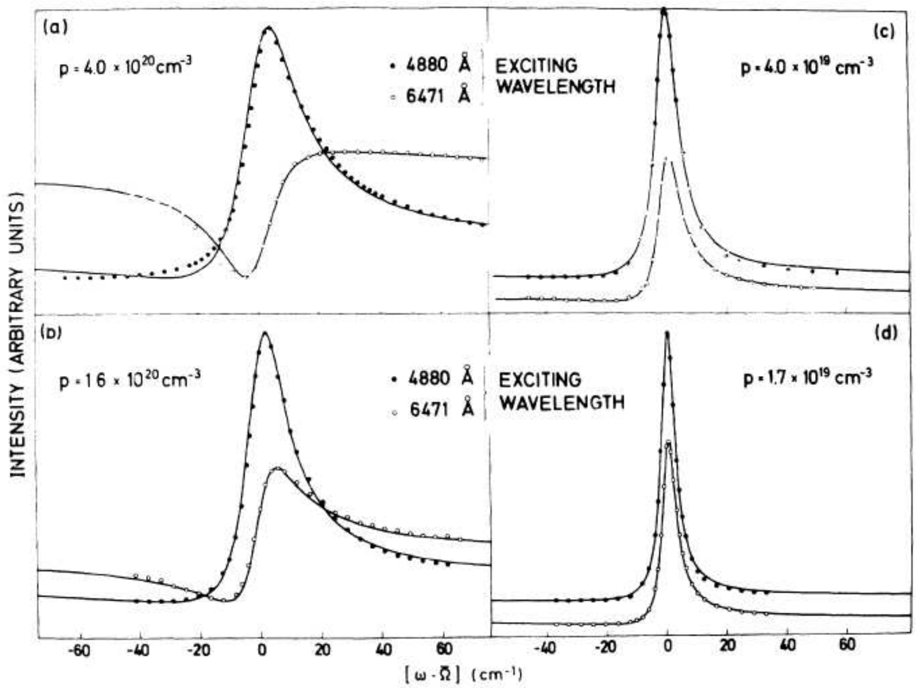
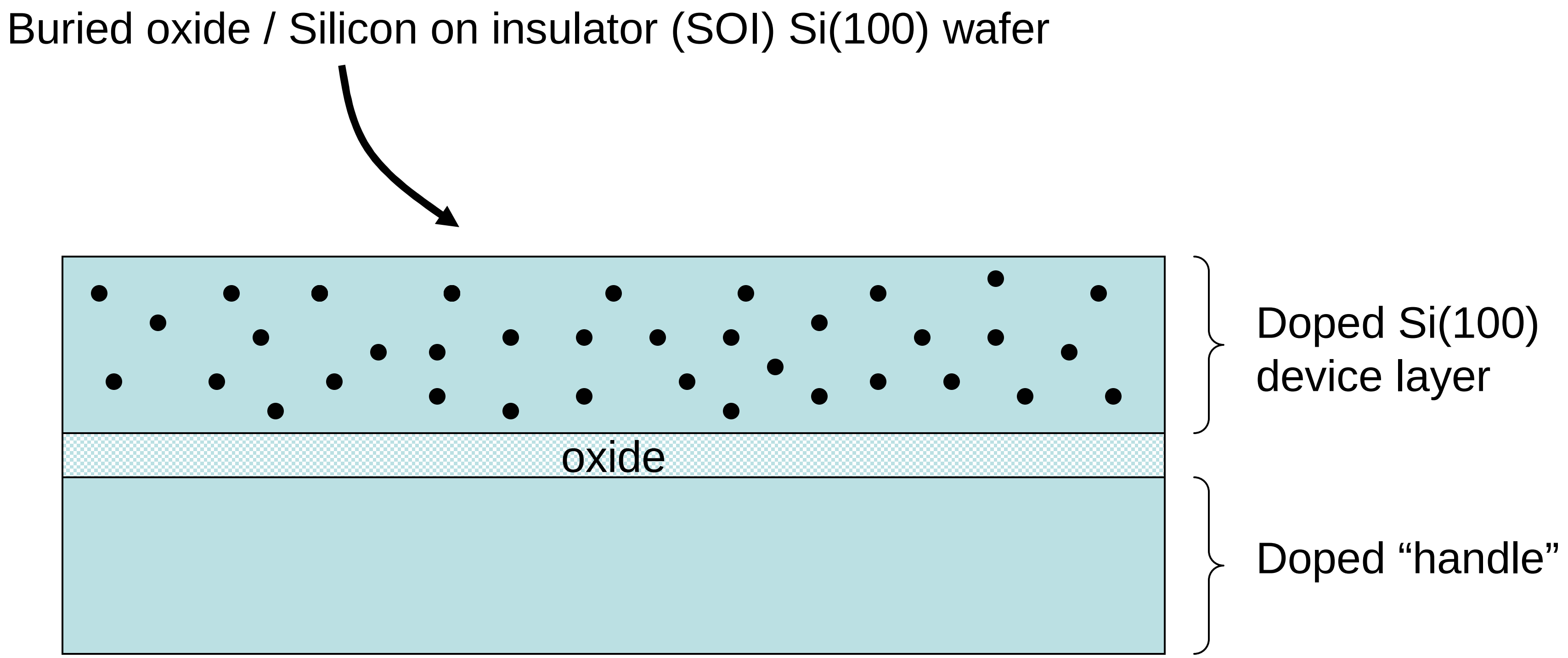


- Resonance / antiresonance behavior depends on strength of the interaction between electronic continuum and discrete phonon states

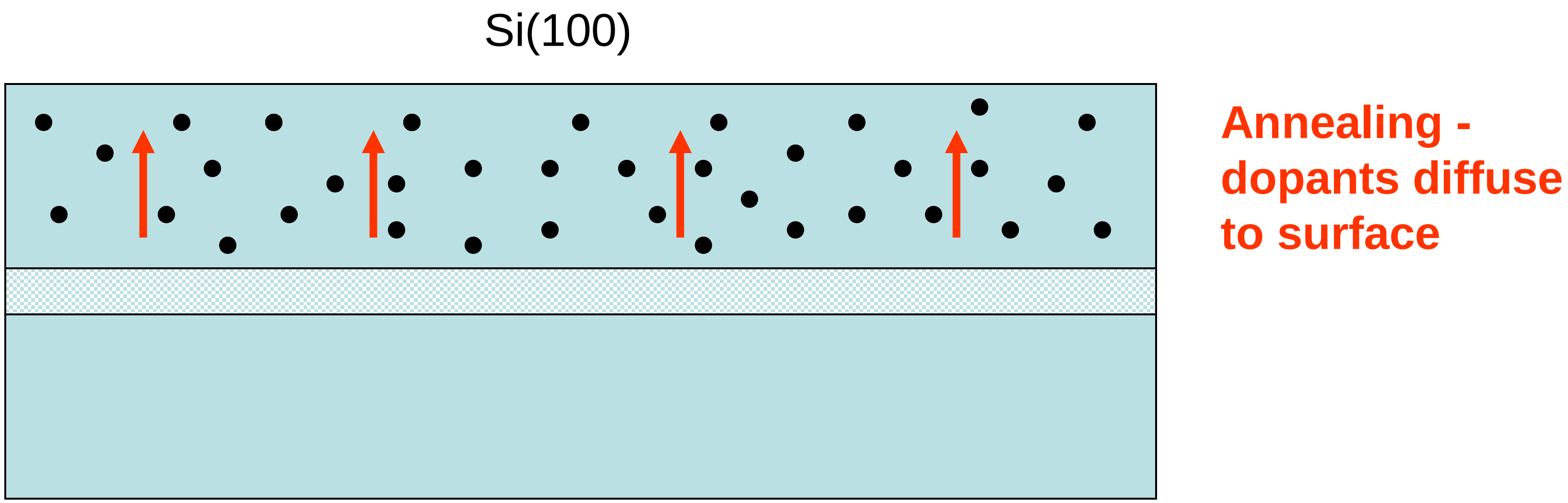
- Fano lineshape:
$$I(\omega) = \frac{(q+\varepsilon)^2}{(1+\varepsilon^2)}$$
$$\varepsilon = (\omega - \omega_0)/\Gamma$$

in which Γ = width parameter
q = asymmetry parameter (q→∞ produces Lorentzian)

Tunable Fano device

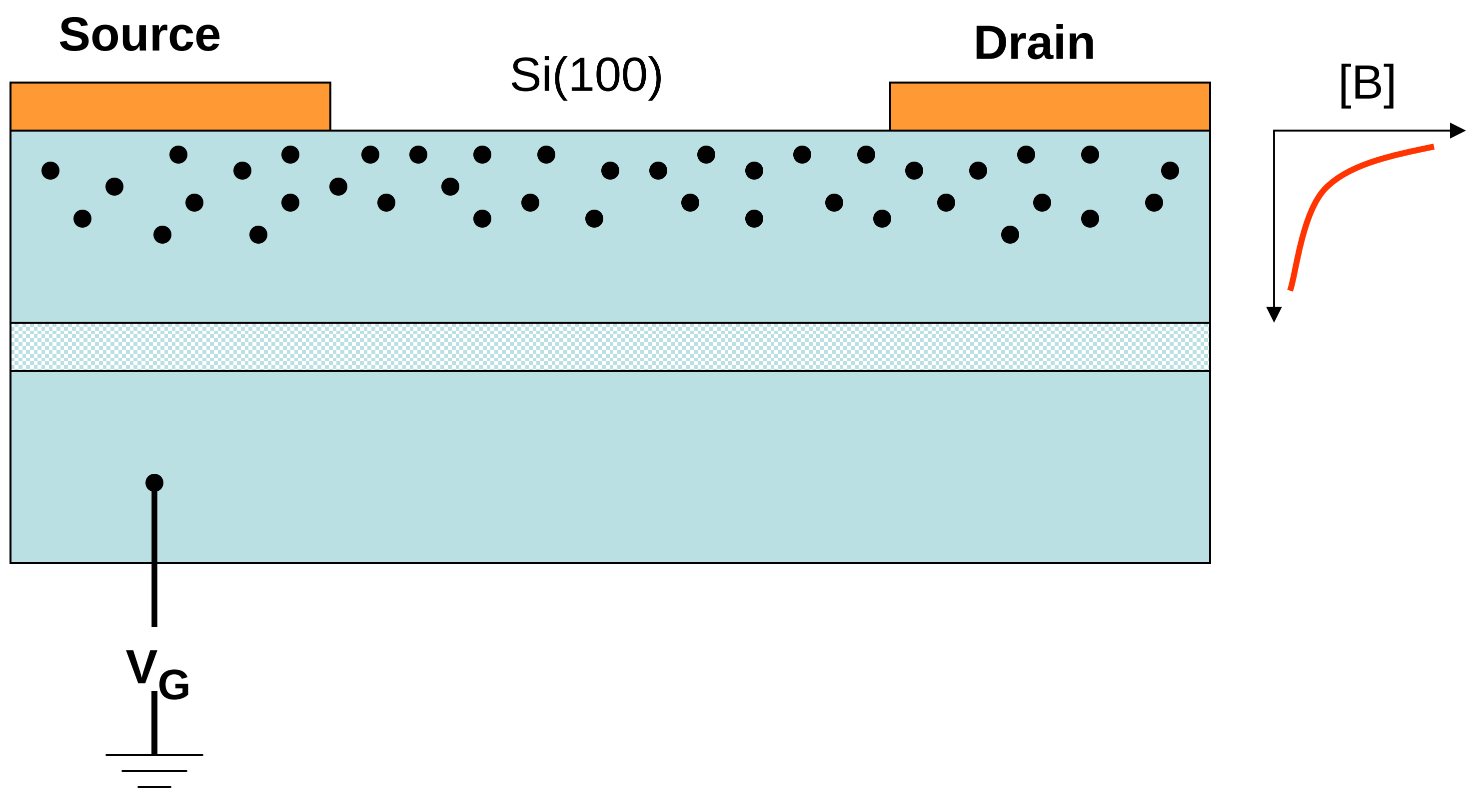


Tunable Fano device



Tunable Fano device

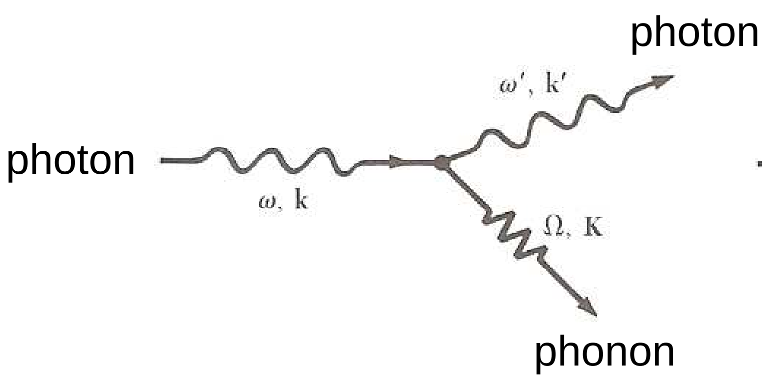
Open questions: range of tunability; transport signature
Next: molecular adsorbates as surface dopants

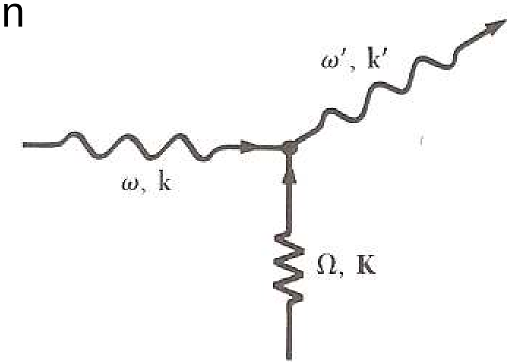


Device building in progress (Jack Chan)

Electron Phonon Interaction in Nanotube-channel FETs

Raman Stokes and anti-Stokes processes:

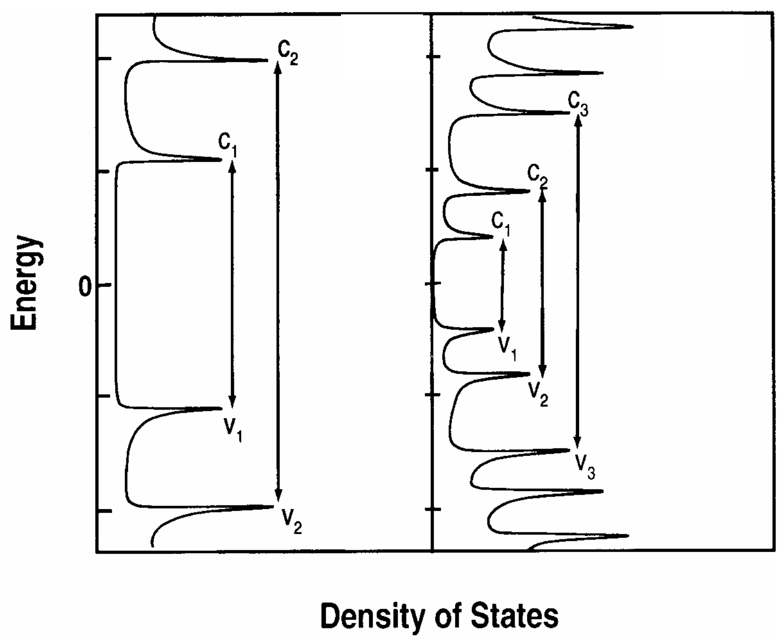




Raman studies on individual nanotube-channel FETs

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

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



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

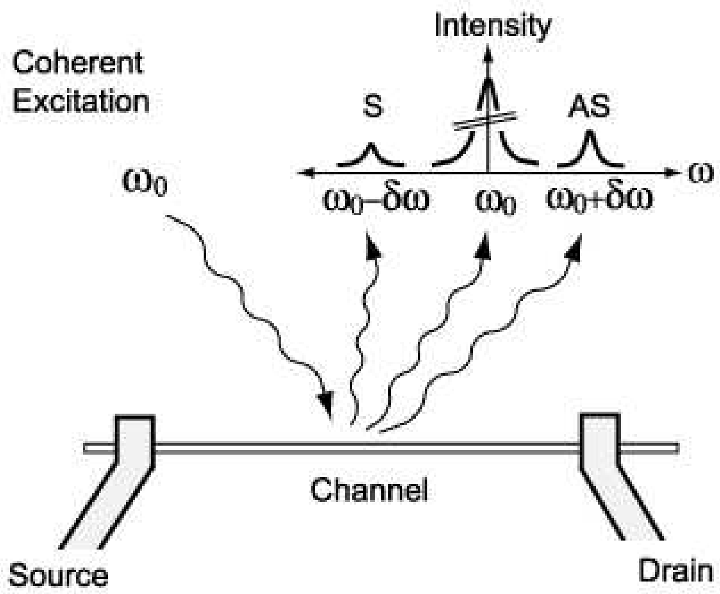
JDOS:

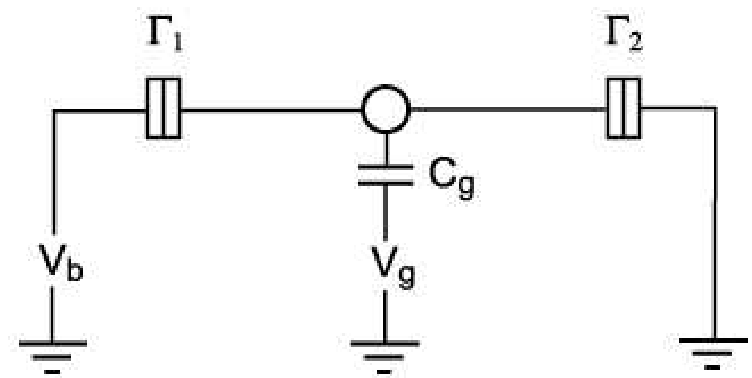
$$g(E) = \mathrm{Re}\left(\sum_i \frac{a_{C-C} E}{d\gamma_0 \sqrt{(E - E_{ii} - i\Gamma_J)(E + E_{ii} + i\Gamma_J)}} \right)$$

References

[1] Richter, Subbaswamy et al.
[2] Raman resonance: Rao, Richter, Bandow, Chase, Eklund, Williams, Fang, Subbaswamy, Menon, Thess, Smalley, Dresselhaus, Dresselhaus

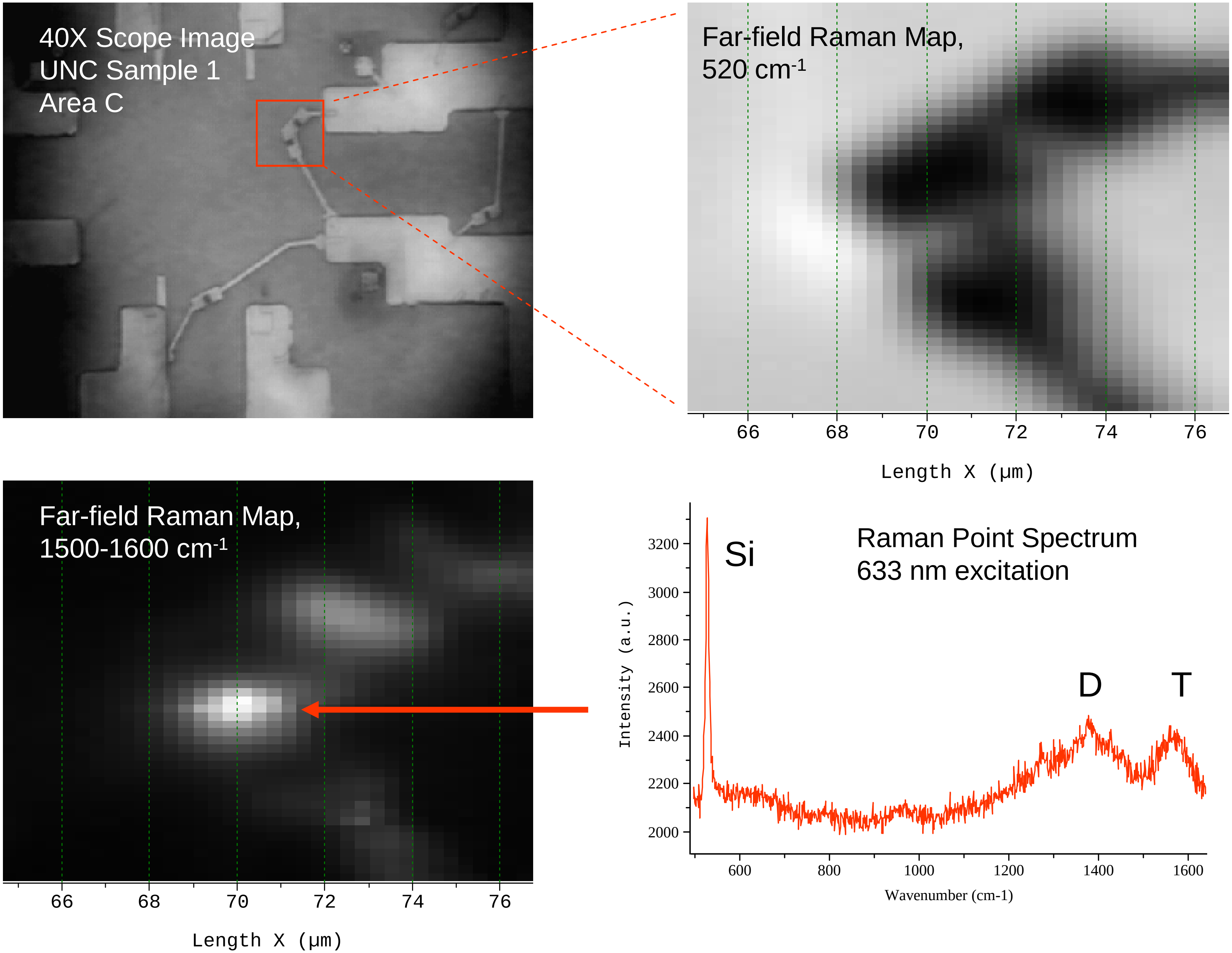
Electron Phonon Interaction in Nanotube-channel FETs



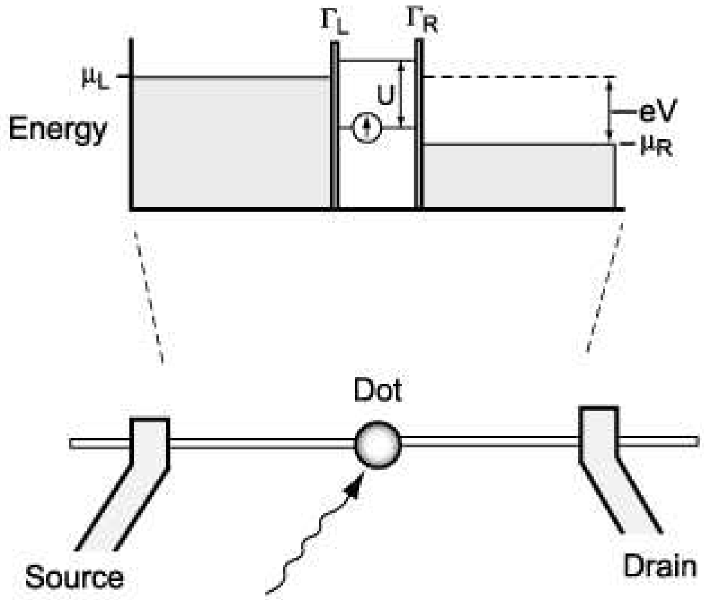


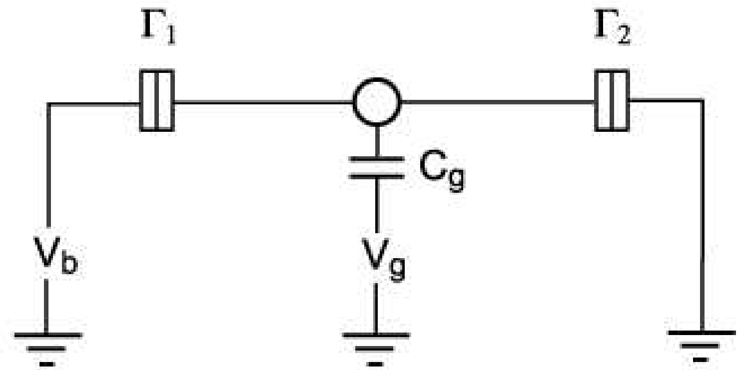
- single-channel measurements possible because of resonance conditions
- current-driven phonons
- work in progress: tube devices by CVD, lithography, Stokes/anti-Stokes measurements

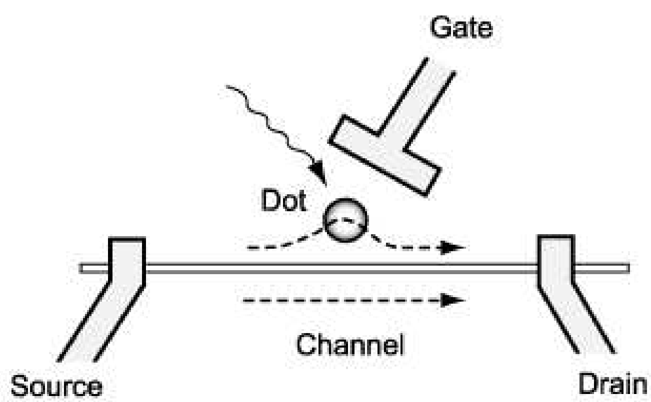
Raman mapping of the nanotube channel

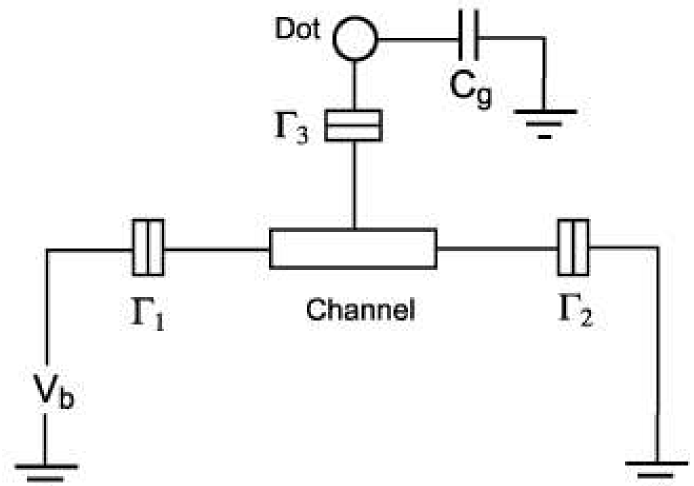


Related studies:

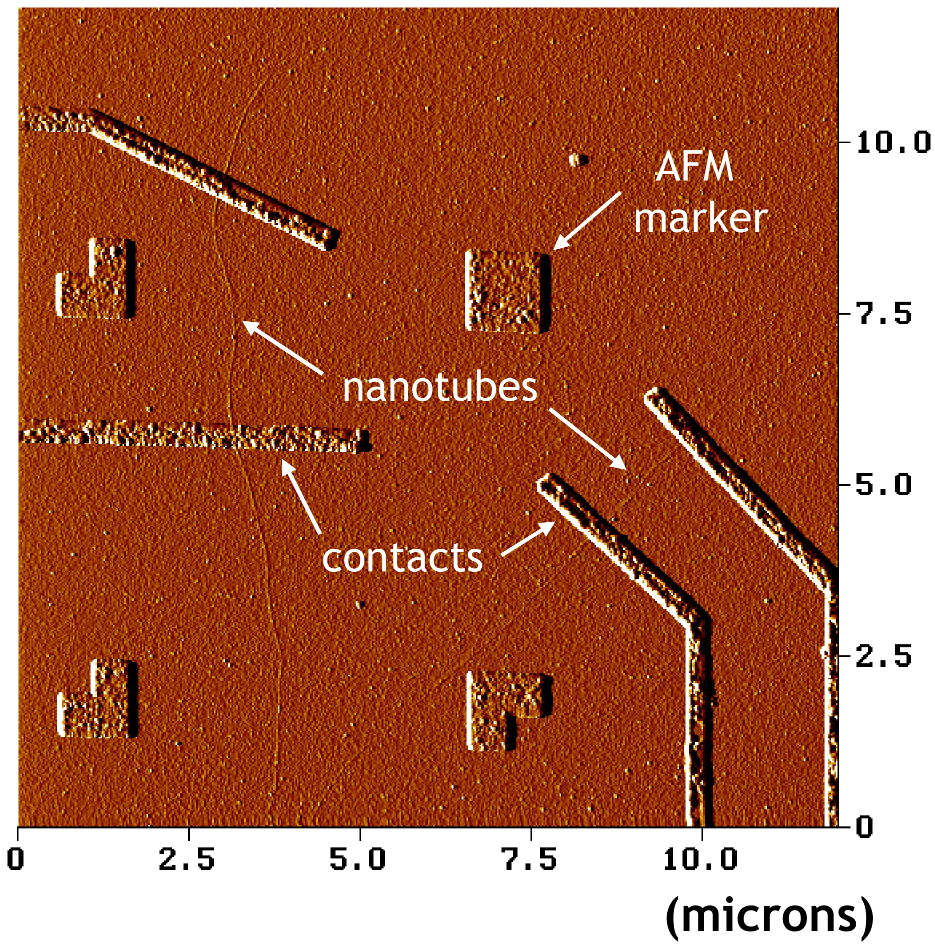






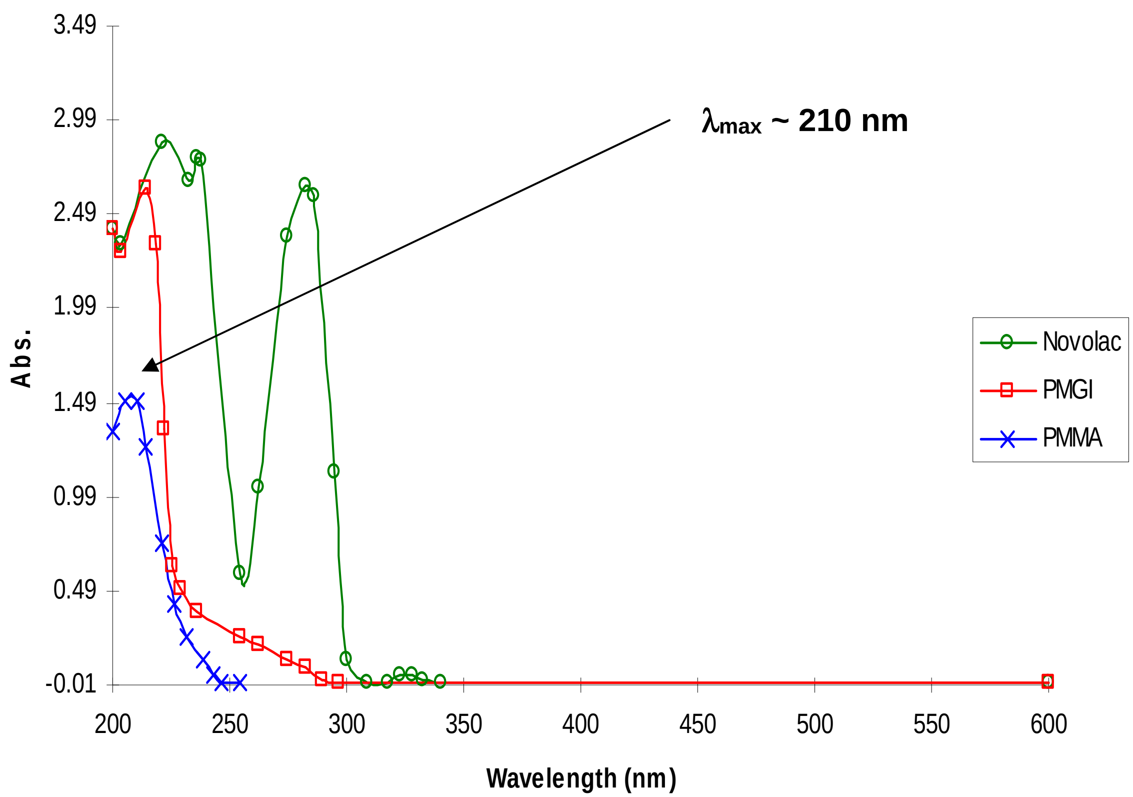


Current work: electron-beam and photolithography



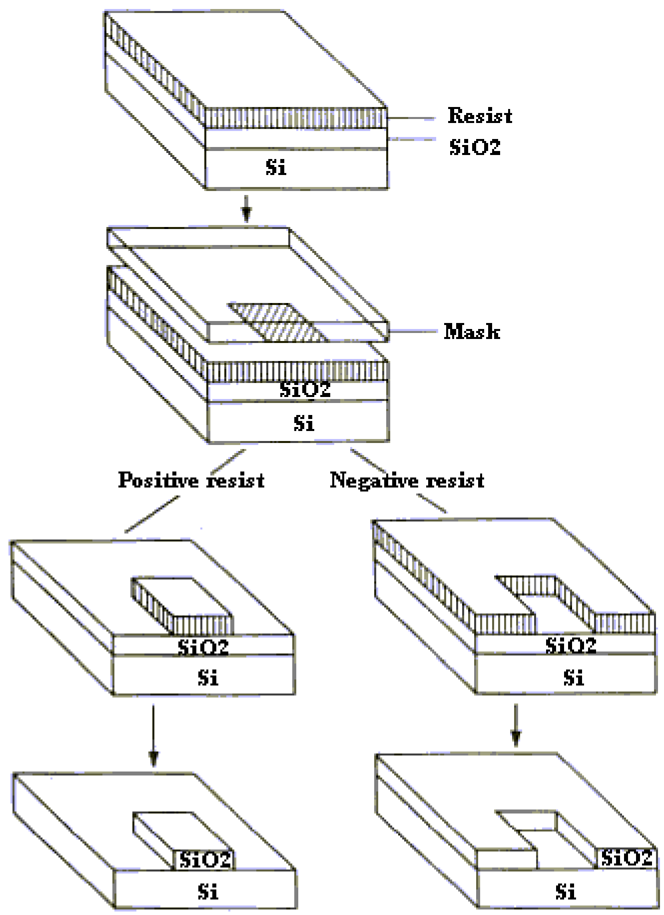
Device fab. collab. @ Delft with Iddo Heller and Jing Kong (MIT)

New lithographic Tools: Near field ultraviolet photolithography



- 5th harmonic from Nd:YAG – 213 nm
- ~0.5 mW average power possible at 20 Hz

Standard Photolithography processes with a mask



(very) Brief Summary of Near-field techniques

• Hans Bethe, "Theory of diffraction by small holes," *Phys. Rev.* **66** , 163-182 (1944):

Very small transmission expected:

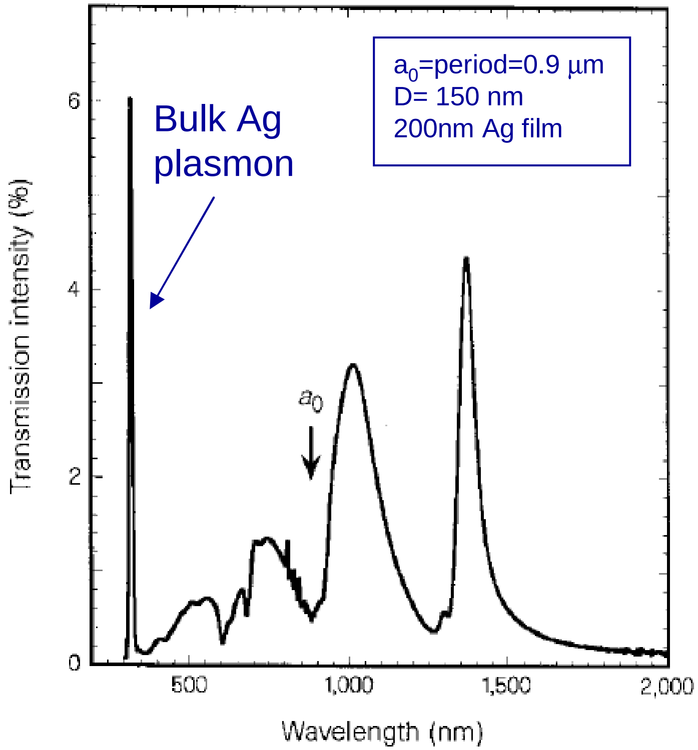
$$T \propto \left(\frac{d}{\lambda}\right)^4$$

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

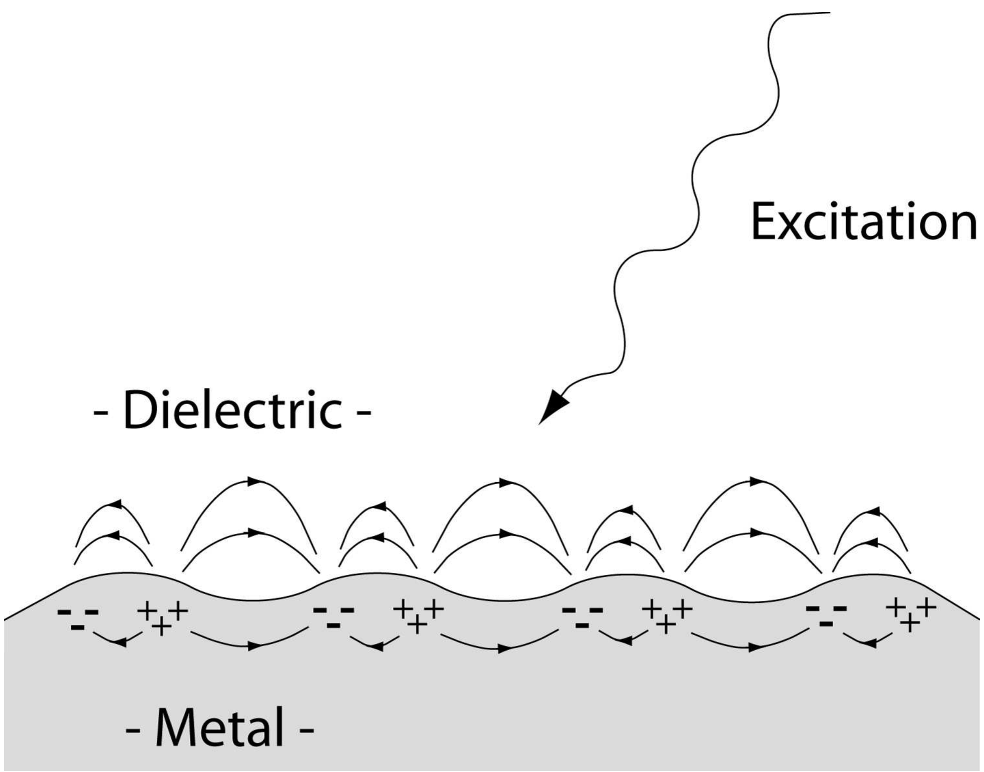
• 1998: Thomas Ebbesen et al., "Extraordinary optical transmission through sub-wavelength hole arrays" *Nature* **391**:

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

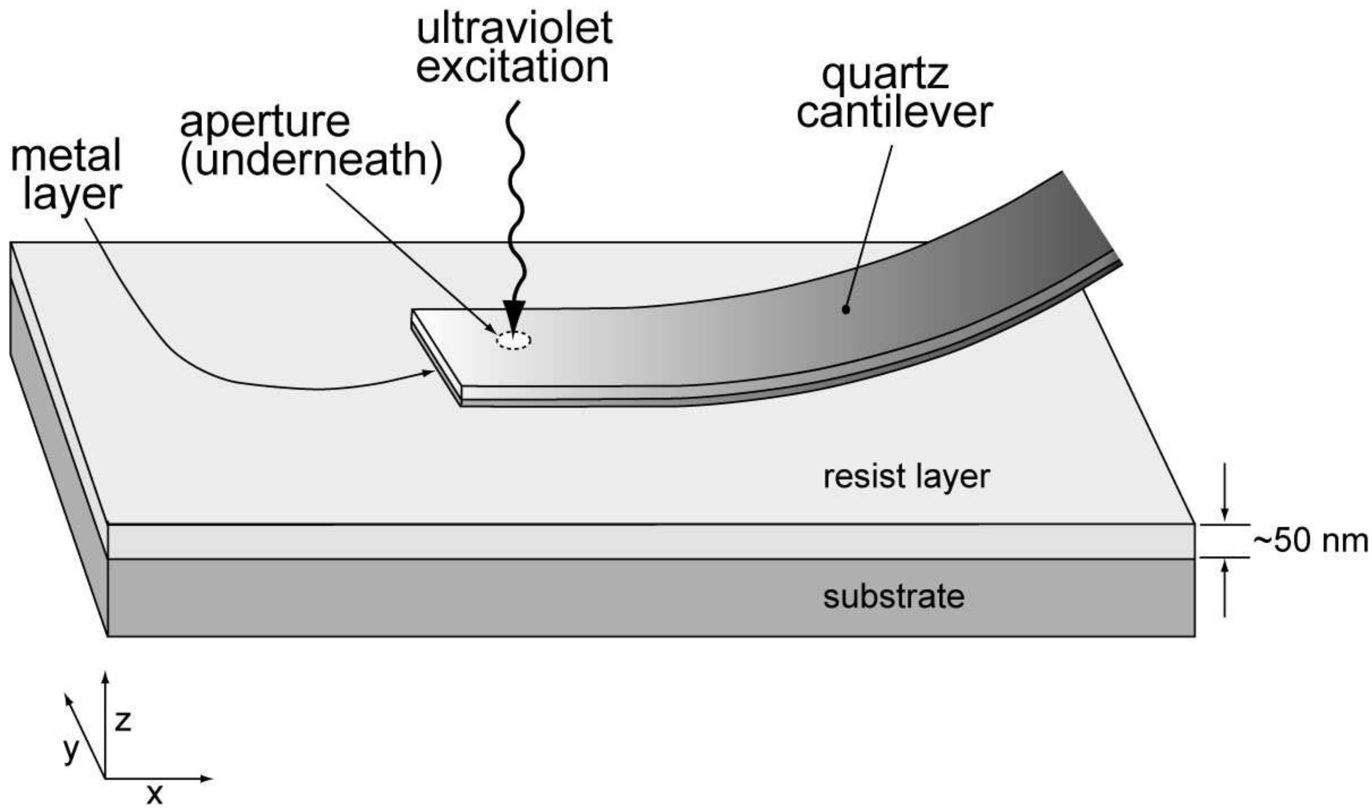
→ T *many* orders of magnitude higher than expected



Interaction of photon with surface plasmon

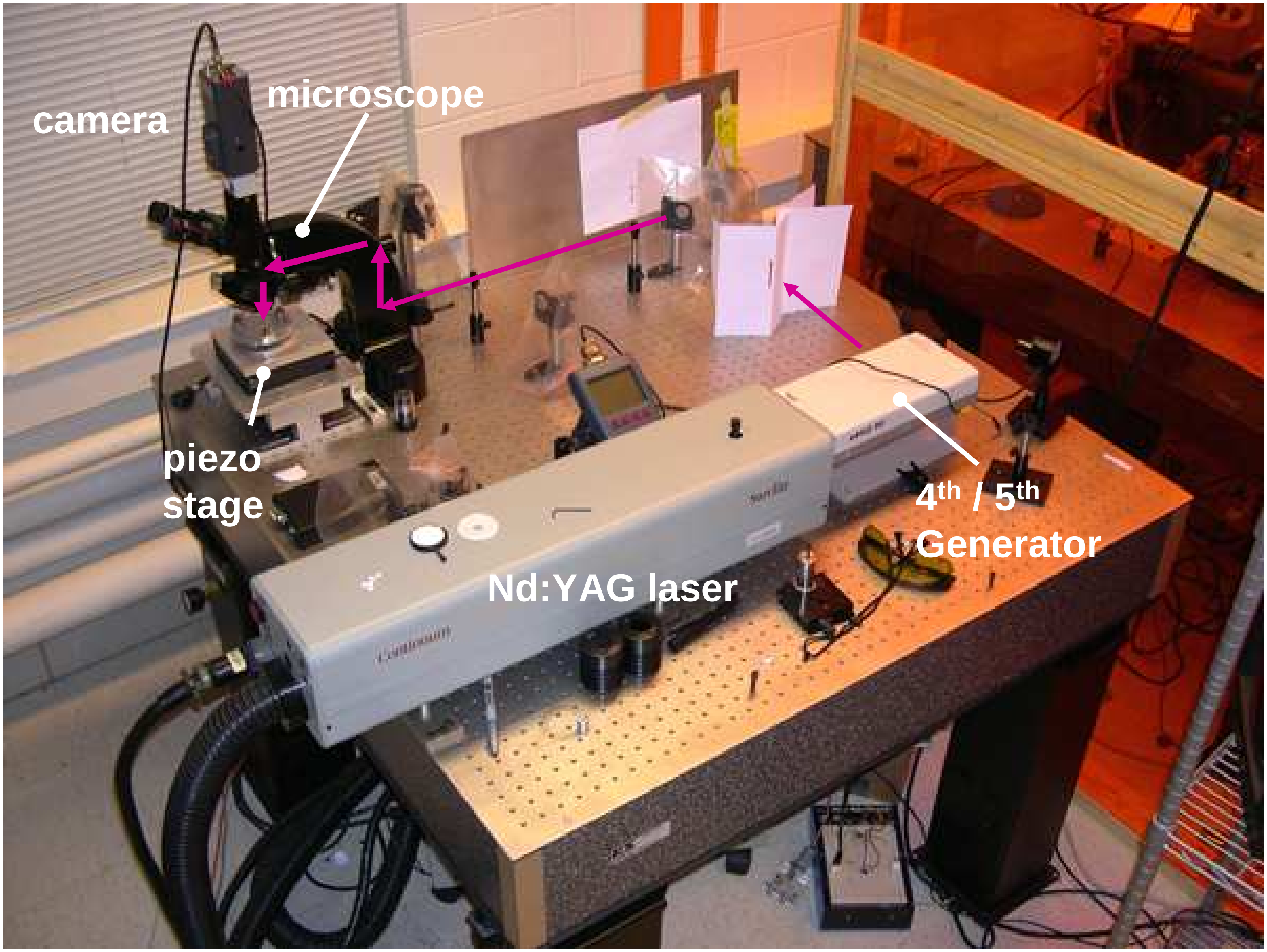


New lithographic Tools: Near field ultraviolet photolithography



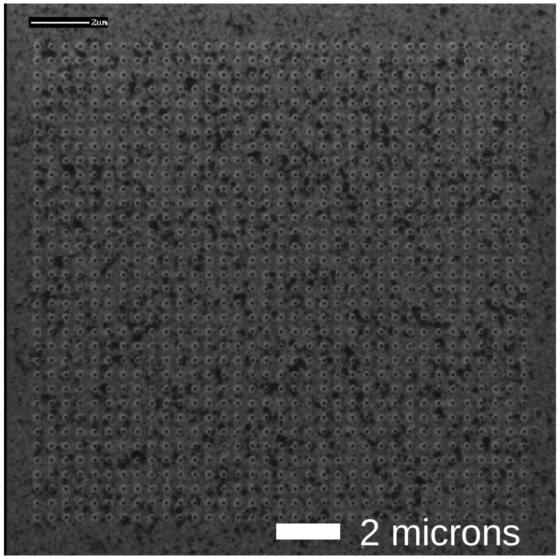
- akin to contact print photolithography but with direct write, scanning aperture
- transmission enhancement through near-field aperture
- resolution: PMMA can be spun to ~few nm (thinner than photoresist)

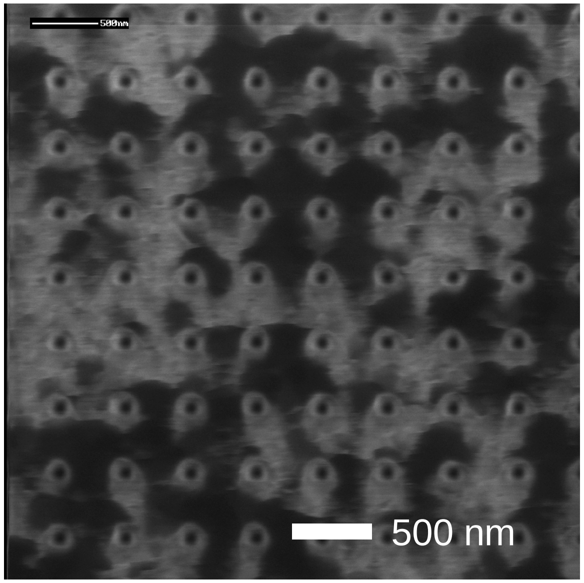
New lithographic Tools: Near field ultraviolet photolithography

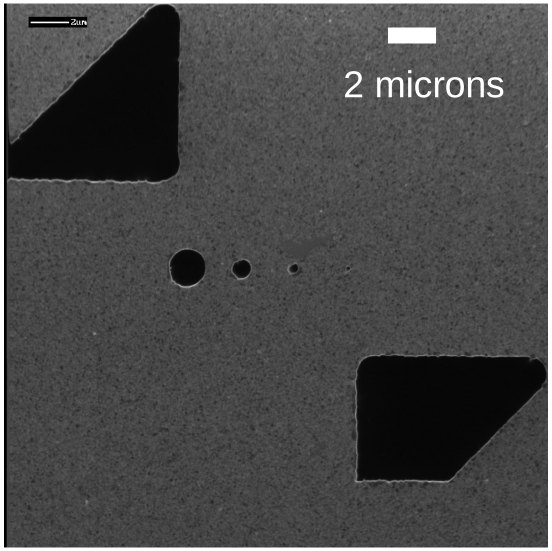


New lithographic Tools: Near field ultraviolet photolithography

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







Fab work: Andrew Spisak
Lithography: Brian Burke

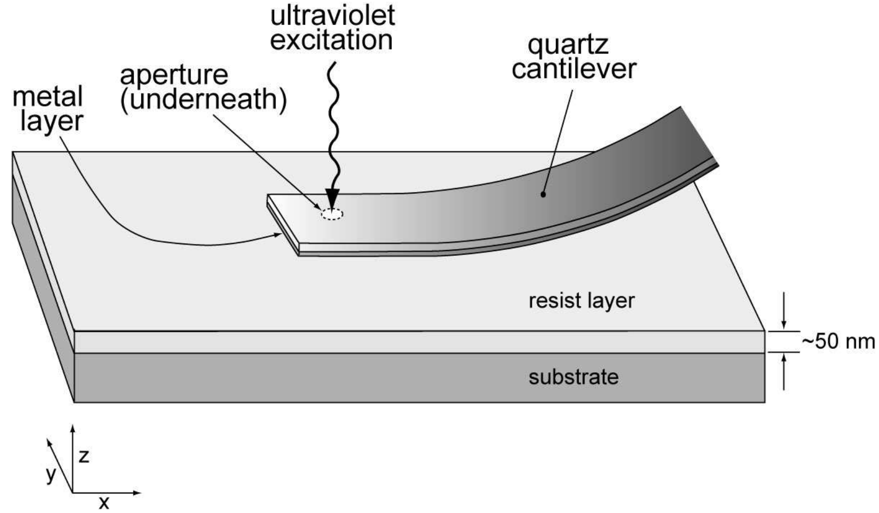
Anticipated benefits:

• 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

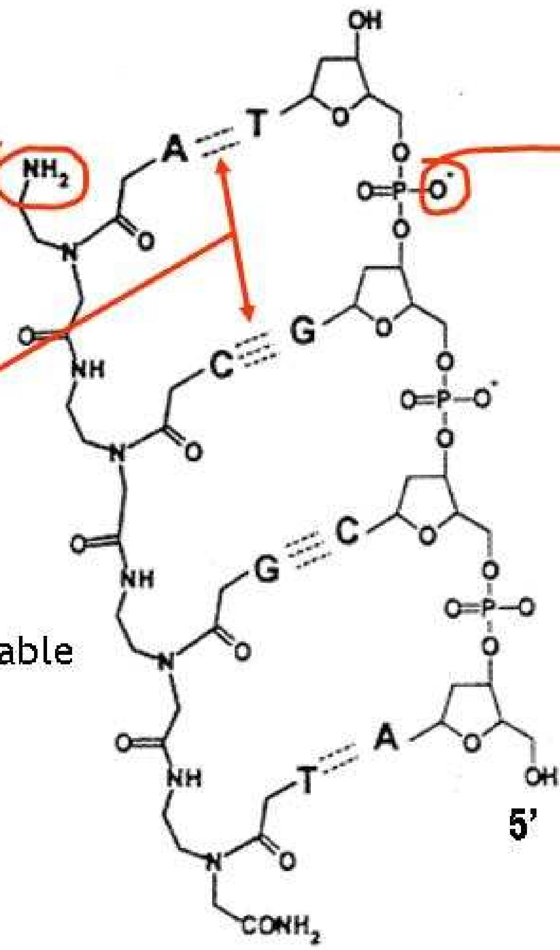
A dreams of the future: conductive wires with Watson-Crick hybridization?

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 ~1^{o}C per base pair, on average

*Solubility can be sequence dependent



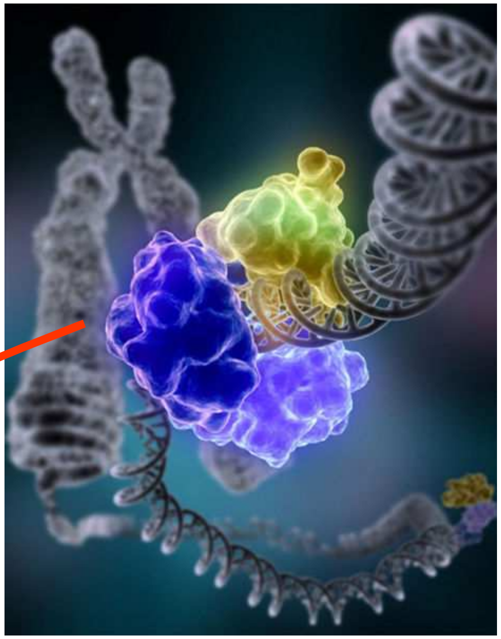
PNA-DNA Duplex
(Nielsen and Haaima, 1997)

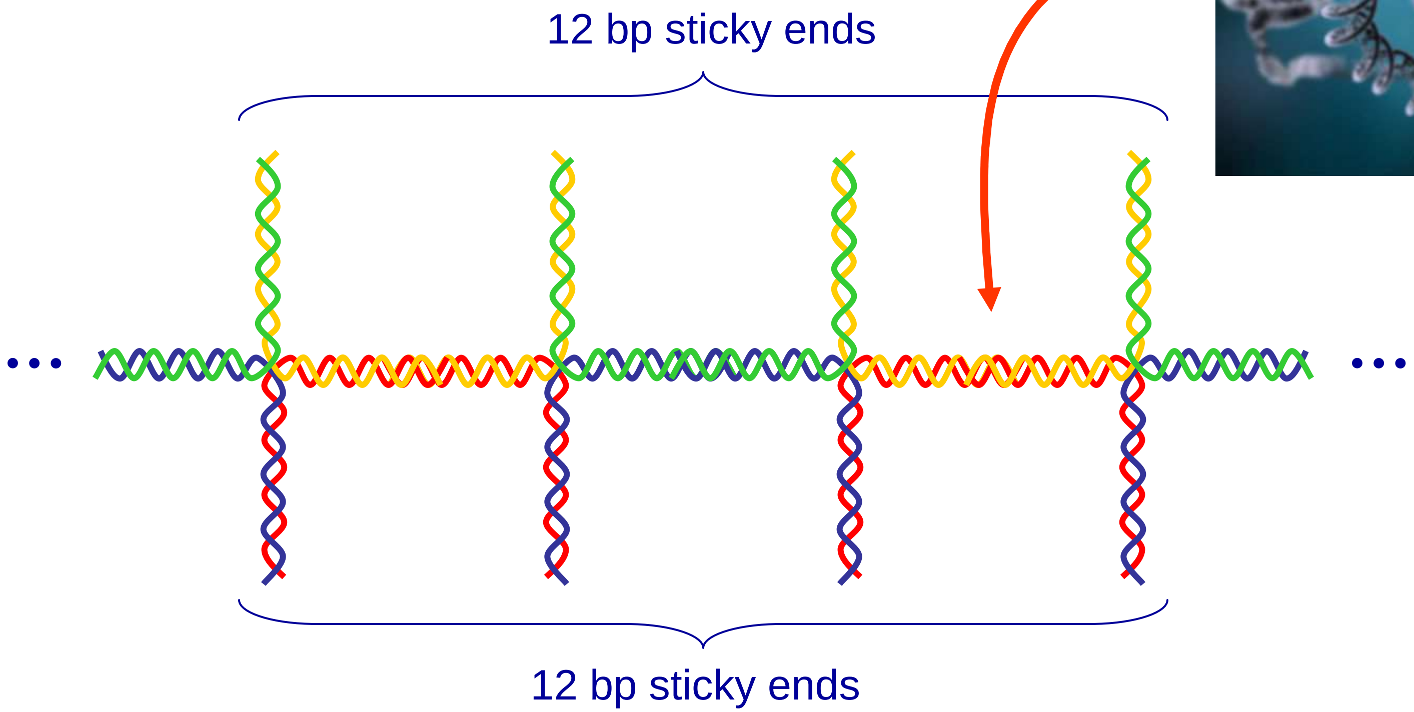
DNA properties

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

Development of conjugated backbone?

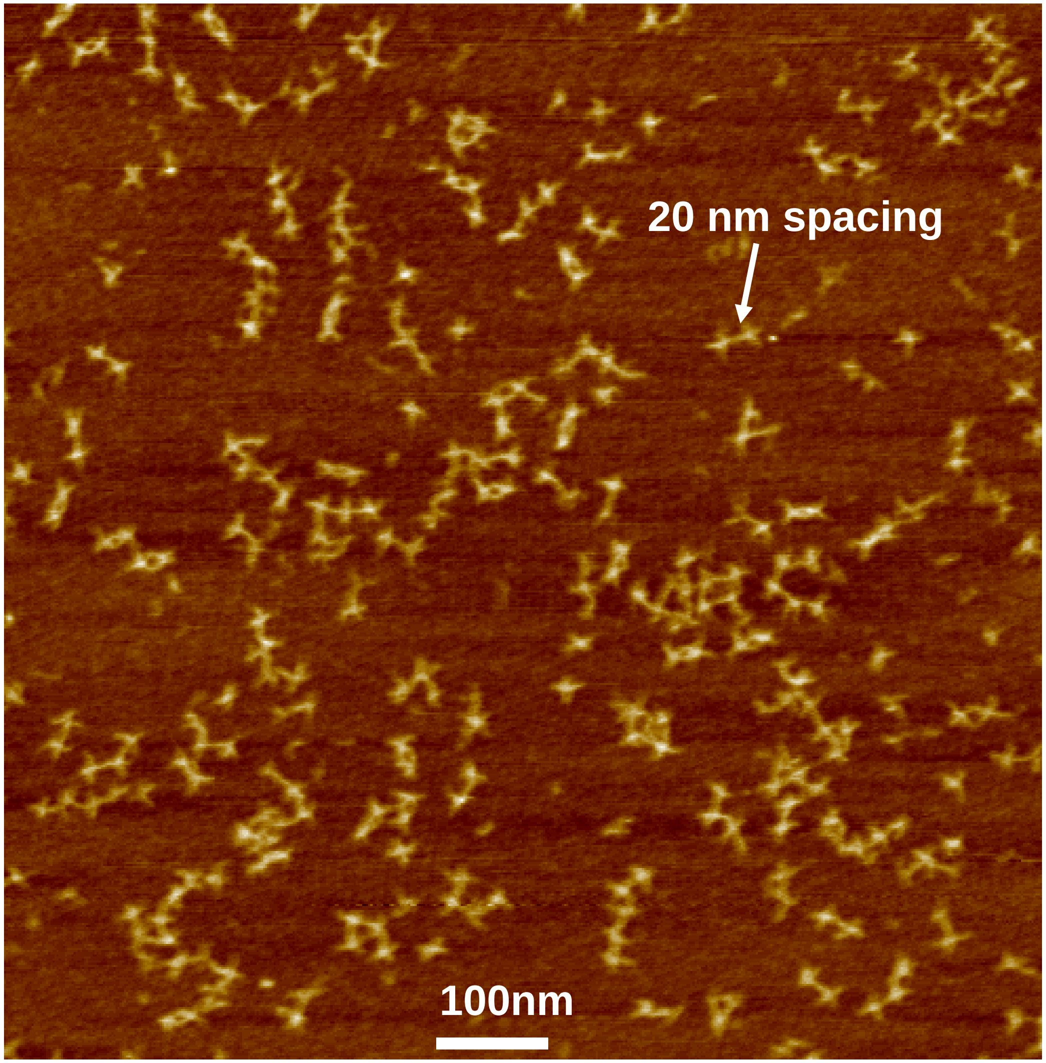
DNA junction scaffolds designed by sequence and assembled by ligase:





Ligase model: Tom Ellenberger,
Washington University School of Medicine

~nm position control in DNA, and limitless structural coding…



Manuscript in prep.

Molecular Electronics- Past, Present & Future

I. Goals
II. History & Recent Events
III. Survey of (our) Current Strategies
IV. Summary of Challenges

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

V. Education

Keith Williams
kwilliams@virginia.edu
9 February 2007

Molecular Electronics- Past, Present & Future

I. Goals
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V. Education

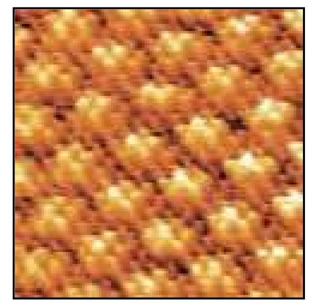
- RET
- SMV
- NUE

Keith Williams
kwilliams@virginia.edu
9 February 2007

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

Nanoscience EasyScan© table top STM



TaS_2, 5.4 nm scan

- 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