united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 35

SPRING COLLEGE ON SCIENCE AT THE NANOSCALE
(24 May - 11 June 2004)

SEMICONDUCTORS; DEVICES

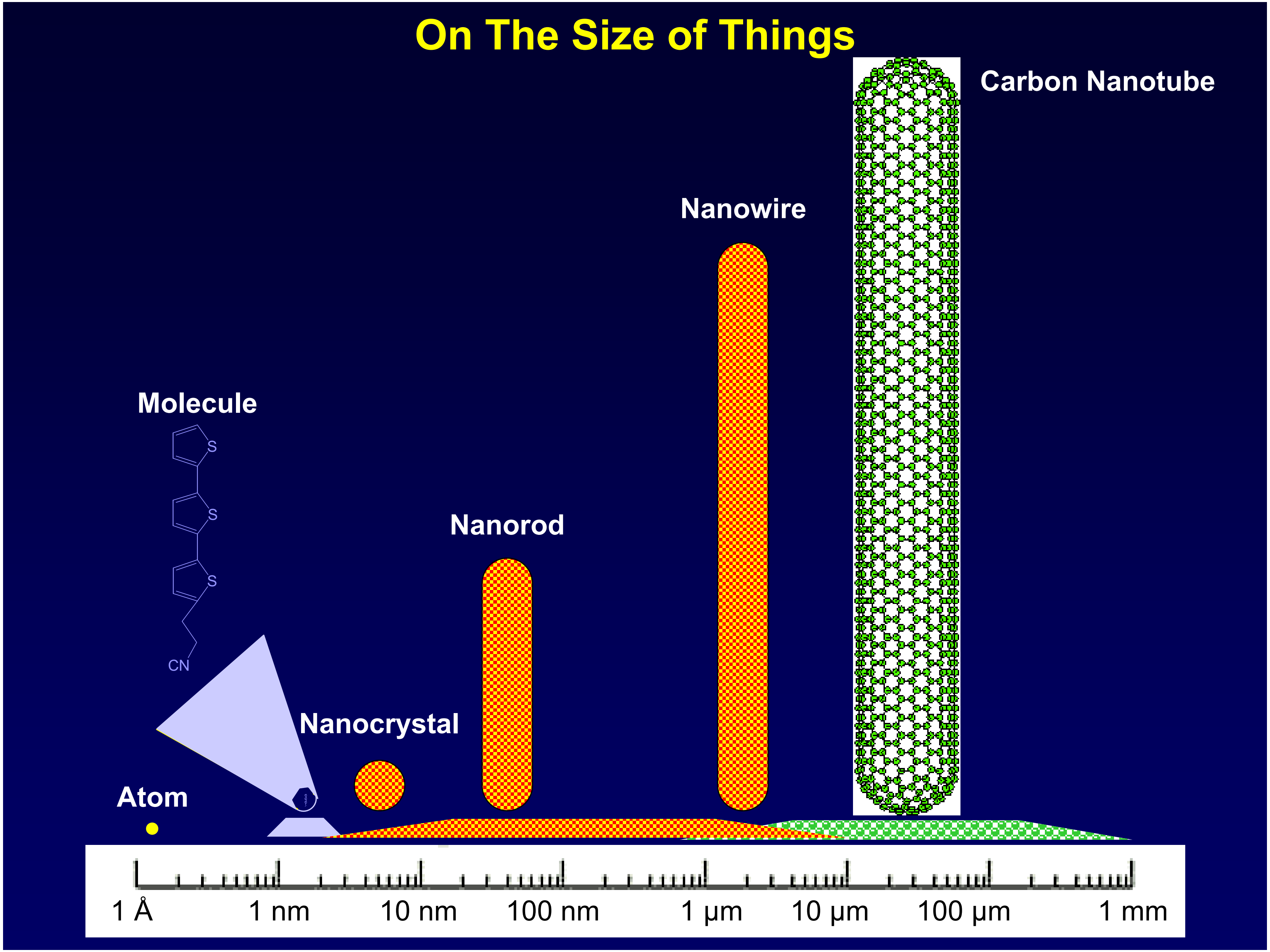
Cherie R. KAGAN
I.B.M. Thomas J. Watson Research Centre
Yorktown Heights, NY, U.S.A.

These are preliminary lecture notes, intended only for distribution to participants.

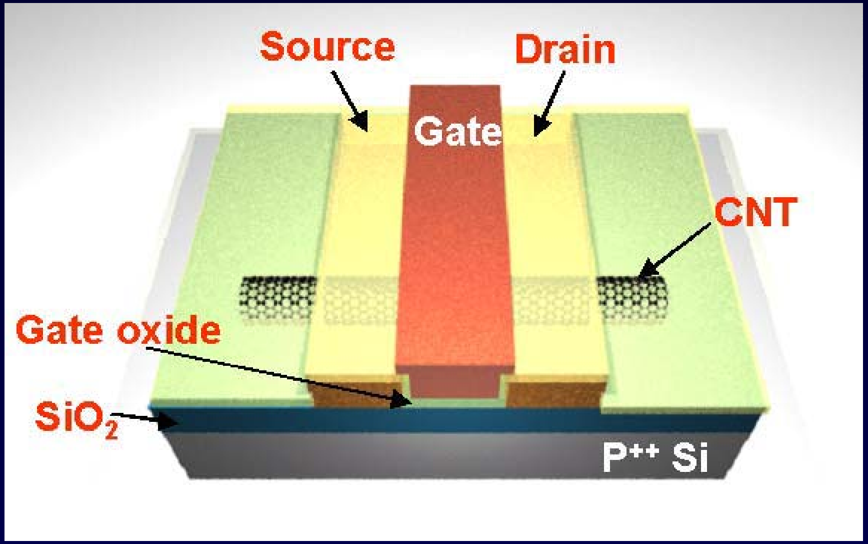
Making Electrical Contact to Molecules

Cherie R. Kagan

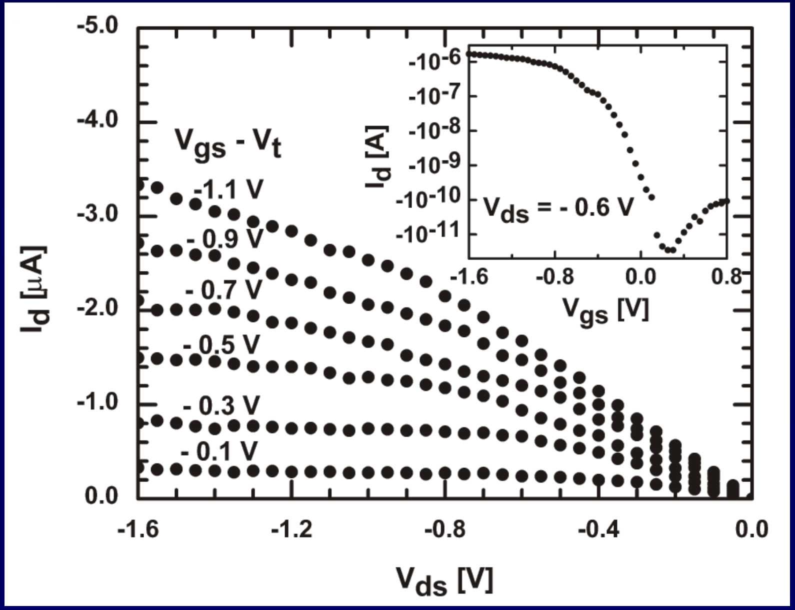
IBM T. J. Watson Research Center
Yorktown Heights, NY


On The Size of Things
Carbon Nanotube
Nanowire
Molecule
S
S
S
CN
Nanorod
Nanocrystal
Atom
1 Å
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm

Carbon Nanotube Transistor



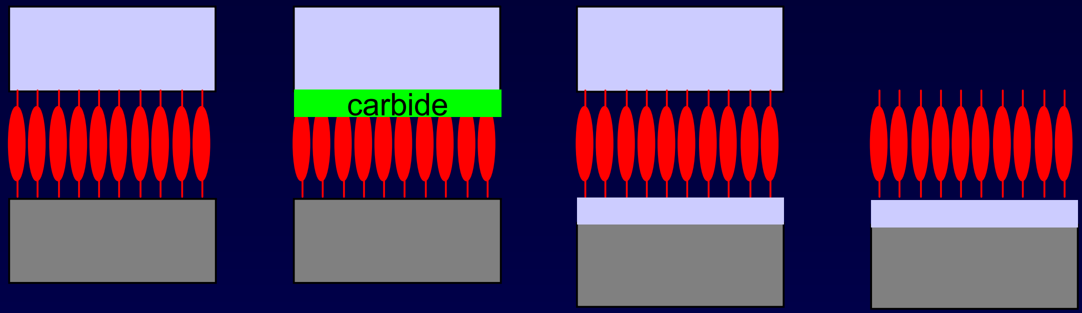
- Channel Length is 300 nm
- Oxide fabricated on top of CNT



S.J. Wind, J. Appenzeller, R. Martel, and Ph. Avouris, *Appl. Phys. Lett*. **80** 3817 (2002).

Challenges in Fabricating Molecular Junctions
Vertical Structures

Local Challenges

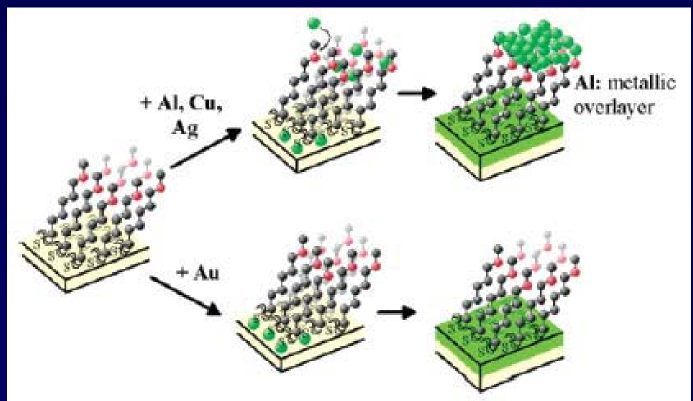


Idealized Structure

Reactive Metal
(Ti)

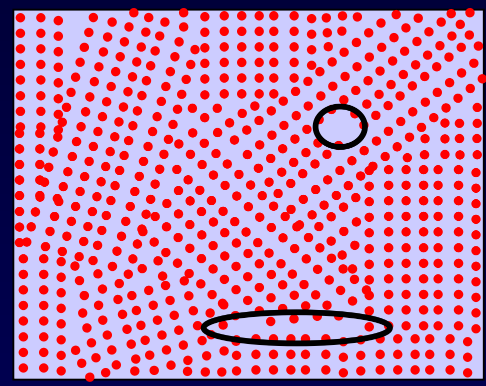
Middle of the
road Metal
Al, Cu, Ag

Unreactive Metal
(Au)



A. V. Walker, T. B. Tighe, O. M. Cabarcos, M. D. Reinard, B. C. Haynie, S. Uppili, N. Winograd, D. L. Allara, *J. Am. Chem. Soc.* **126**, 3954 (2004).

Global Challenges



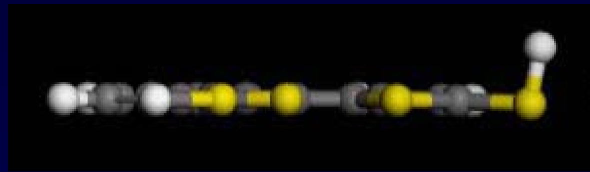
Metal penetration through defects in monolayers

- domain boundaries
- voids

Challenges in Fabricating Molecular Junctions: Lateral Geometry

α-terthiophene thiol

rotated



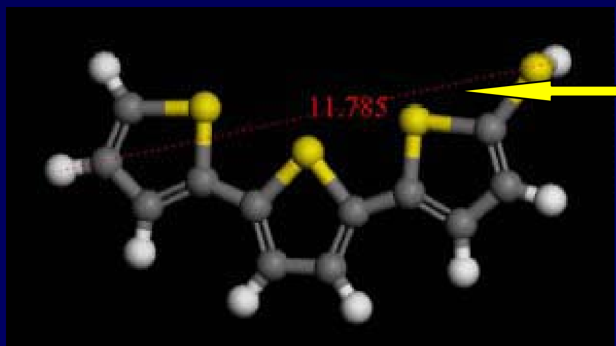
molecule's planarity provides:

good π-overlap, conductivity

rigidity, reducing solubility

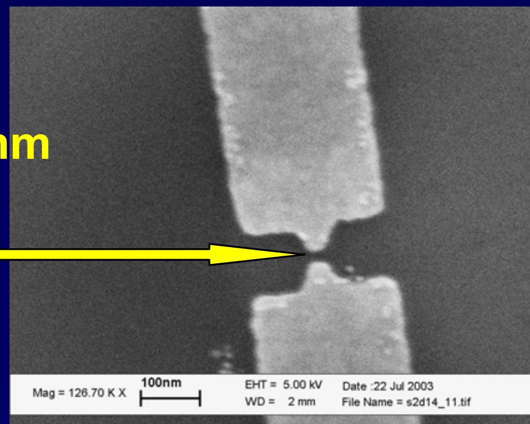
distance

Limits length of molecule



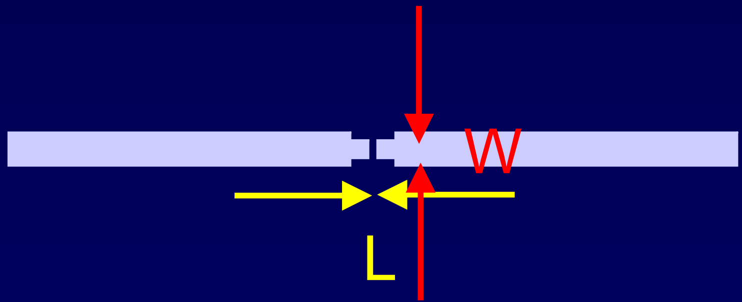
~1.2 nm

~17 nm



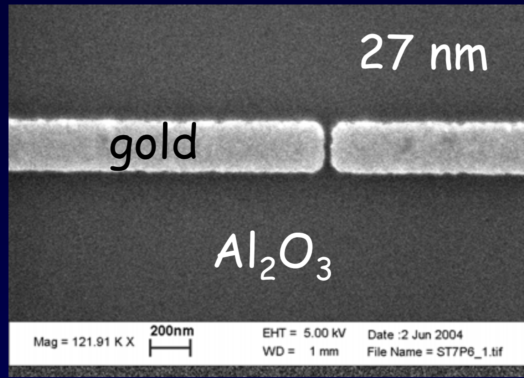
Limitations of e-beam Lithography

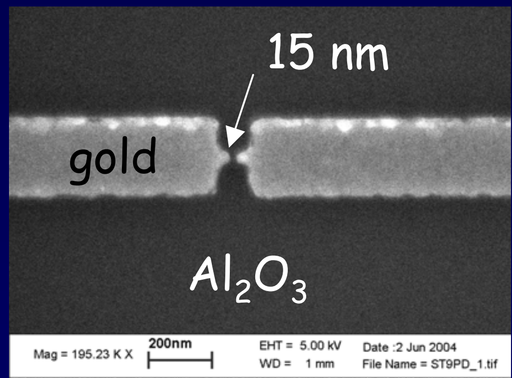
Design



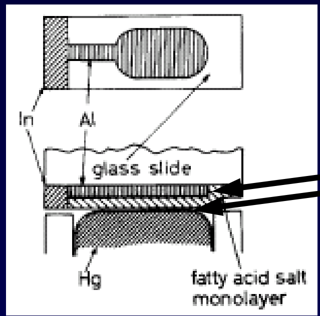
As L is narrowed, W must be reduced to achieve lift-off

Product

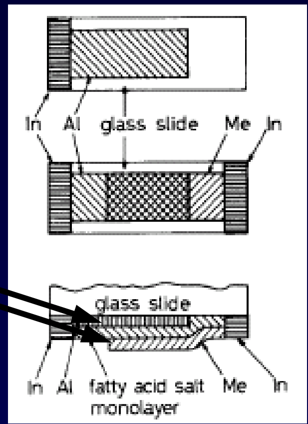




First Examples of Transport Measurements in Molecular Junctions
Kuhn – 1971
Tunneling through Fatty Acids



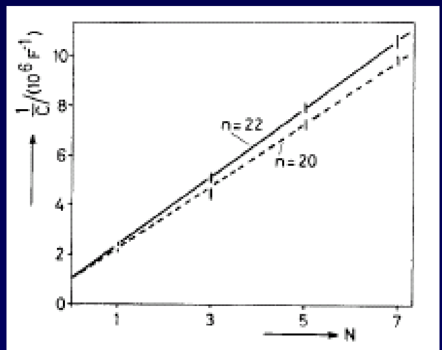
native oxide layer



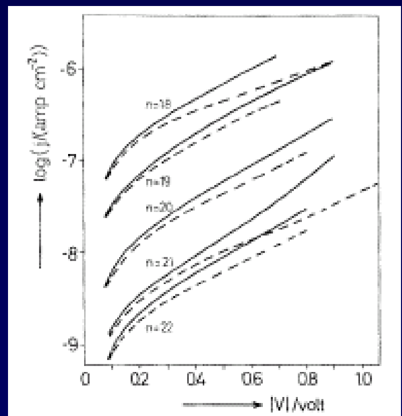
Fatty acids: $CH_3(CH_2)_nCOOH$

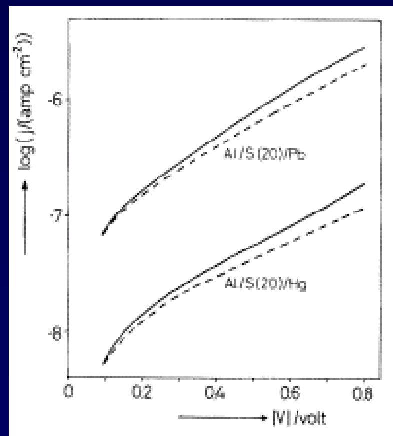
Metal Salts, example: $[CH_3(CH_2)_nCOOH]_2Cd$

Metal: Pb, Al, Ag, Au



$$1/C=(\epsilon_0 F)^{-1}(d_{ox}/\epsilon_{ox}+Nd/\epsilon)$$





$$\sigma_t=(e^2/h^2)(2m\varphi)^{1/2}\exp[-(2d/\hbar)(2m\varphi)^{1/2}]$$

(for small voltages V),

$$\sigma_t=(e^3V/8\pi h\varphi d)\exp[-(4d/3eV\hbar)(2m\varphi^3)^{1/2}]$$

(for large voltages V),

Note: For Ag, Au comment on care not to overheat monolayer during evaporation

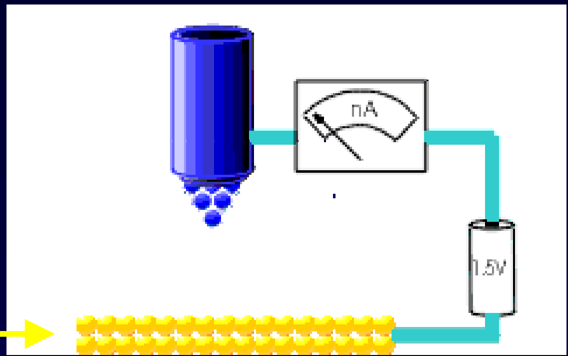
B. Mann, H, Kuhn, *J. Appl. Phys.* **42**, 4398 (1971).

Scanning Tunneling Microscopy of Molecluar Assemblies

Map density of states

Not measure of molecular conductance

Metal

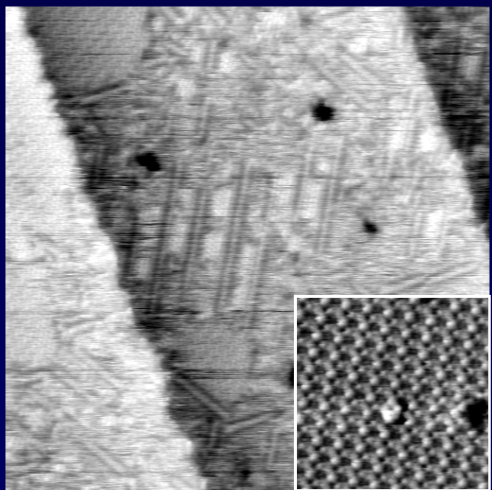


$d_{tip\text{-}sample} \leq 10$ Å

$$I \propto \exp\left(\frac{2\sqrt{2m\Phi\hbar}}{d}\right)$$

Ordered versus Dis-ordered Assembly

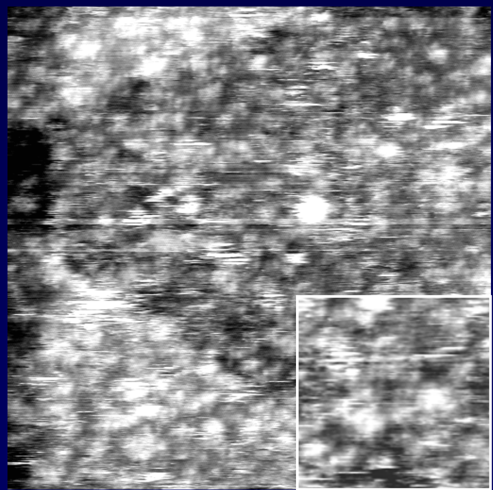
hexanethiol



10 nm

50 nm

1,1'-biphenyl-4,4'-dithiol



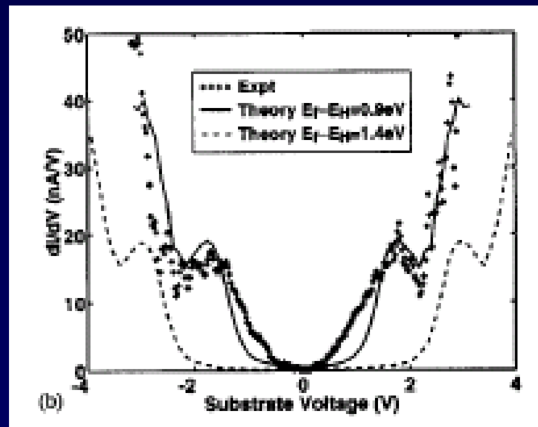
5 nm

60 nm

C. R. Kagan, A. Afzali, R. Martel, L. M. Gignac, P. M. Solomon, A. G. Schrott, B. Ek, *Nano Letters*, **3**, 119 (2003).

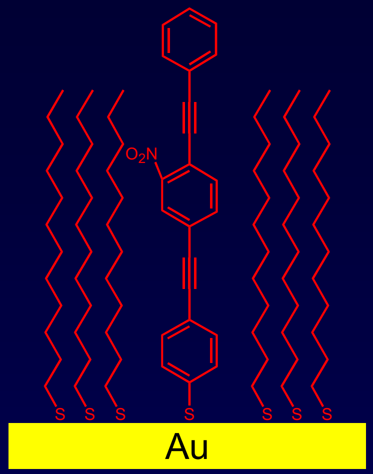
Spectroscopy

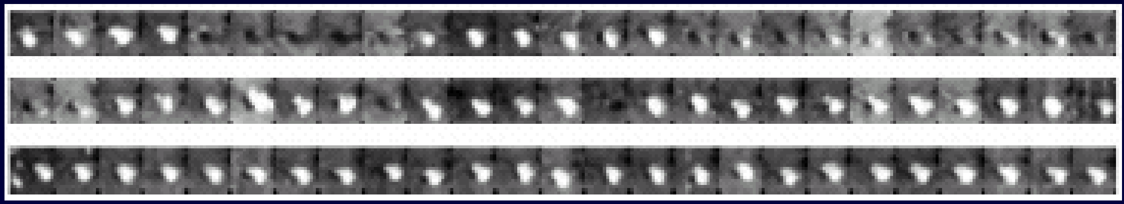
α,α'-xylyl dithiol



W. Tian, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, C. P. Kubiak, *J. Chem. Phys.* **109,** 2874 (1998).

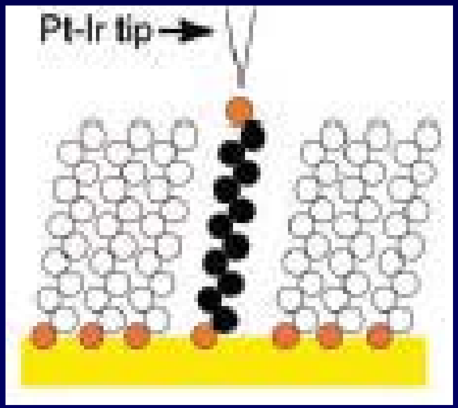
Scanning Tunneling Microscopy: Stochastic Switching in Assembled Molecules

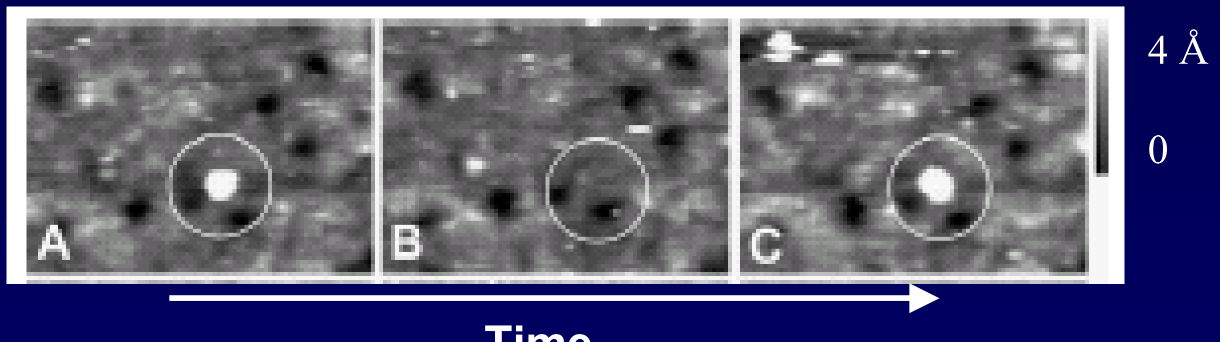




Time interval between frames 6 min.

Z. J. Donhauser, B. A. Mantooth, K. F. Kelly, L. A. Bumm, J. D. Monnell, J. J. Stapleton, D. W. Price Jr., A. M. Rawlett, D. L. Allara, J. M. Tour, P. S. Weiss, *Science* **292**, 2303 (2001).

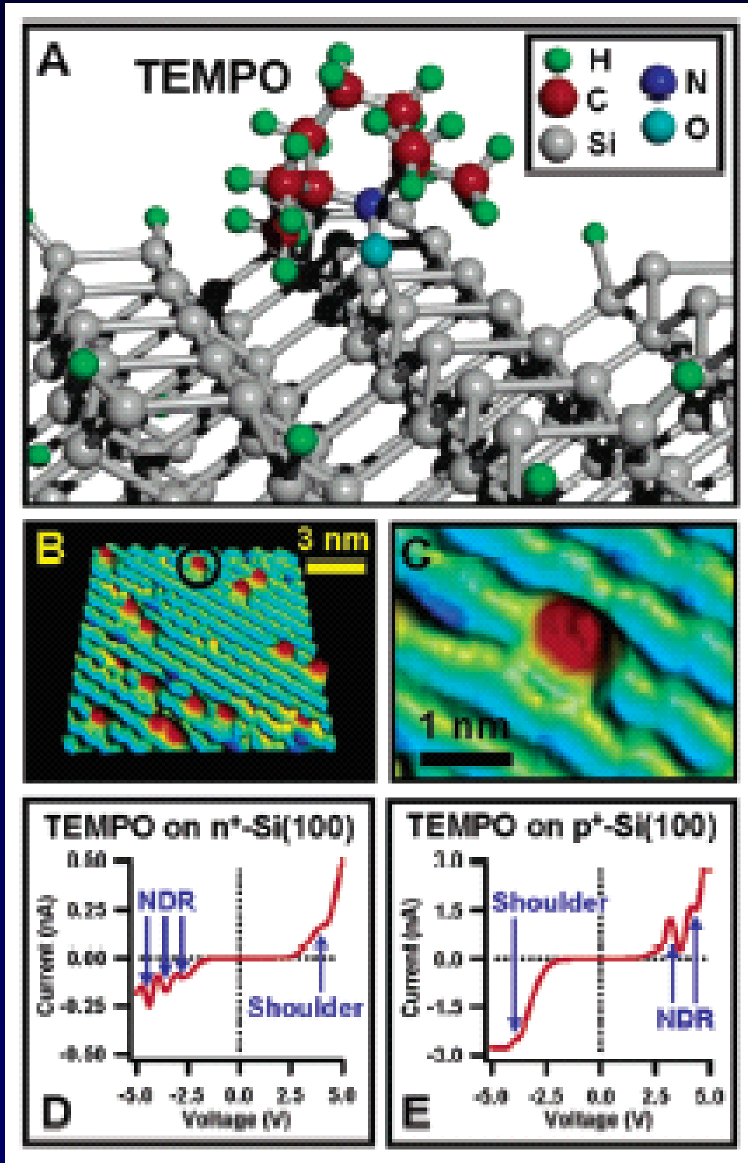




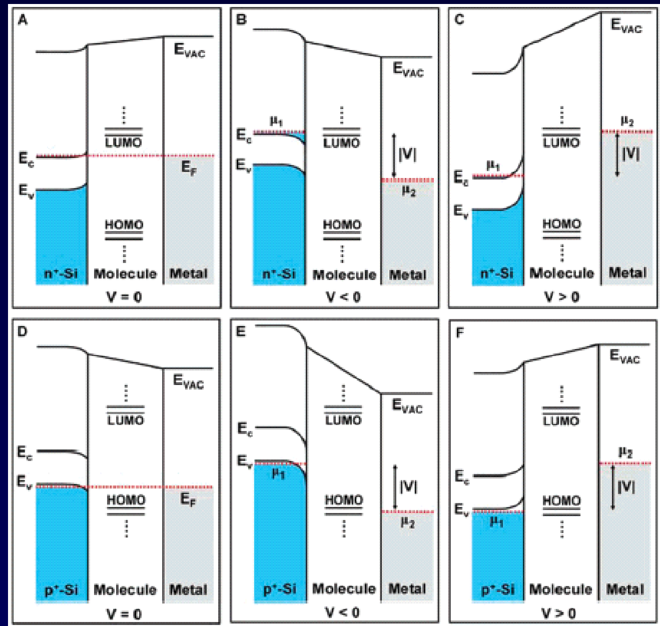
G. K. Ramachandran, T. J. Hopson, A. M. Rawlett, L. A. Nagahara, A. Primak, S. M. Lindsay, *Science* **300**, 1413 (2003).

Stochastic switching – arise from Au-S bond breaking?

STM Measurements of Molecules on Si

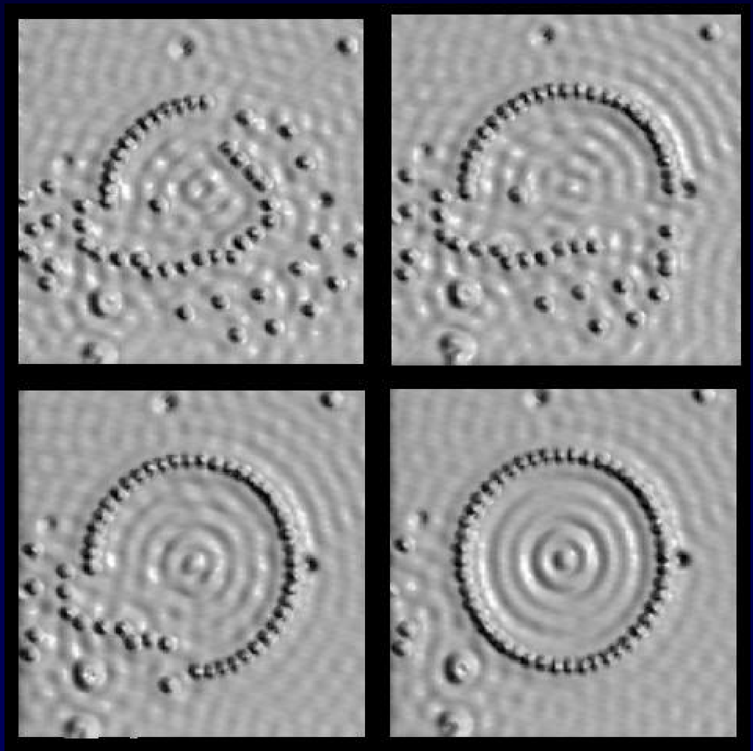


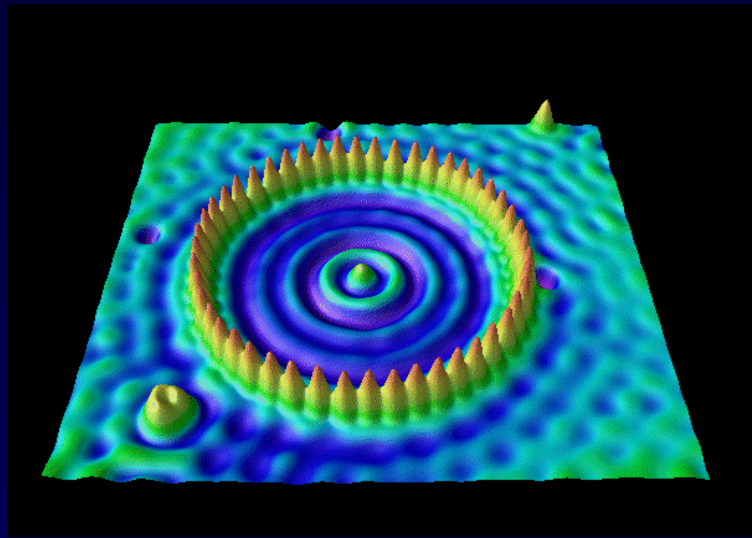
- NDR when molecular levels cross Si band edge
- Shoulder whne molecular levels cross metal Fermi level



N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, M. C. Hersam, *Nano Lett.* **4**, 55 (2004).

Scanning Tunneling Microscopy of Atoms

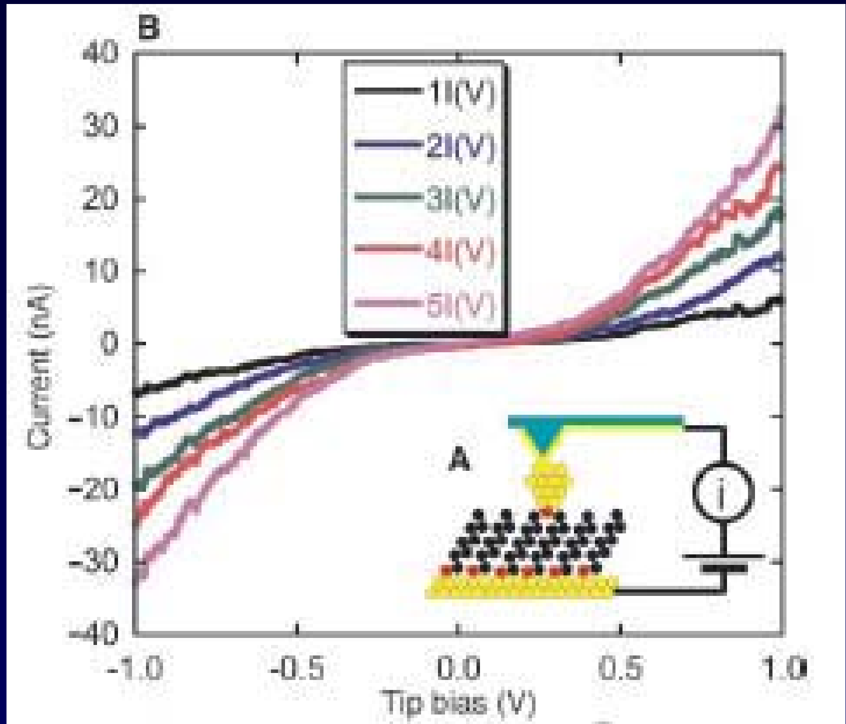




Fe adatoms on Cu (111)

M.F. Crommie, C.P. Lutz, D.M. Eigler. *Science* **262**, 218-220 (1993).

Conductive Probe AFM

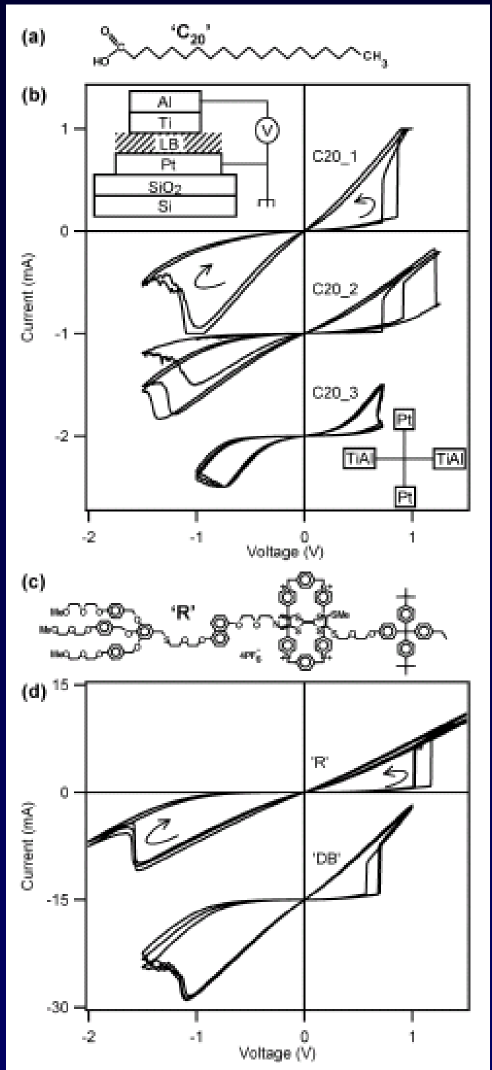


Two-physical contacts allows measurements of conductance

Metal nanocrystal makes "better" contact through covalent bond to S atom on molecule
and
provides more reliable contact as it is not as dependent on applied force

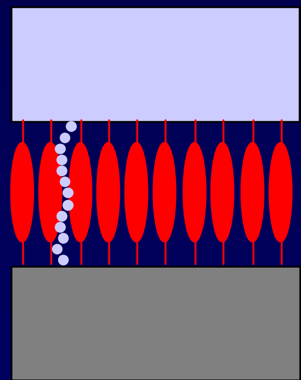
X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, S. M. Lindsay, *Science* **294**, 571 (2001).

Metal-Molecule-Metal Sandwiches/Crossbars



I-V characteristics are independent of the molecular chemistry

Metal filament formation?
Known to give similar characteristics even in thin organic and oxide films for ~40 years

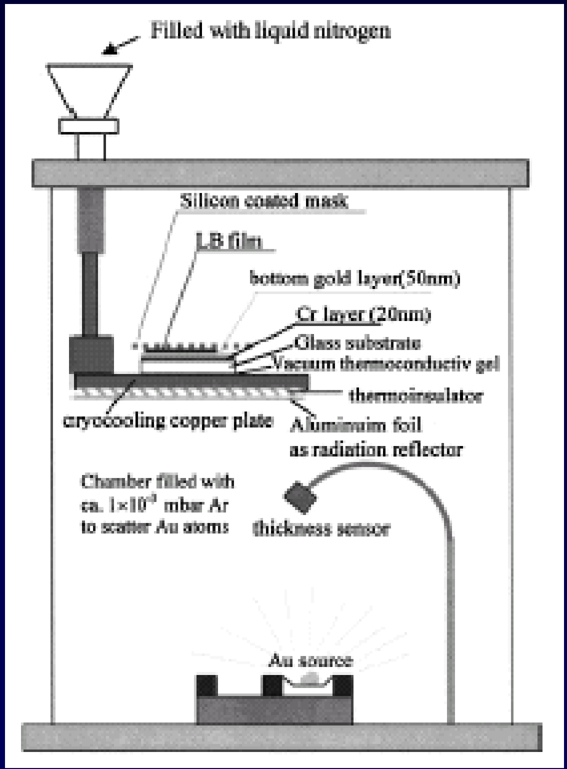


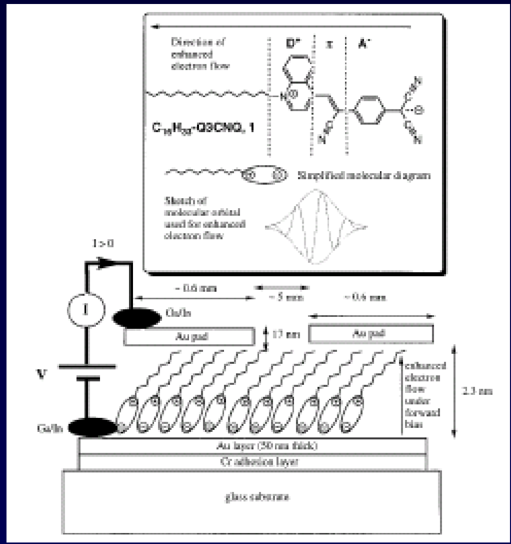
D. R. Stewart, D. A. A. Ohlberg, P. A. Beck, Y. Chen, and R. Stanley Williams, J. O. Jeppesen, K. A. Nielsen, J. Fraser Stoddart, *Nano Lett.* **4**, 133 (2004).

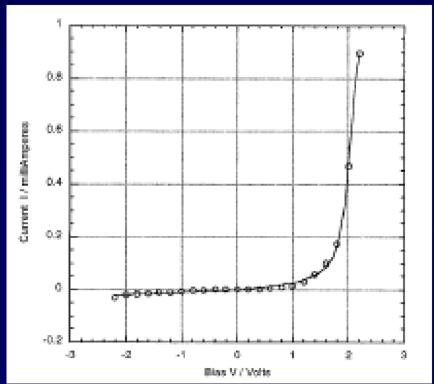
Cold-Gold Evaporation:
Metal-Molecule-Metal Rectifying Junctions

Langmuir-Blodgett monolayer of

hexadecylquinolinium tricyanoquinodimethanide

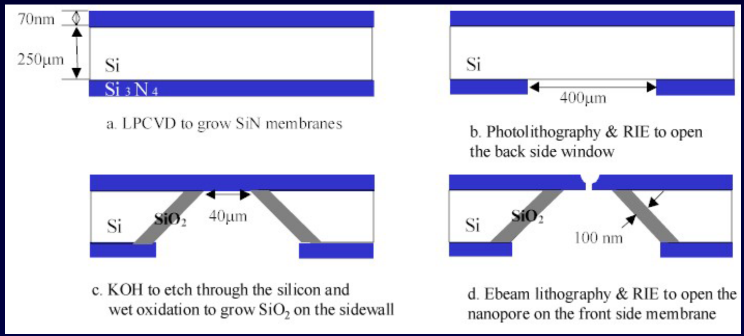




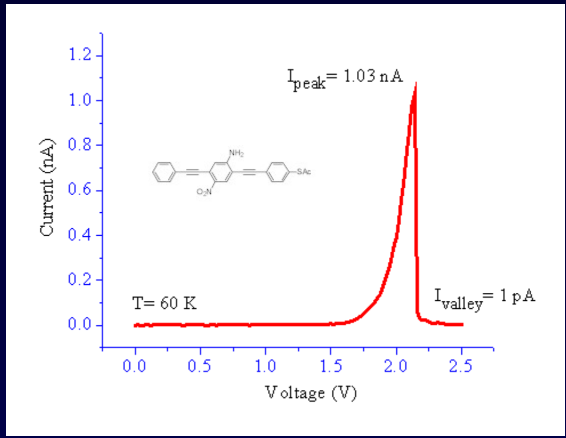


R. M. Metzger, T. Xu, I. R. Peterson, *J. Chem. Phys. B* **105,** 7280 (2001).

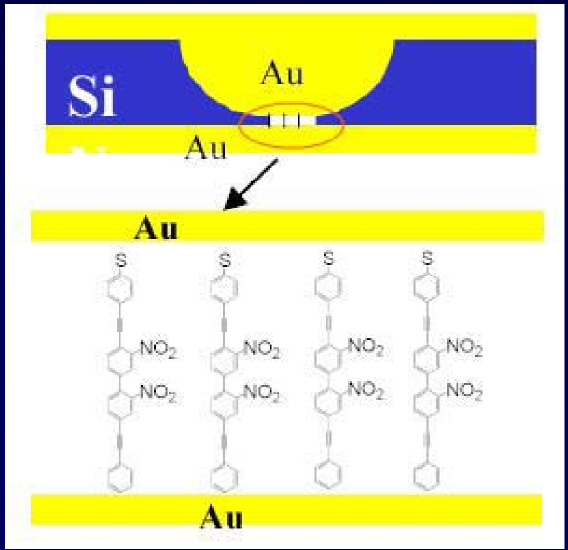
Nanopore Geometry

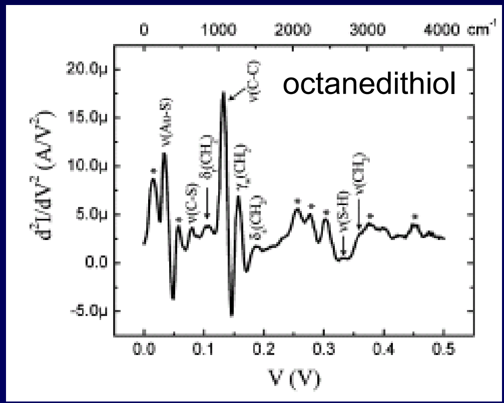


M. A. Reed, Yale University



J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **286**, 1550 (1999).



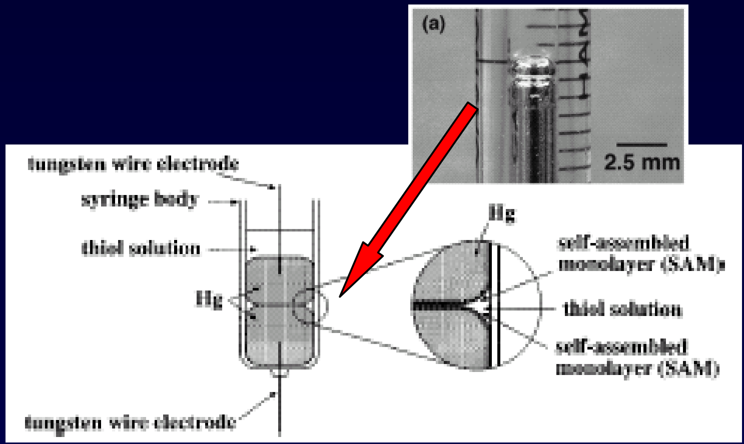


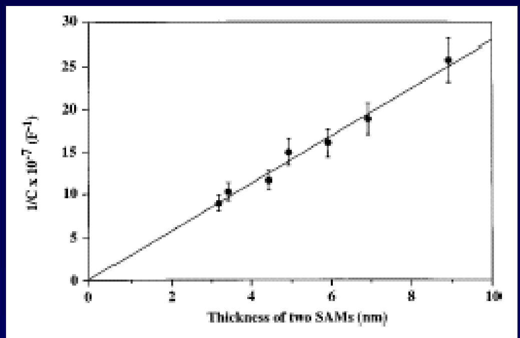
W. Wang, T. Lee, I. Kretzschmar, M. A. Reed, *Nano Lett.* **4**, 634 (2004).

Decrease probed area to small ~ 30 nm dimension to reduce the probability of defects

Using Hg as an Electrode

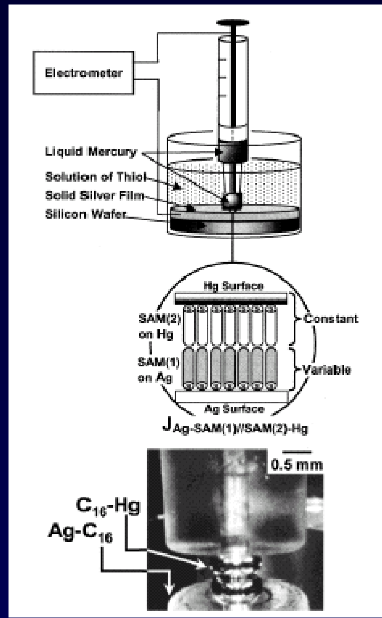
Hg-SAM/SAM-Hg Junctions

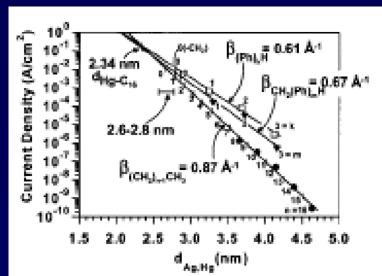




M. A. Rampi, O. J. A. Schueller, G. M. Whitesides, *App. Phys. Lett.* **72**, 7281 (1998).

Hg-SAM/SAM-Au or Ag Junctions





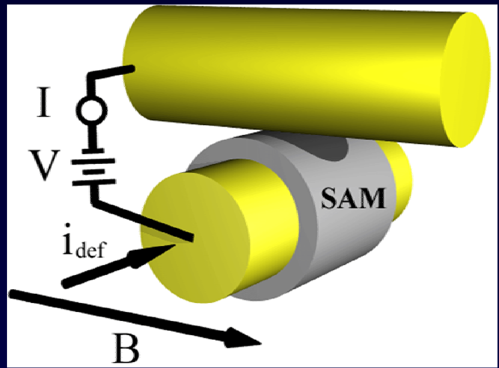
$$I \cong I_0[e^{-\beta(1)d_{SAM(1)}}][e^{-\beta(2)d_{SAM(2)}}]$$

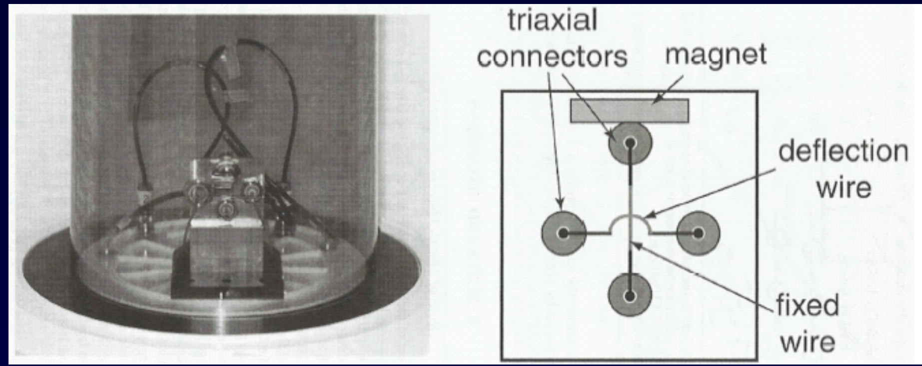
$$I \cong I_0 \gamma e^{-\beta(1)d_{SAM(1)}} \quad (3)$$

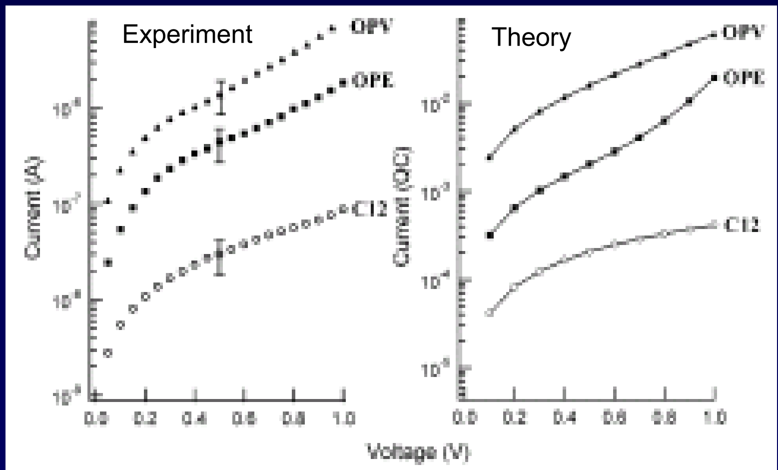
R. E, Holmlin, R. Haag, M. L. Chabinyc, R. F. Ismagilov, A. E. Cohen, A. Terfort, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* **123**, 5075 (2001).

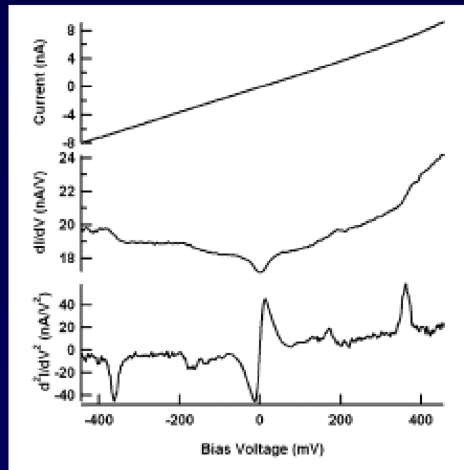
Crossed-Wire Junctions

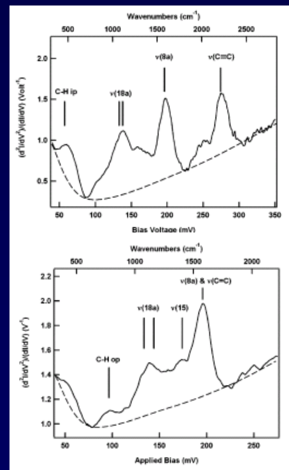
Lorenz Force deflection









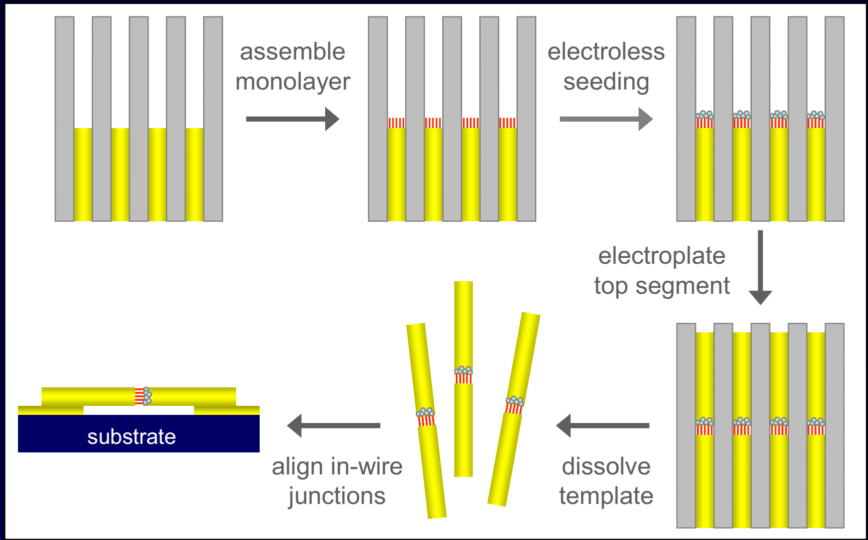


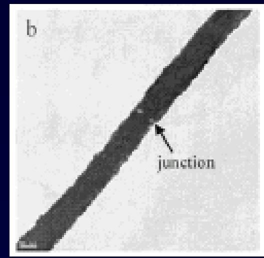
I-V characteristics

Inelastic Tunneling Spectroscopy

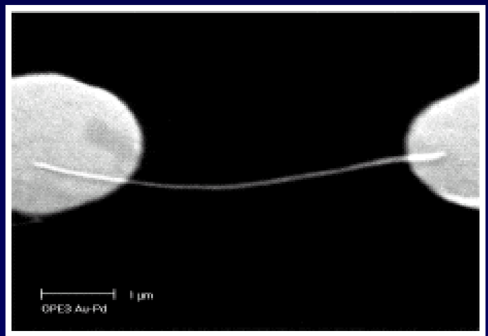
S. Gregory, *Phys. Rev. Lett.* **64**, 689 (1990).
J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, J. C. Yang, T. L. Schull, J. Naciri, M. H. Moore, R. Shashidhar, *J. Am. Chem. Soc.* **124**, 10654 (2002).
J. G. Kushmerick, J. Lazorcik, C. H. Patterson, R. Shashidhar, D. S. seferos, G. C. Bazan, *Nano Lett.* **4** , 639 (2004).

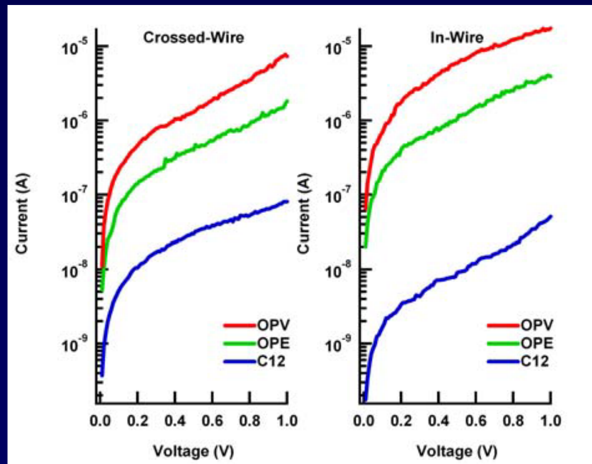
In-wire Junctions





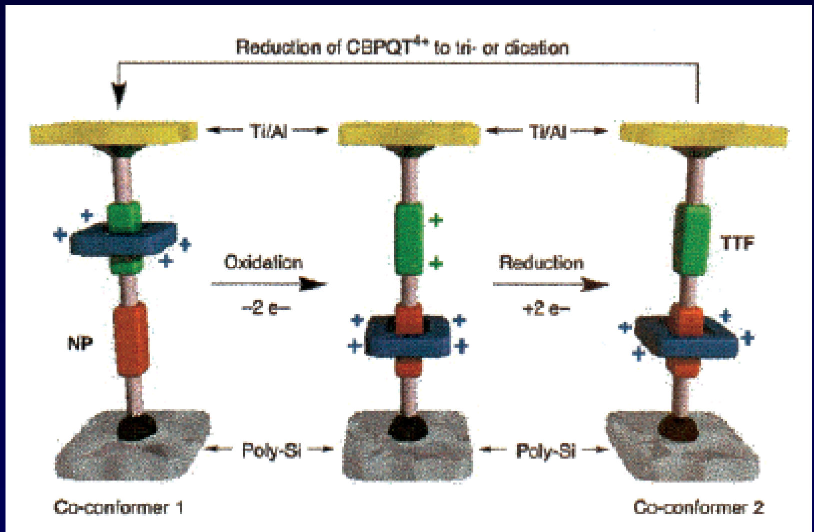
J. K. N. Mbindyo,T. E. Mallouk, J. B. Mattzela, I. Kratochvilova, B. Razavi, T. N. Jackson, T. S. Mayer, *J. Am. Chem. Soc.*, **124**, 4020 (2002).

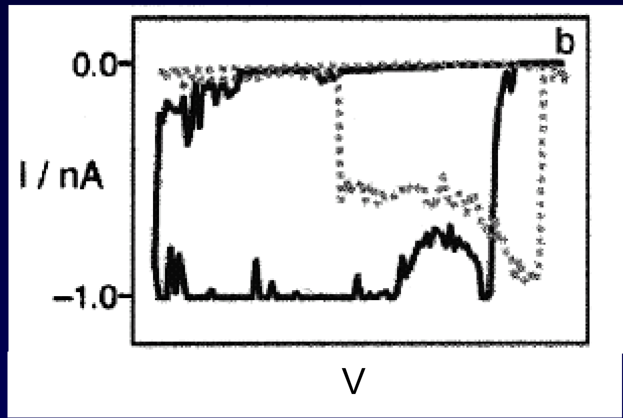




L. T. Cai, H. Skulason, J. G. Kushmerick, S. K. Pollack, J. Naciri, R. Shashidhar, D. L. Allara, T. E. Mallouk, T. S. Mayer, *J. Phys.Chem. B* **108**, 2827 (2004). J. G.Kushmerick, D. L. Allara, T. E. Mallouk, T. S. Mayer, *MRS Bulletin*, June (2004).

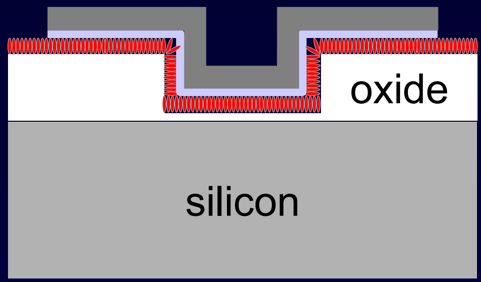
Metal-Molecule-Semiconductor Junction





C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **123**, 12632 (2001).

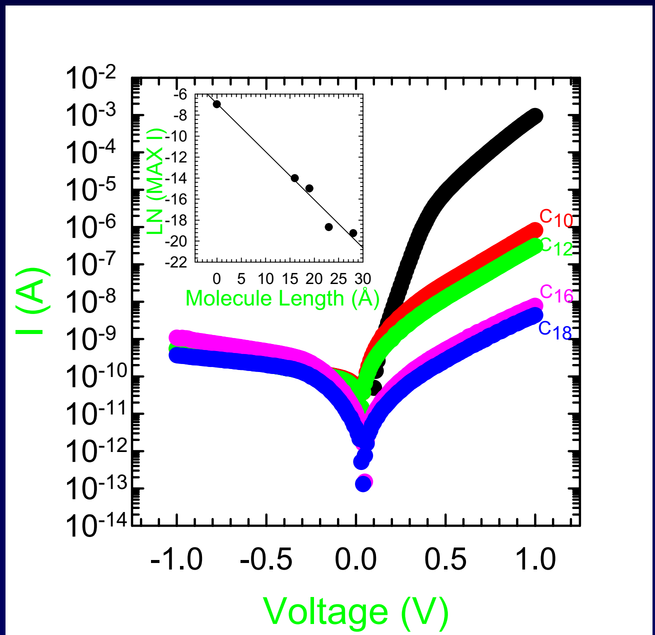
Sandwich Structures on Semiconducting Surfaces

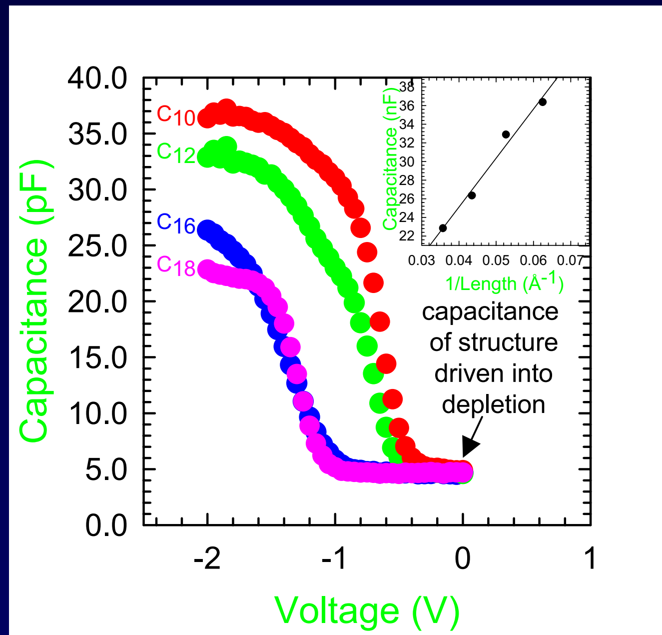


Metal-Insulator-Semiconductor Diodes

• Advantage: MIS control possible
unlike metal-insulator-metal
(good portion of MIM literature incorrect)

• assemble molecules of varying chain length





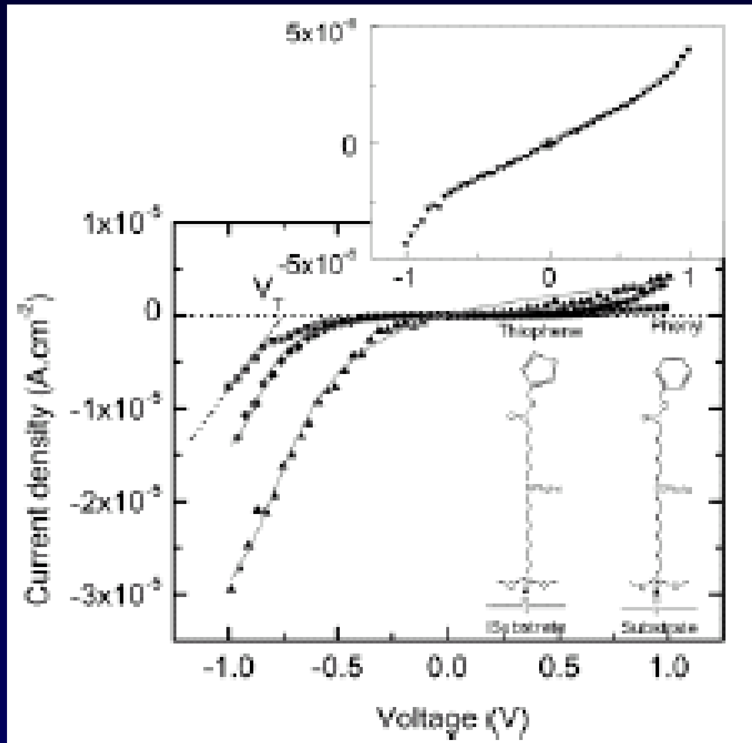
calculated capacitance agrees with MIS diode
having organic molecules + ~10 Å SiO_2 native oxide

C. R. Kagan, C. T. Black

+ photoresponse measurements to understand barrier heights

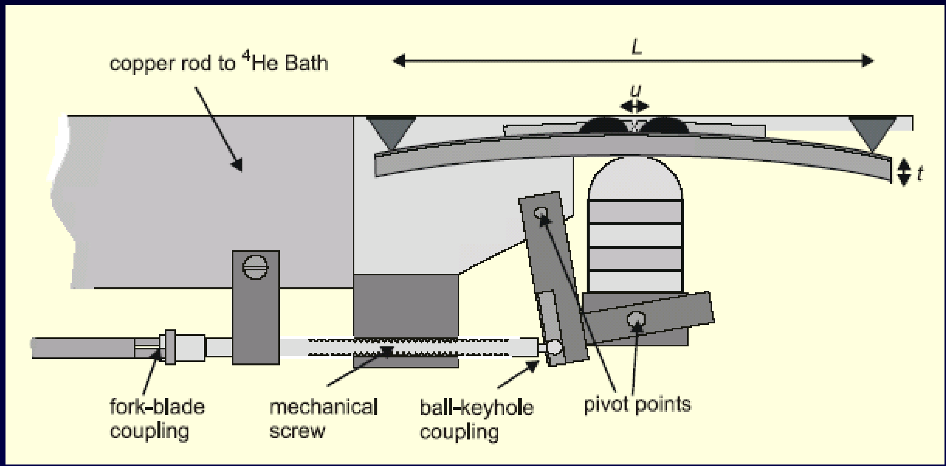
D. Vuillame et. al. Apl. Phys. Lett. **69**, 1646 (1996).

Molecular Junctions: Rectifiers on Si

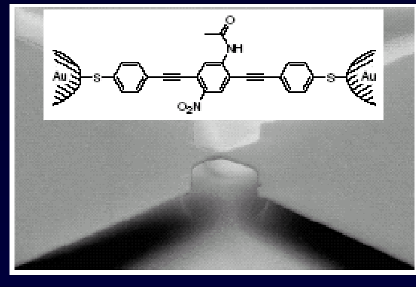


S. Lenfant, C. Krzeminski, C. Delerue, G. Allan, D. Vuillaume,
Nano Lett **3**, 741 (2003).

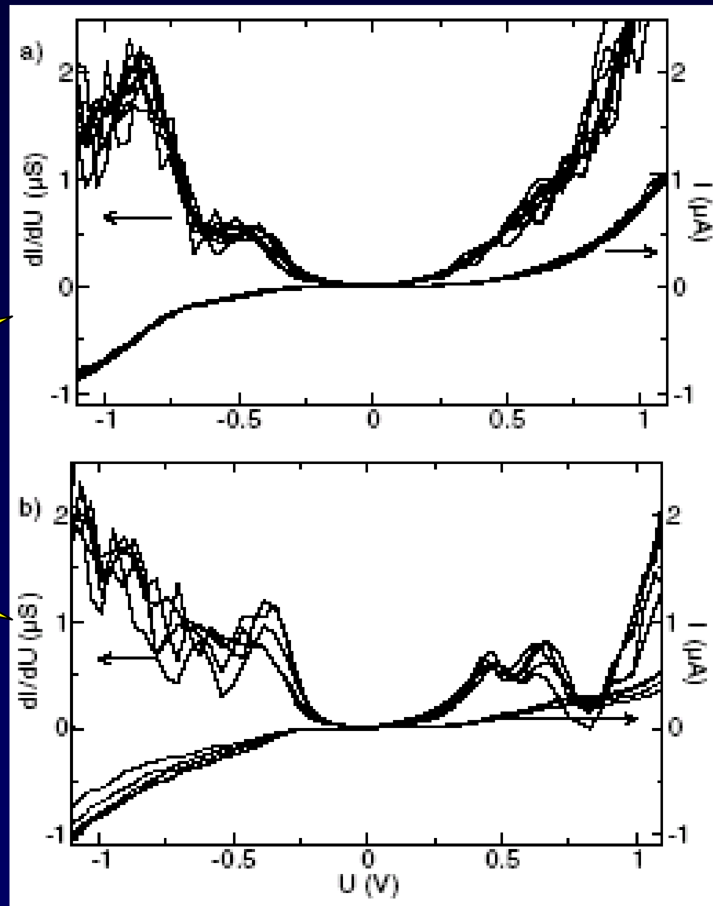
Mechanically Controllable Break Junctions



J. van Ruitenbeek

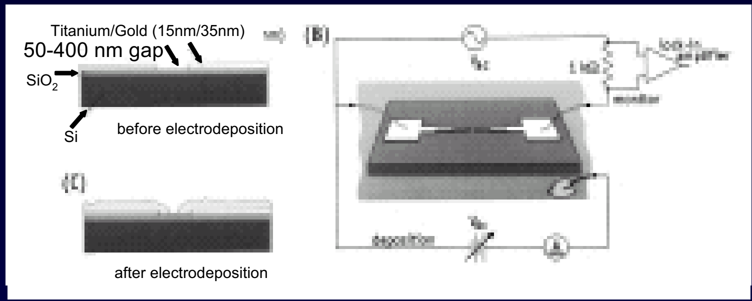


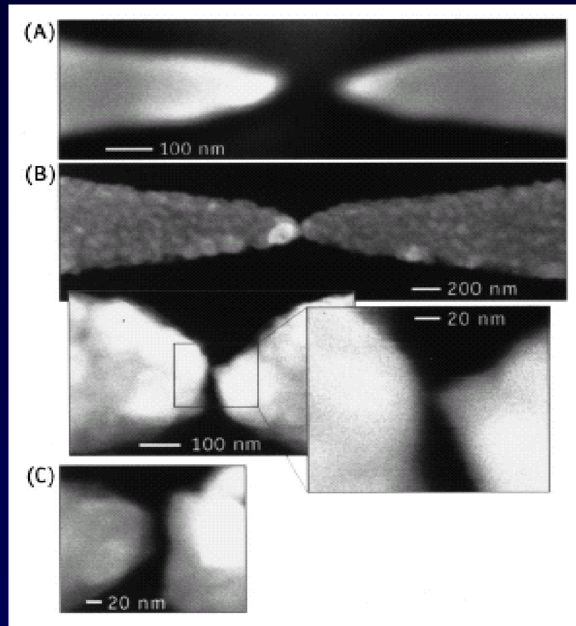
before and after reconfiguration of the molecule in the junction



J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, H. v. Löhneysen, *Phys. Rev. Lett.* **88**, 176804 (2002).

Electrochemical Deposition/Re-dissolution to Form Atomic Scale Gaps





In Solution:

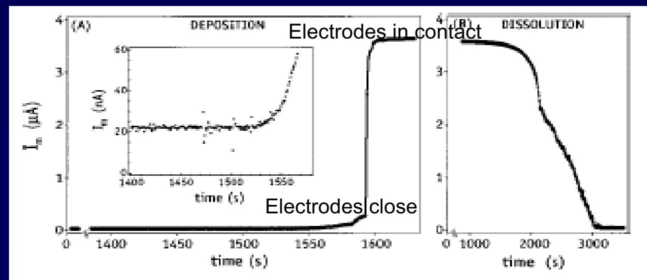
0.01 M potassium cyanaurate [$KAu(CN)_2$]

buffer ~*p*H 10 composed of:

1 M potassium bicarbonate (KHCO3) and

0.2 M potassium hydroxide KOH

Cyanaurate accepts electron, liberating cyanide, depositing Au



Au counterelectrode

V_{app}=-0.5—0.6V on both electrodes

Monitor I with 4 mV ac bias at 1 Hz, monitor across resistor with lock-in

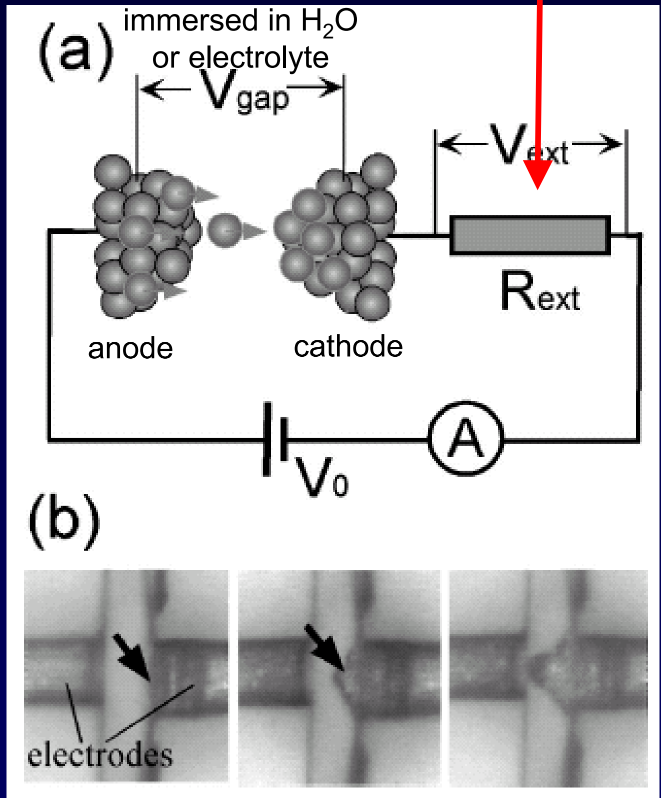
A. F. Morpurgo and C. M. Marcus, D. B. Robinson, *App. Phys. Lett.* **74**, 2084 (1999).

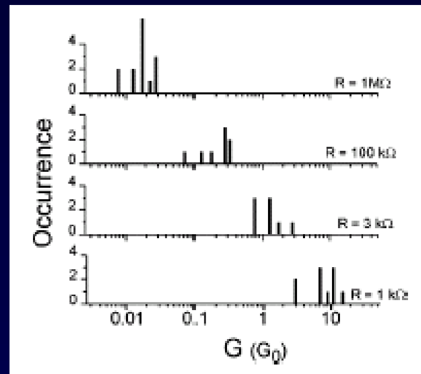
Similarly for Pt electrodes

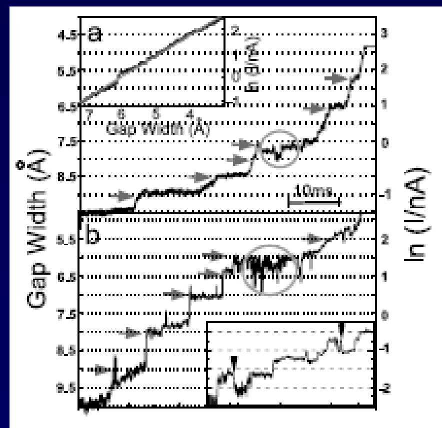
Gaps ~1-20 nm

Self-Terminating Electrochemical Method to the Formation of Atomic-scale Gaps

Provides built-in self-termination
$1/R_{ext} < G_0$, small gap with conductance determined by tunneling
$1/R_{ext} > G_0$, conductance with multiple of G_0





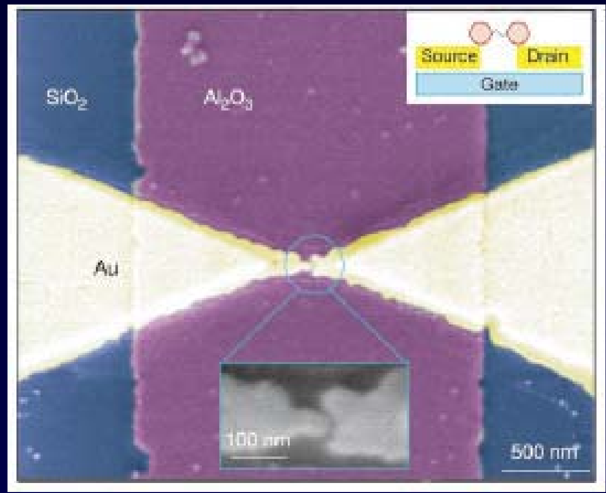


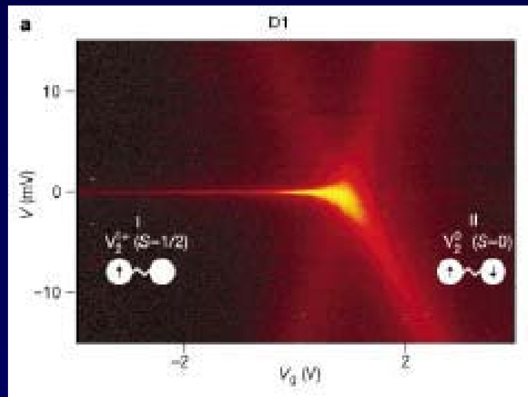
$$V_{gap} = \frac{R_{gap}}{R_{gap} + R_{ext}} V_0 ,$$

R_{gap} depends on tunneling current and leakage current
Leakage current depends on electrode geometry and electrolyte concentration

S. Boussaad and N. J. Tao, *App. Phys. Lett.* **80**, 2398 (2002).
H.X. He, S. Boussaad, B.Q. Xu, C.Z. Li, N.J. Tao, *J. ElectroAnal. Chem.* **522**, 167 (2002)

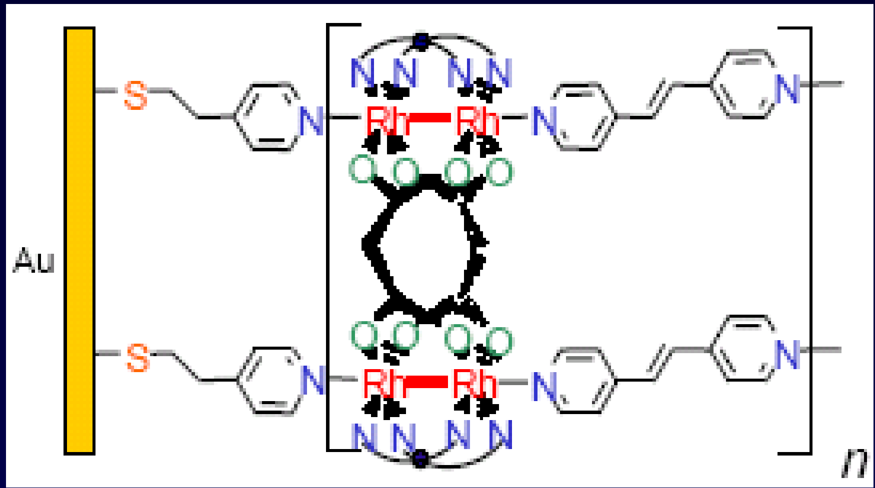
Electromigration Junctions

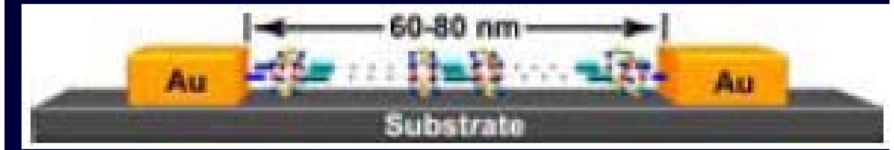




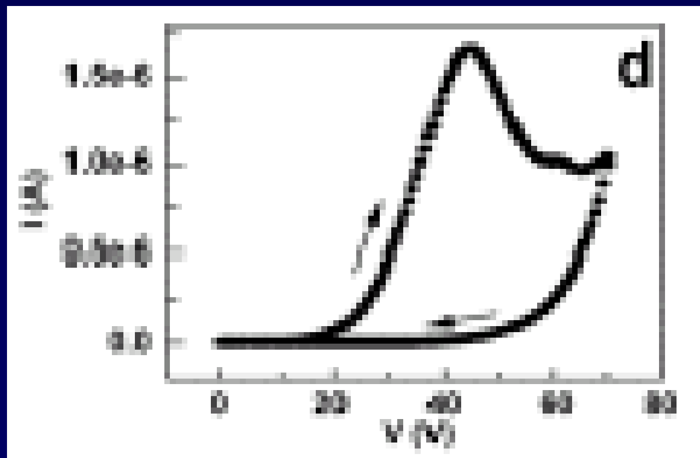
J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, D. C. Ralph, *Nature* **417**, 722 (2002); W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **417**, 725 (2002).

Bridging the Gap





Layer-by-layer Chemistry to meet the dimensions of standard lithographically defined electrodes



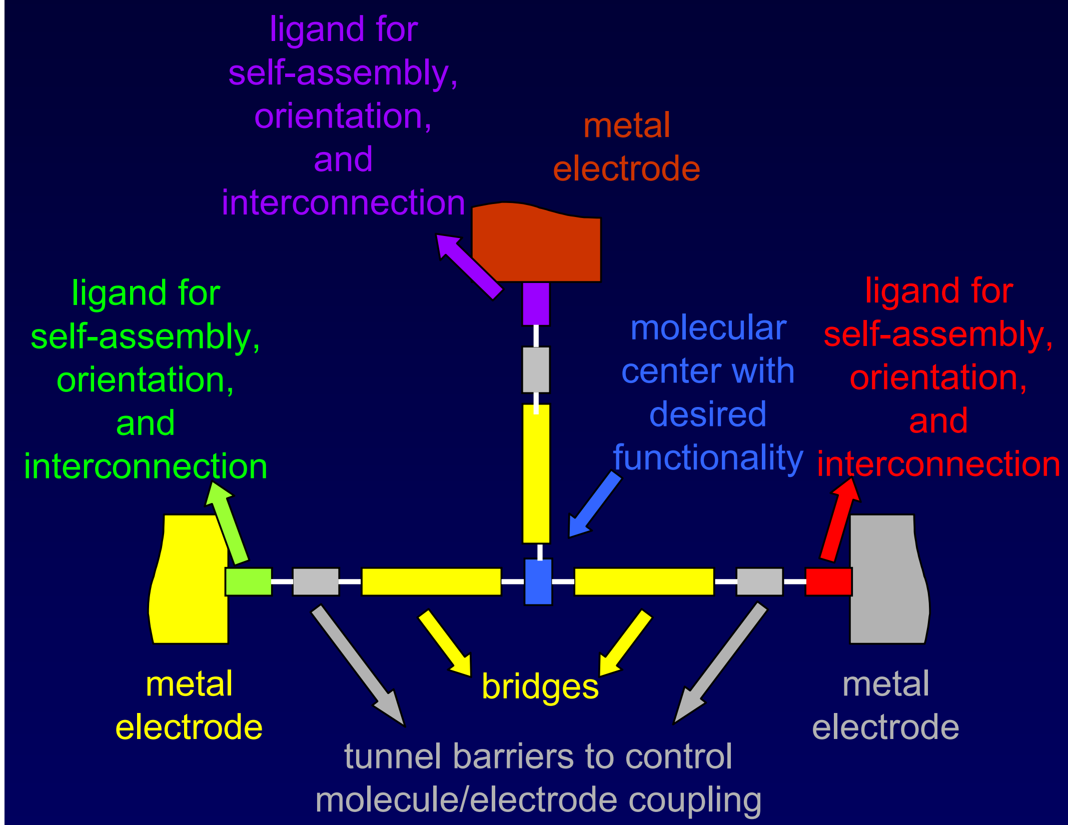
C. Lin, C. R. Kagan *JACS*, **125**, 336 (2003)

The Chemistry of Molecular Assembly

Cherie R. Kagan

IBM T. J. Watson Research Center
Yorktown Heights, NY

Molecular Materials and Devices

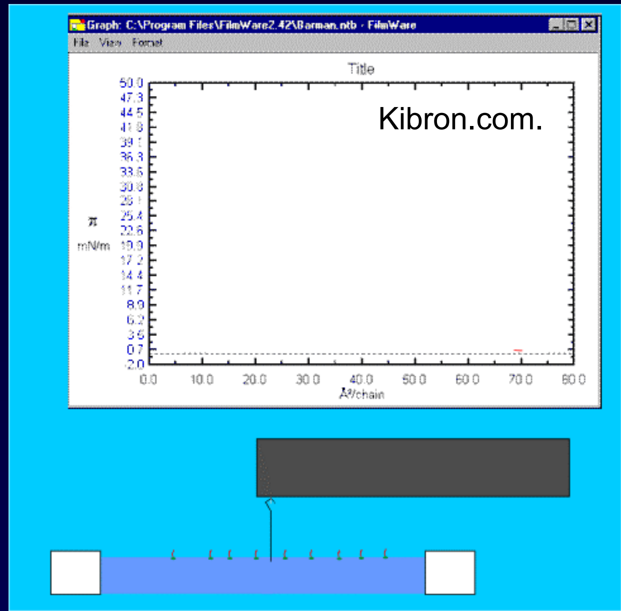


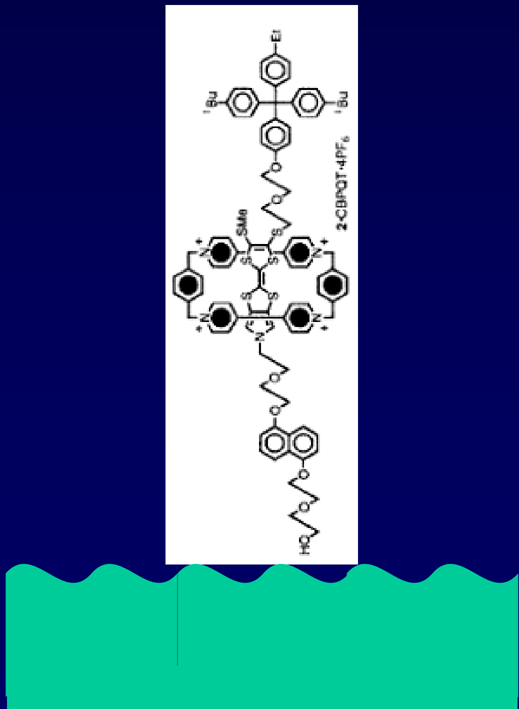
Build desired functionality into single molecules

Understand the physics and design of molecules and molecular devices to control:

switching potential
switching time/mechanism
reversibility/stability
room T operation
solubility
self-assembly/orientation
molecule-contact resistance/coupling
….. And the list goes on!

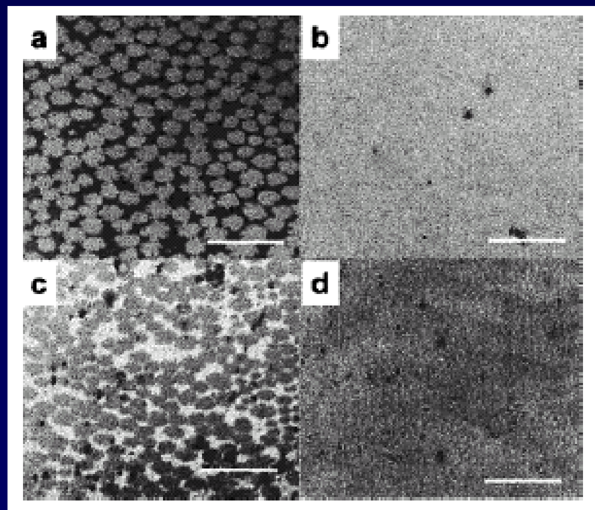
Physical Monolayers on a Langmuir-Blodgett Trough





H_2O

6.4 mM $CdCl_2$

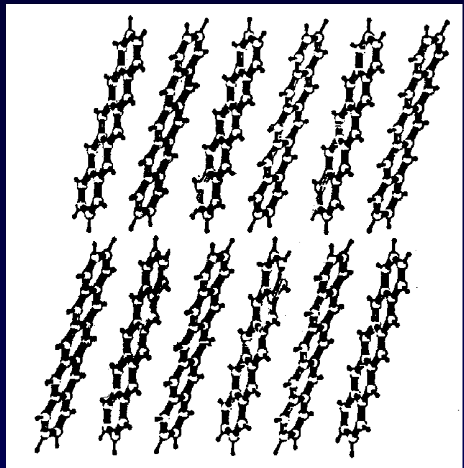


100 µm

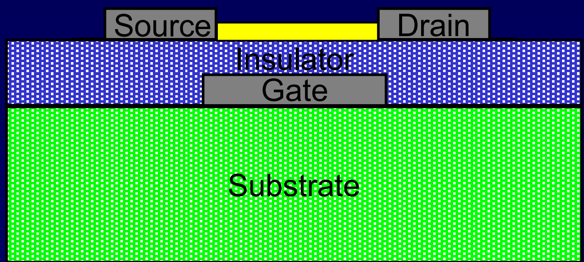
C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **123**, 12632 (2001).

Physical Assembly As in Thin Film Organic Devices

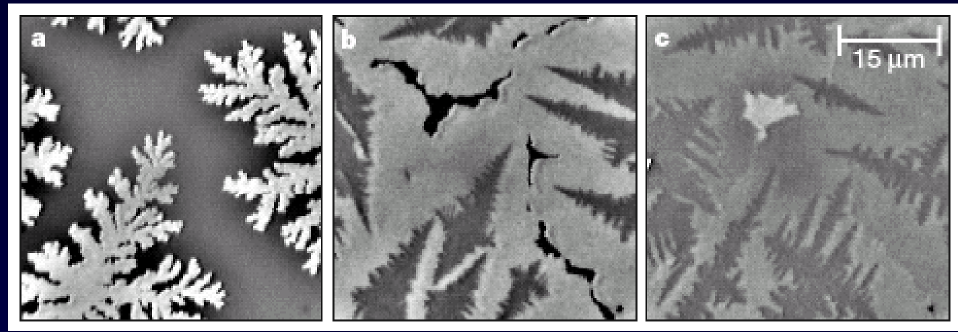
Intermolecular Charge Transport



Collective property of molecules

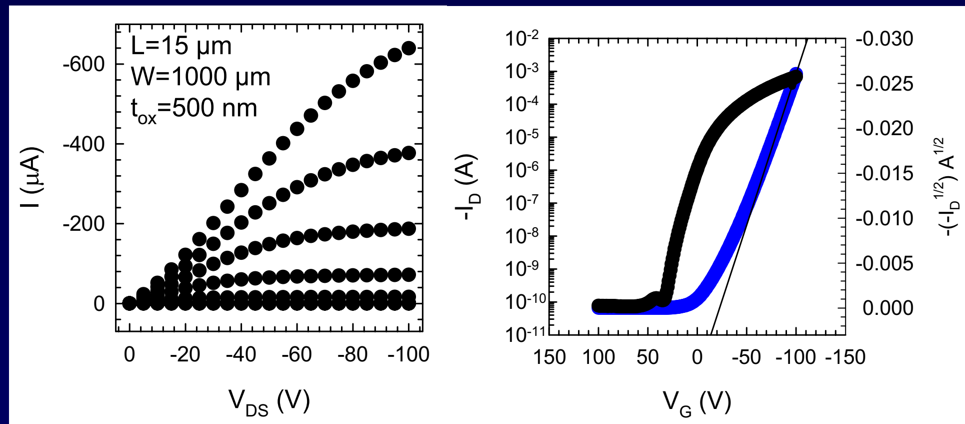


Channel Lengths ~ μm



Low-energy electron microscope monitoring pentacene growth on Si(001)

F. J. Meyer zu Heringdorf, M. C. Reuter, R. M. Tromp, *Nature* **412**, 517 (2001).

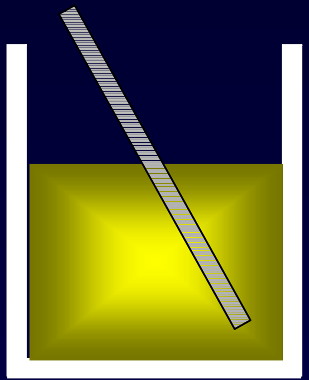


Mobility = 0.5 cm^2/V-sec

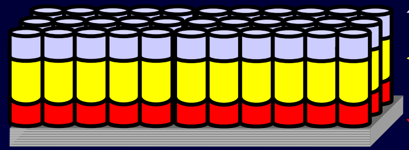
$I_{ON}/I_{OFF} = 10^7$

C. R. Kagan, A. G. Schrott

Chemical Assembly on Surfaces



Immerse substrate in solution of surface-active molecular species for seconds to hours

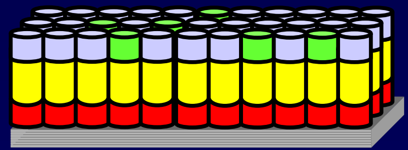


Closely-packed ordered SAM

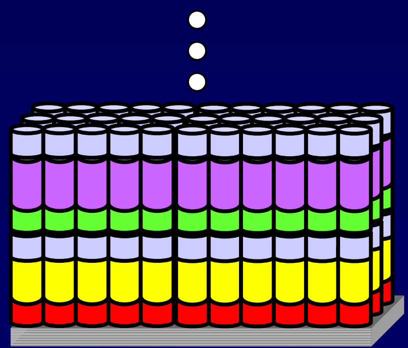
tail group
Interacts with adjacent or added molecules, air, electrodes

Intermolecular interactions (van der Waals, π–π, ...)

Surface-active head group providing chemisorption to the surface



Different tail groups may interact through hydrogen bonding, dipolar interactions



Reactive tail groups for multilayer assembly

Interactions:

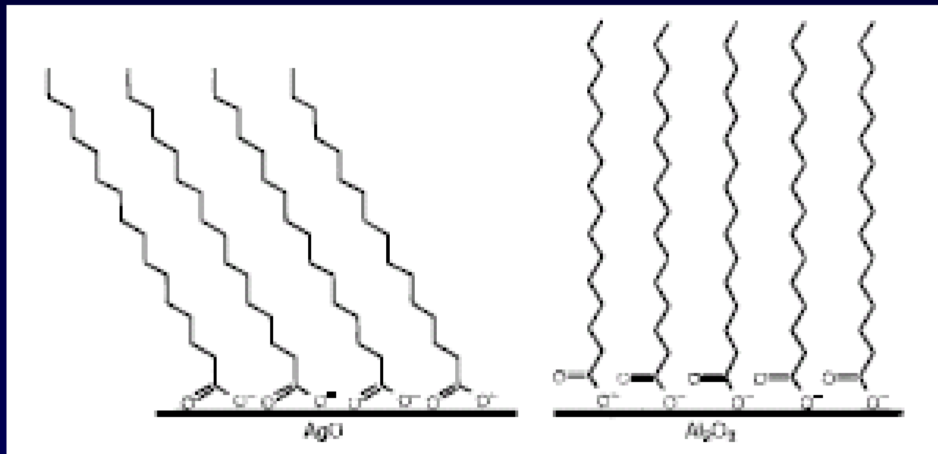
- molecule-molecule
- molecule-substrate
- molecule-solvent

Affects:
ordering, growth, wetting, ….

A. Ulman, *Chem. Rev.* **96**, 1533 (1996).

Classic Example of Fatty Acids

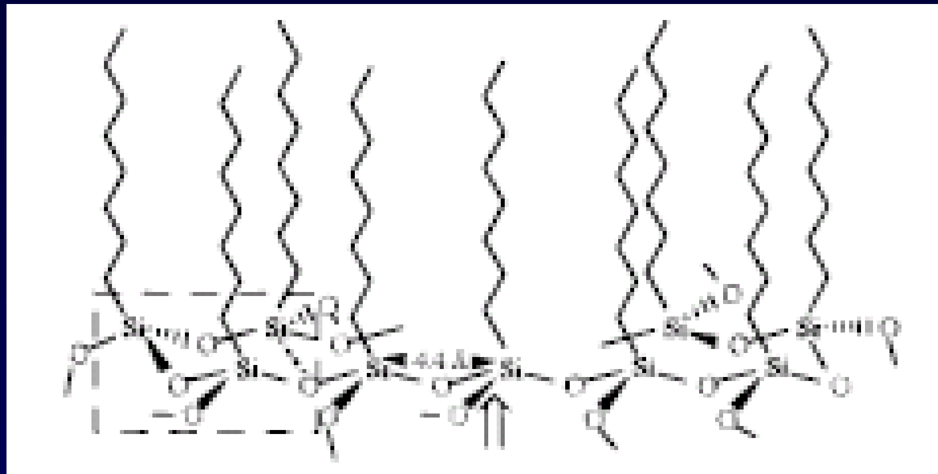
Example:
$C_nH_{2n+1}COOH$ + metal containing surface ⟶



acid-base reaction between carboxylic acid and surface metal cation

Classic Example of Silanes

silane + hydroxylated surface surface →

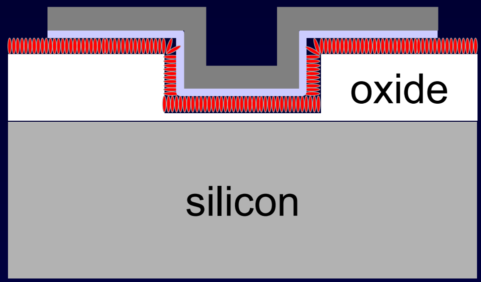


Driving force:
Polysiloxane connected to surface silanol
or other hydroxylated surface

Note: monolayer formation is highly sensitive to surface water

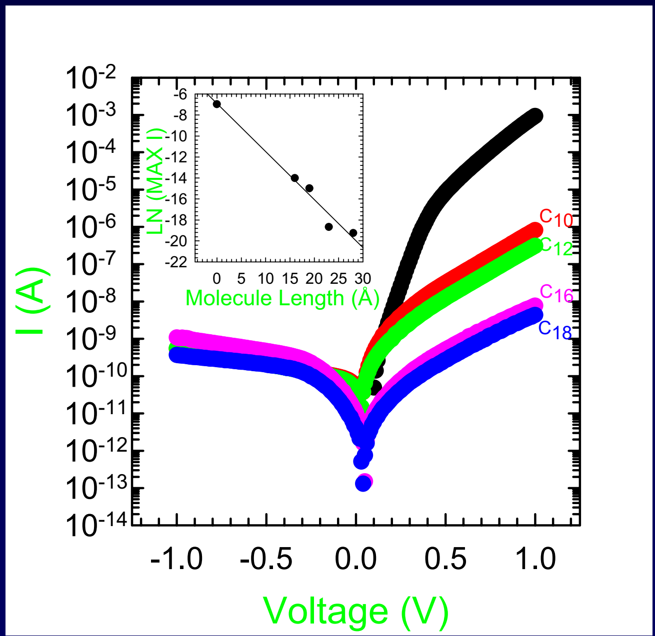
Kuhn, 1971

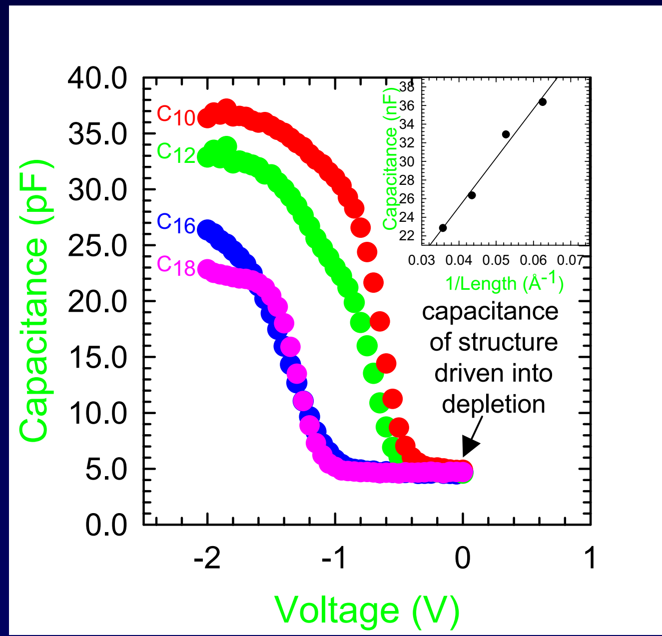
Understanding the Fabrication and Characteristics of Molecular Devices



Metal-Insulator-Semiconductor Diodes

- Advantage: MIS control possible unlike metal-insulator-metal (good portion of MIM literature incorrect)
- assemble molecules of varying chain length





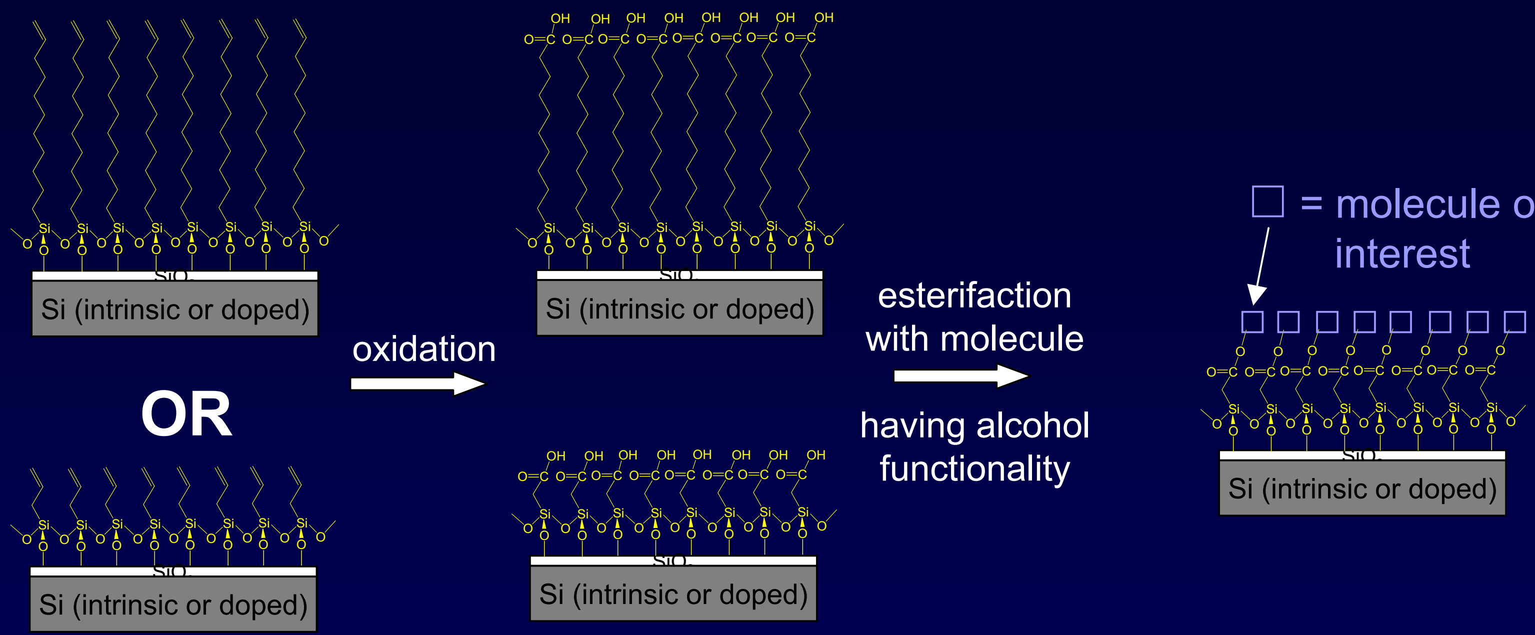
calculated capacitance agrees with MIS diode having organic molecules + ~10 Å SiO_2 native oxide

C. R. Kagan, C. T. Black

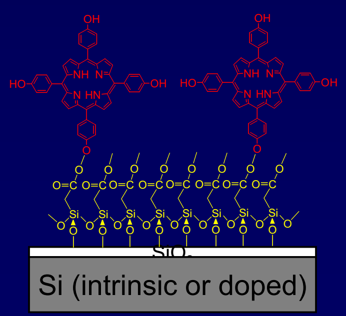
+ photoresponse measurements to understand barrier heights

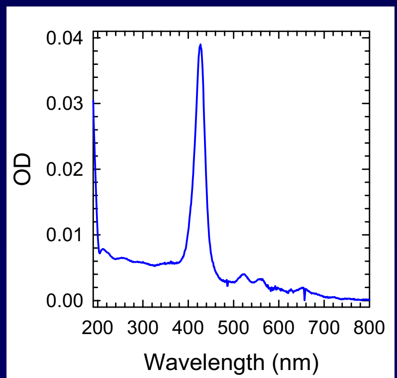
D. Vuillame et. al. Apl. Phys. Lett. **69**, 1646 (1996).

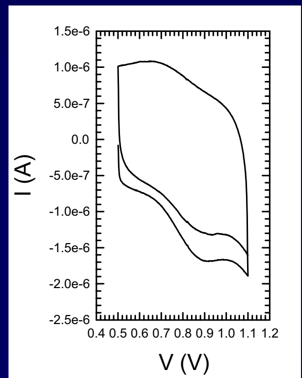
Chemistry to Covalently Bind Molecules to Oxides



Example: tetrahydroxyphenylporphine







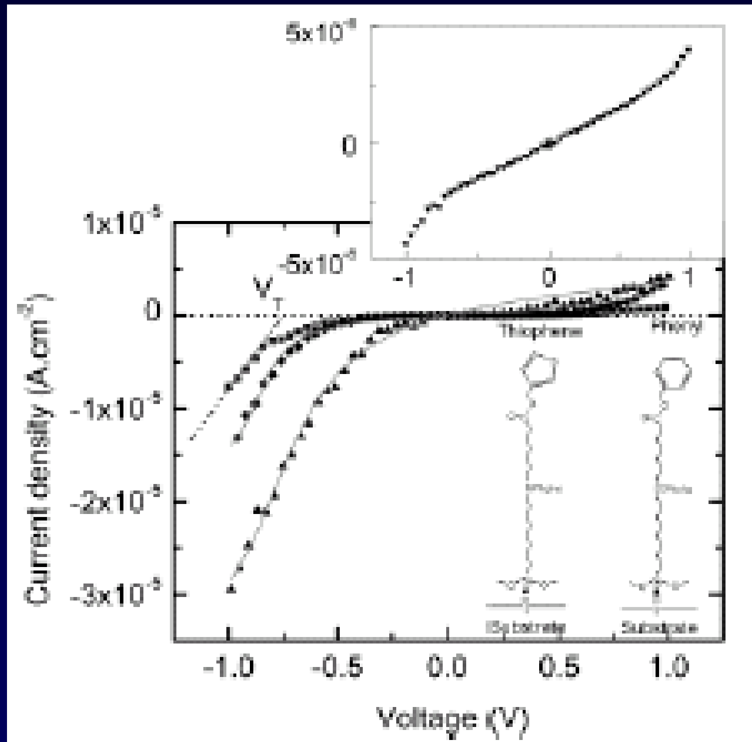
Molecules tried :
- porphyrins
- ferrocene
- pyrene
- anthracene
- all-trans retinol

Works for alcohols, phenols, …..?

D. Vuillame Appl. Phys. Lett. **76**, 1339 (2000).

Kagan/Afzali

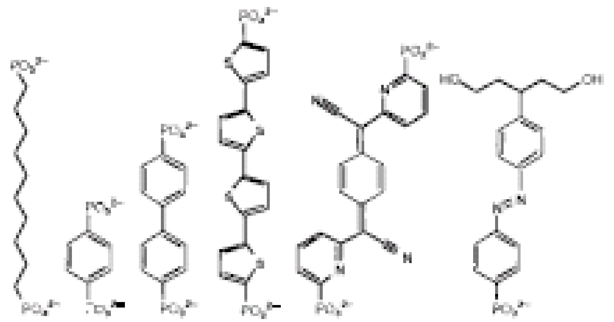
Molecular Junctions:
Rectifiers on Si



S. Lenfant, C. Krzeminski, C. Delerue, G. Allan, D. Vuillaume,
Nano Lett **3**, 741 (2003).

Other Head Group Chemistries for Self-Assembly on Oxide Surfaces

Phosphonic Acids –



I II III IV V VI

Figure 14. Different diphosphonic acids used in self-assembled multilayer preparation.

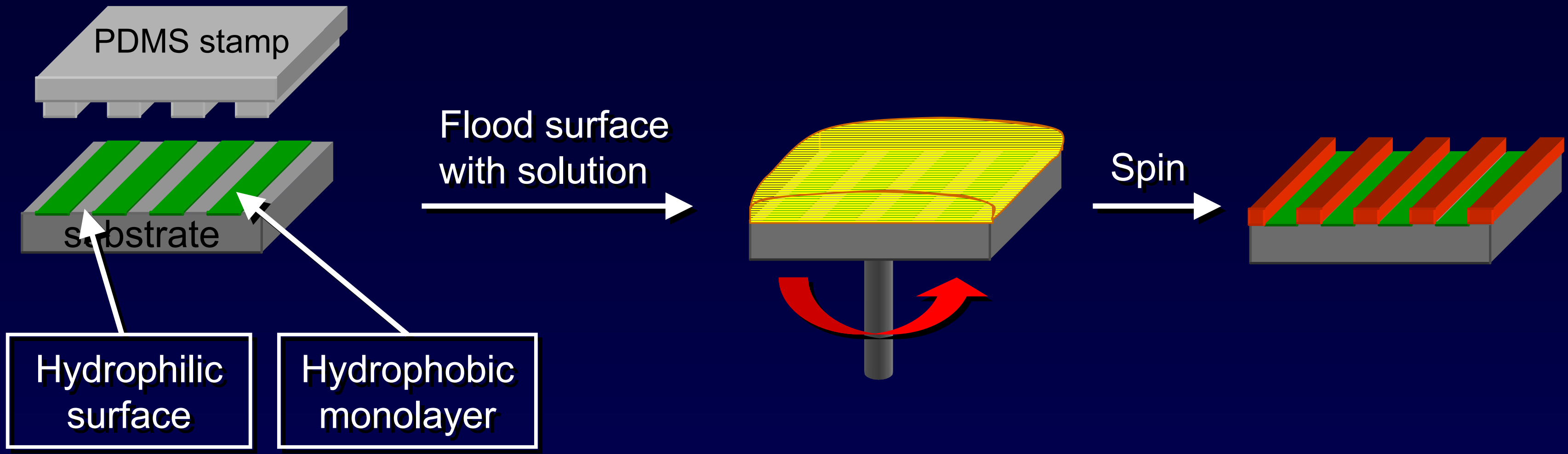
$+ Zr^{4+} \longrightarrow$ Zirconium Phosphate Multilayers

H. Lee, L. J. Kepley, H. G. Hong, T. E. Mallouk, *J. Am Chem. Soc.* **110**, 618 (1988).

H. Lee, L. J. Kepley, H. G. Hong, S. Akhter, T. E. Mallouk, *J. Phys. Chem.* **92**, 2597 (1988).

T. M. Putvinski, M. L. Schilling, H. E. Katz, C. E. D. Chidsey, A. M. Musjsce, A. B. Emerson, *Langmuir* **6**, 1567 (1990)/

Patterning Organic-Inorganic Hybrid Materials



Organic Monolayer

Differentiates the Chemical Nature

Of the Substrate Surface

To pattern subsequently

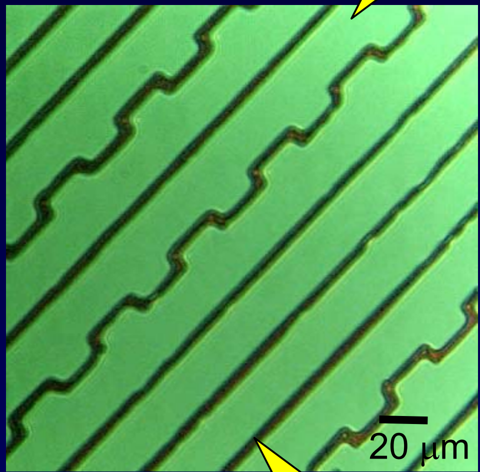
Solution deposited thin films

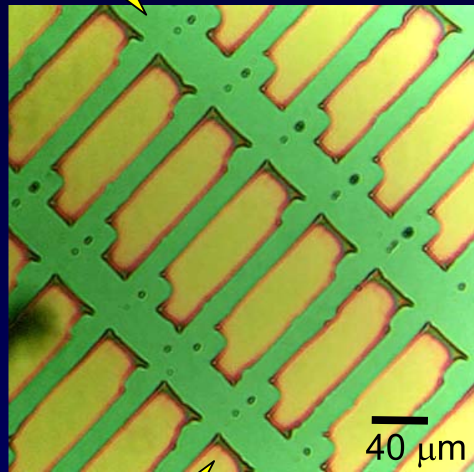
- Simple
- Low-cost
- Low-temperature
- Parallel Process/Additive
- Avoid potentially damaging post processing steps

C. R. Kagan, T. L. Breen, L. L. Kosbar, *App. Phys. Lett.* **79**, 3536 (2001).

Patterned Organic-Inorganic Hybrid Thin Films
Example: Hydroxamic acids on Oxide Surfaces

Hydrophobic monolayer – repels hybrid material





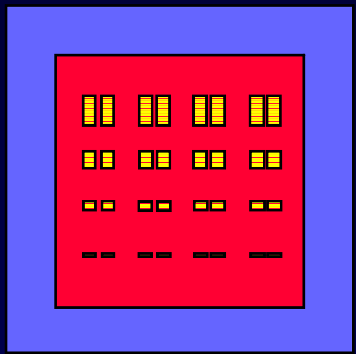
Hybrid material selectively deposits on hydrophilic oxide surface

Hydrophobic monolayer – hexadecylhydroxamic acid

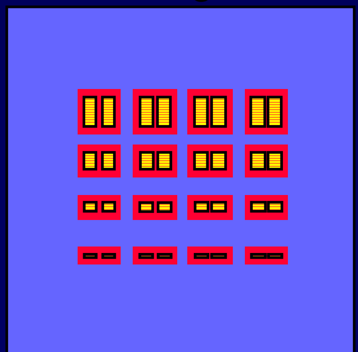
Substrate – $ZrO_2/SiO_2/Si$

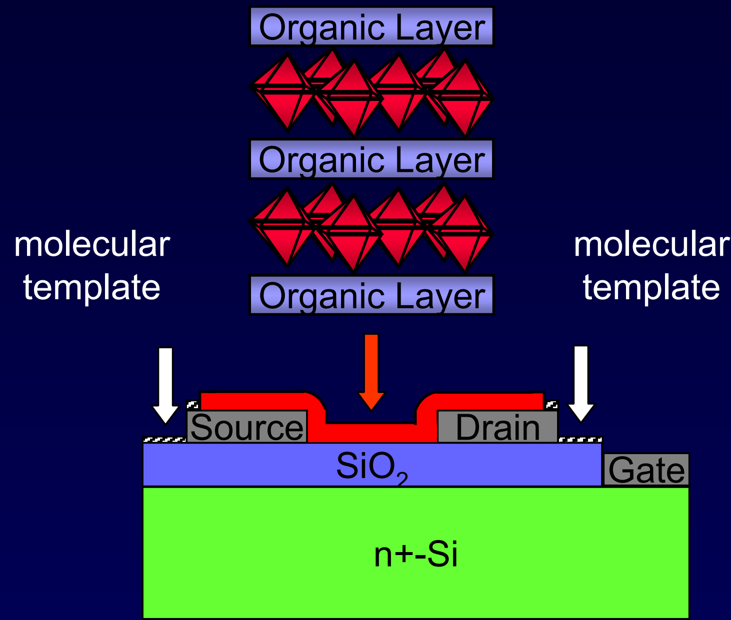
Patterned Organic-Inorganic Hybrid Thin Film Transistors

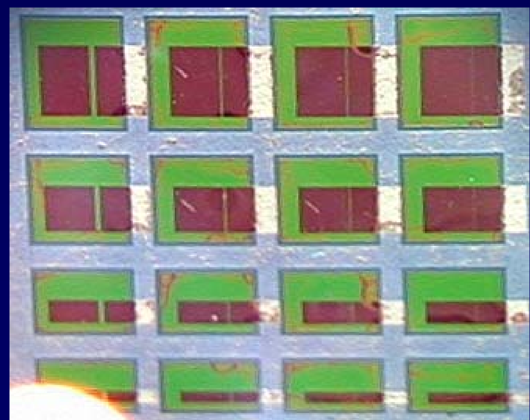
Unpatterned



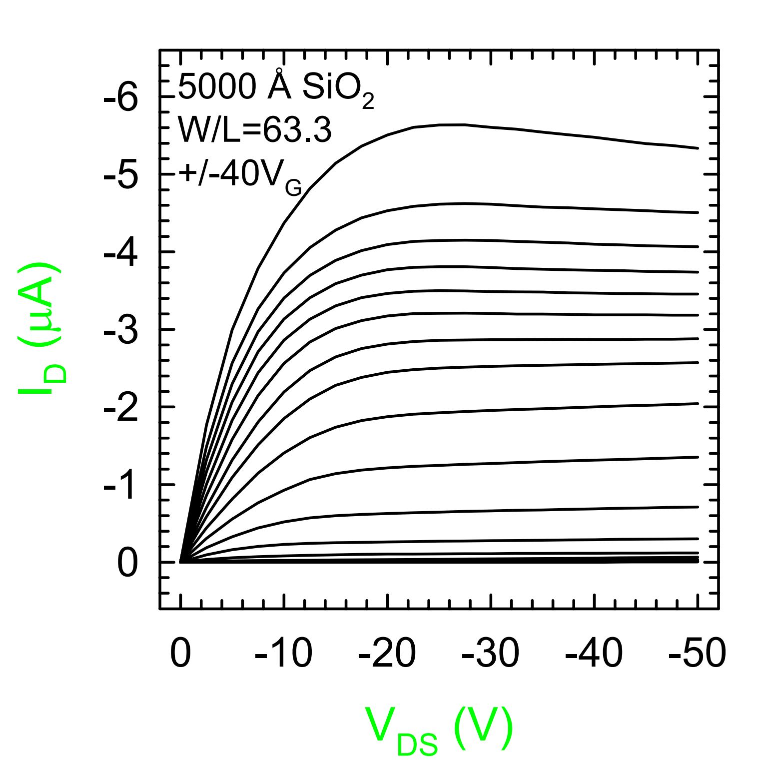
Isolate devices from each other and from back gate



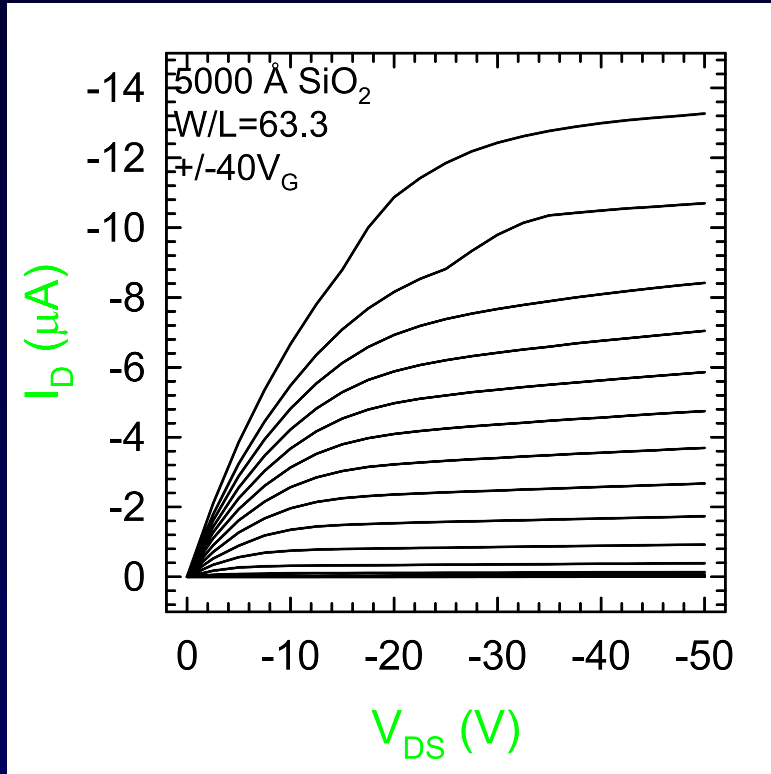




Organic-Inorganic Hybrid Material $(C_6H_5C_2H_4NH_3)_2SnI_4$ Patterned Devices

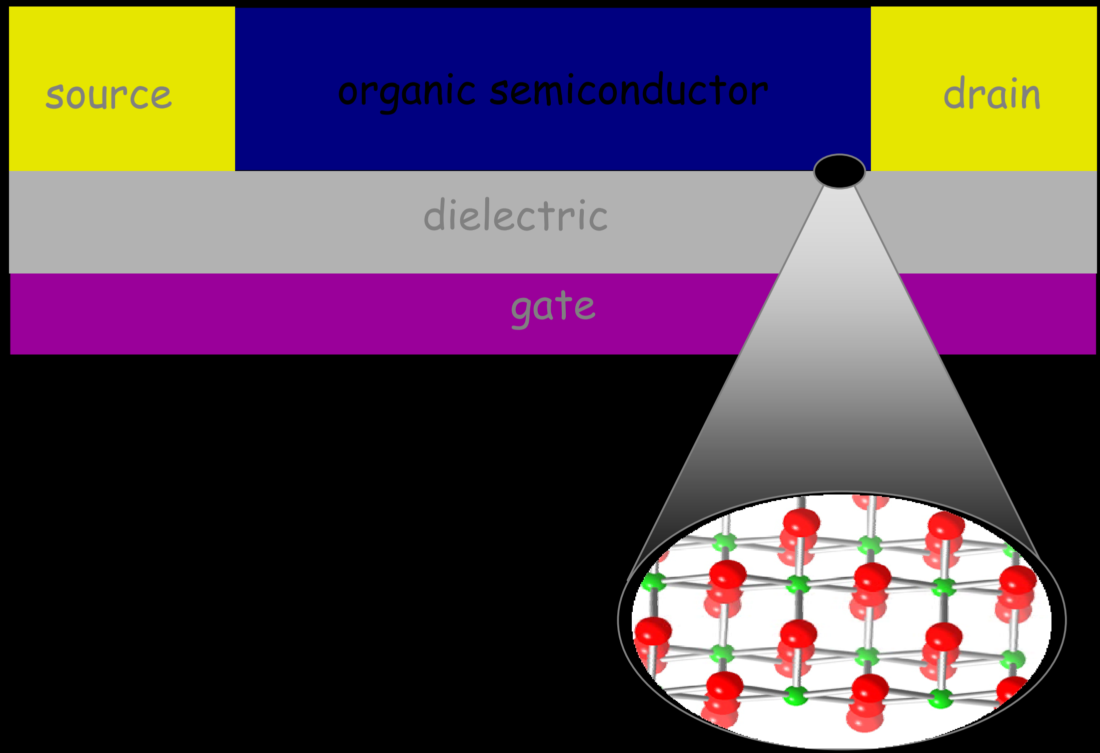


Template:
Octadecylphosphonic acid
μ= 0.1 cm^2/V-sec
I_{ON}/I_{OFF} ~ 10^4

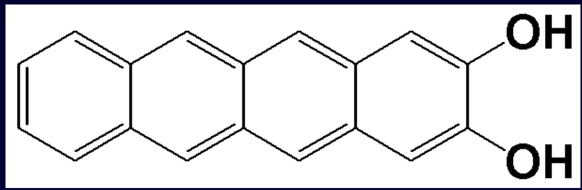


Template:
fluorinated alkylsilane
μ= 0.52 cm^2/V-sec
I_{ON}/I_{OFF} ~ 10^5

Self-Assembly of linear acenes on gate oxides



Self-Assembly on High K-Dielectrics



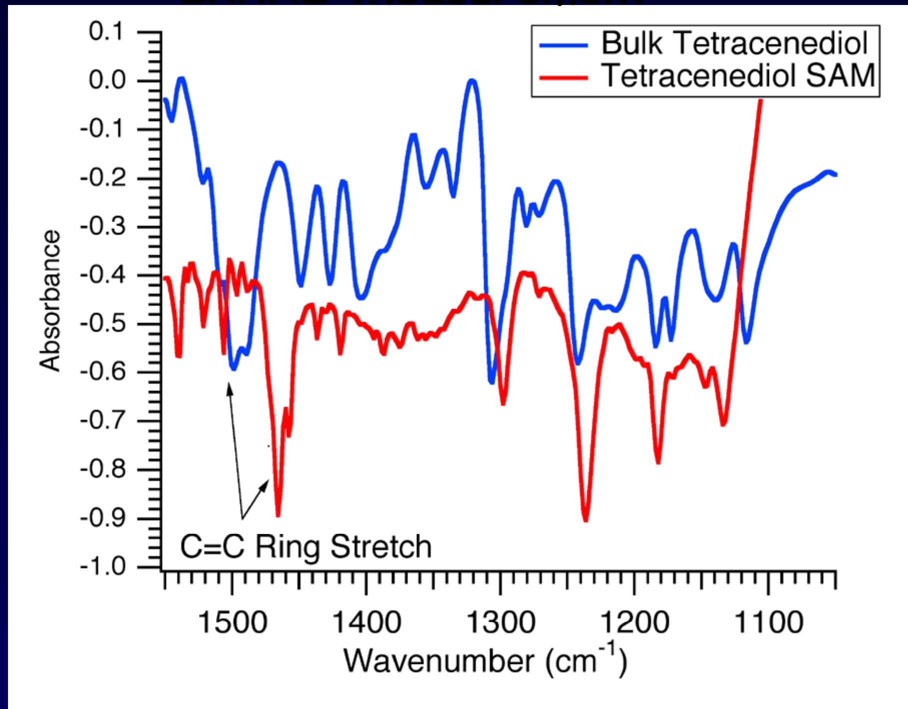
THF solution with
Al_2O_3 Surface

Water Contact Angle:
Advancing = 76º
Receding = 63º

XPS

	15º	35º	70º
O	31.4	36.4	41.2
C	47.1	36.3	26.2
Al	21.4	27.2	32.5
C/Al	2.20	1.34	0.81

IRRAS Measurement

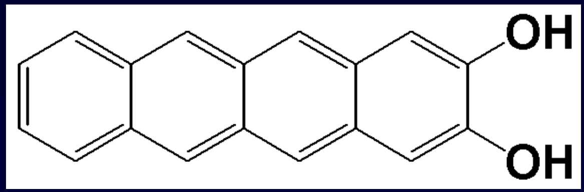


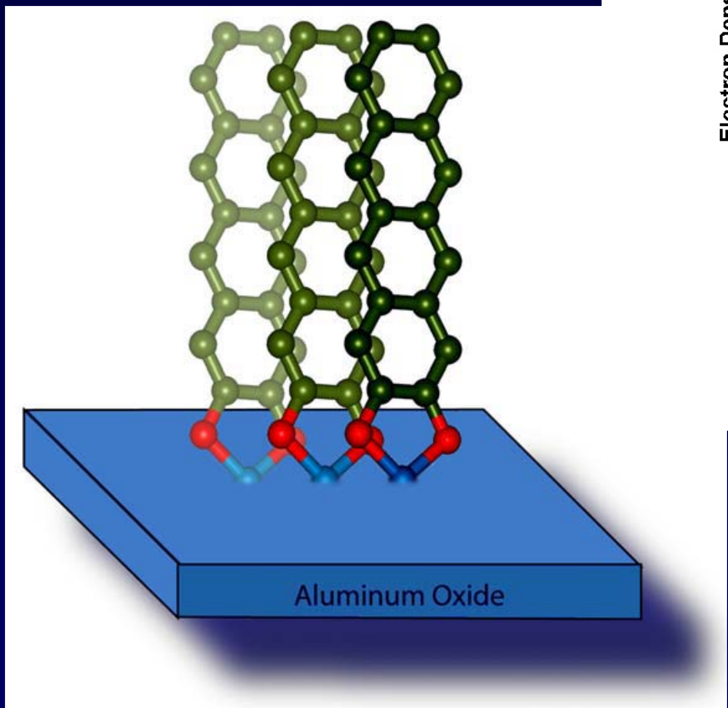
Ellipsometry:
Measured Thickness =14.8 Å
Calculated: 14 Å

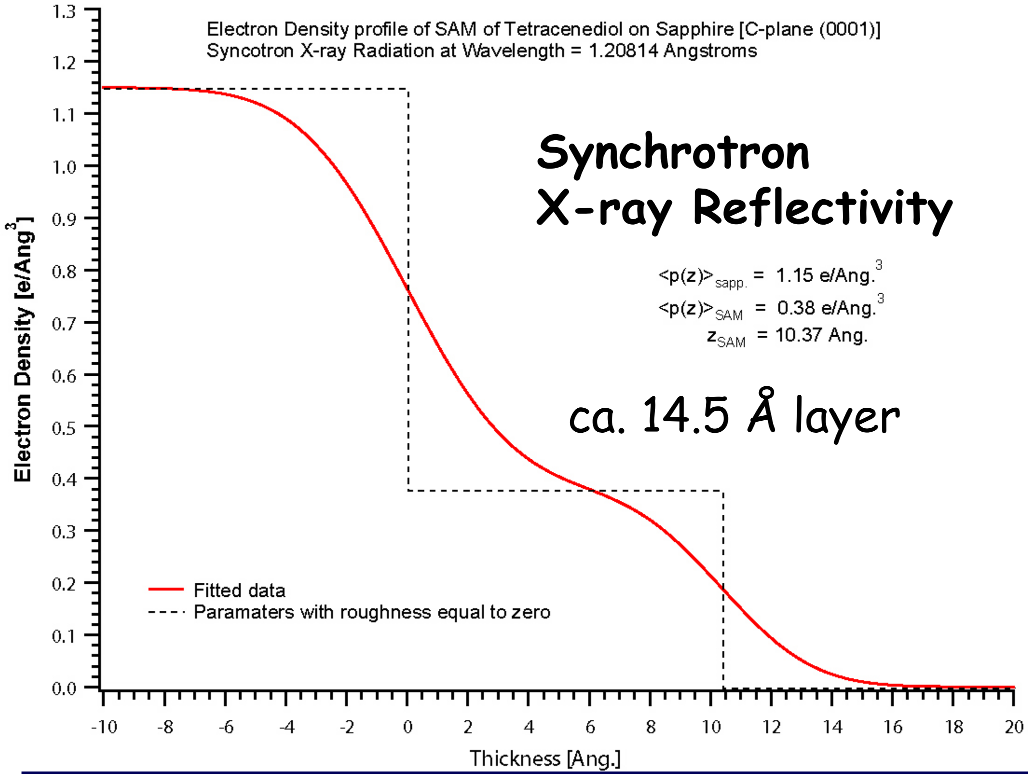
Also: HfO_2, ZrO_2, and Y_2O_3

George Tulevski, Qian Miao, Colin Nuckolls (Columbia)

Monolayers on sapphire crystals







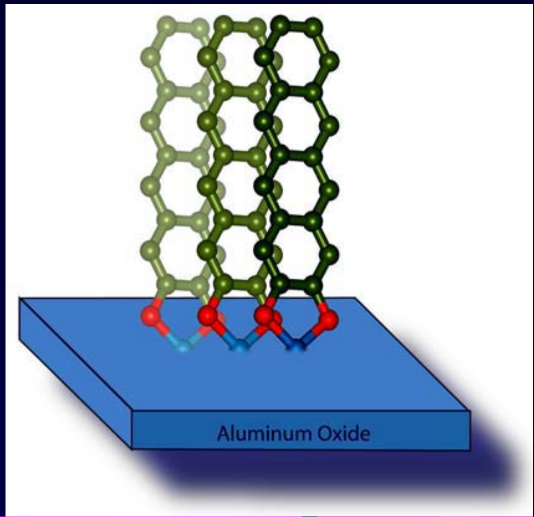
<u>electron density</u>

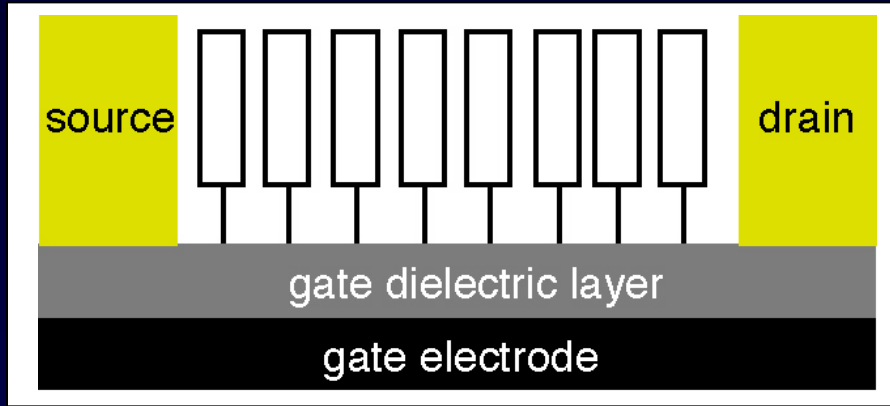
0.38 $e^-/Å^3$ for monolayer

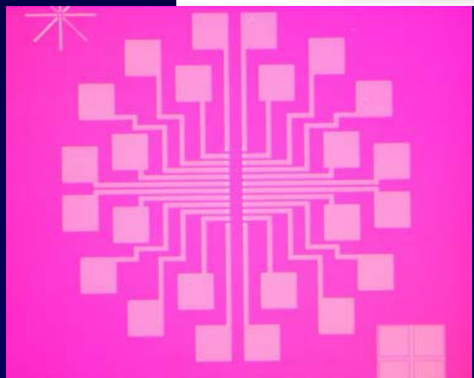
0.39 $e^-/Å^3$ for tetracene crystal

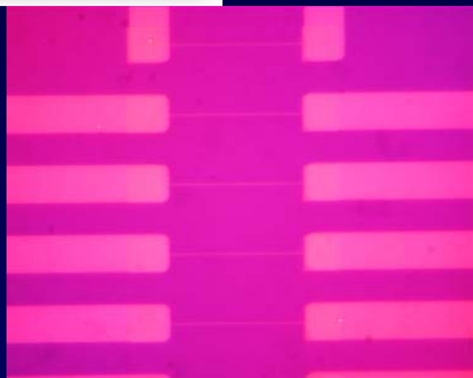
Columbia: George Tulevski, Qian Miao, Colin Nuckolls, **BNL:** Masafumi Fukuto, Ben Ocko, Ron Pindak, **IBM:** Cherie Kagan

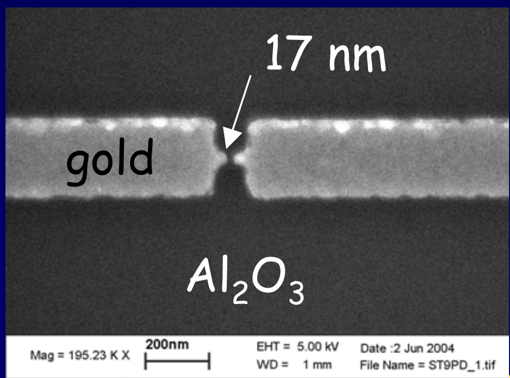
Monolayer devices

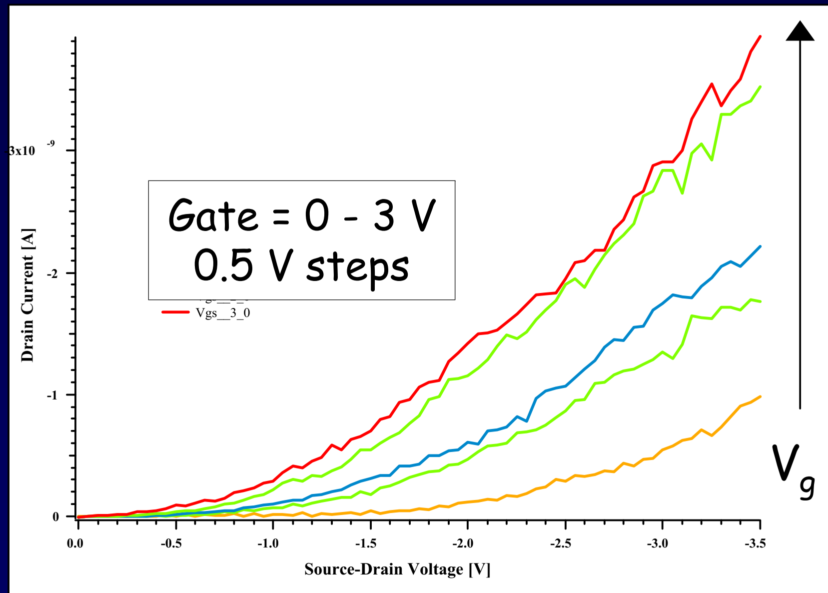








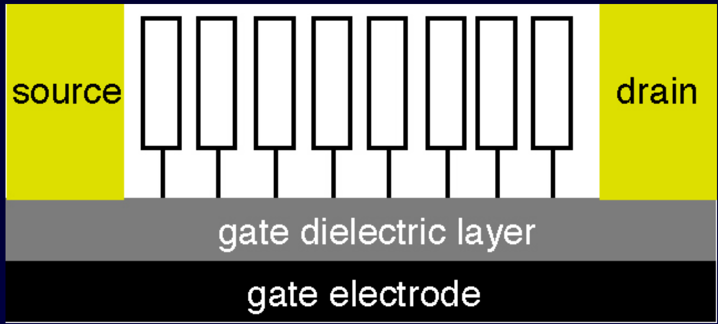




Yield of similar devices: approx. 90%

George Tulevski, Qian Miao, Colin Nuckolls (Columbia), Cherie Kagan

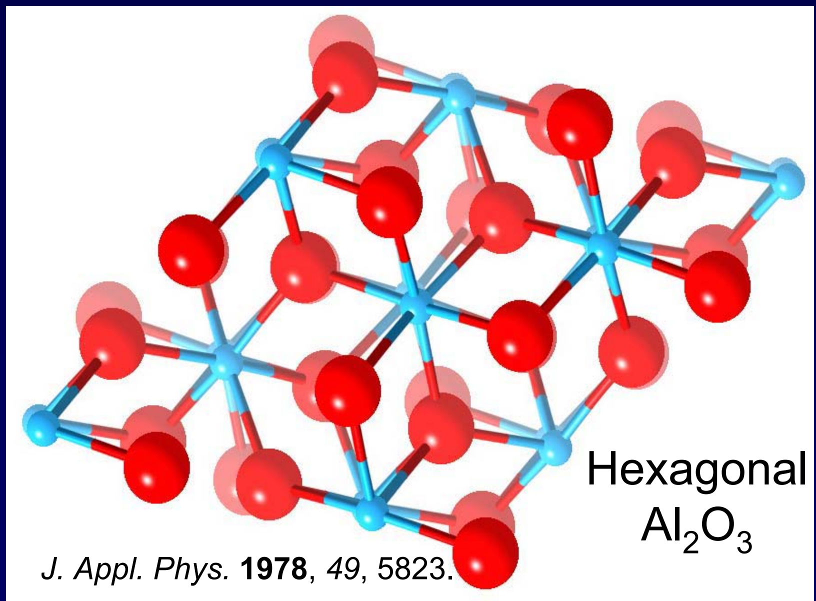
The next step: tune the three interfaces



Source/Drain:
Gold (adhesion layer?)
Platinum
Derivatized

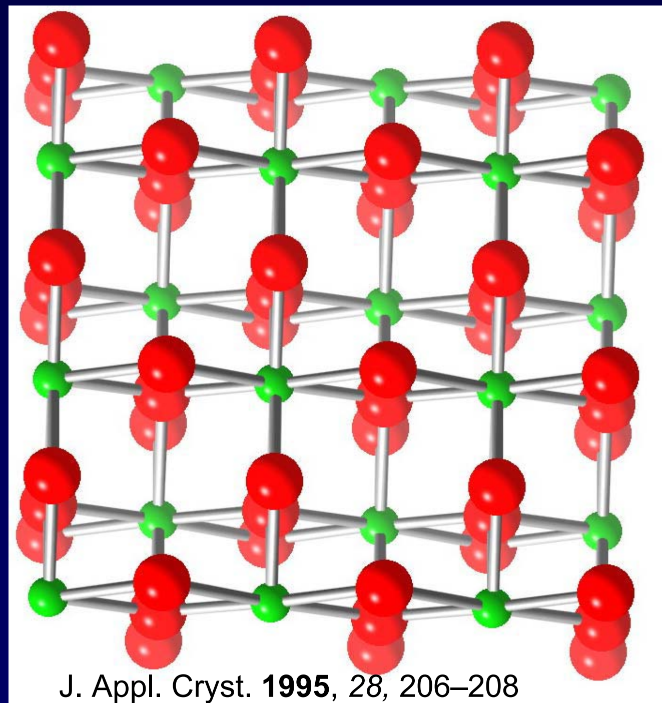
Gate dielectric:
Aluminum oxide
Hafnium oxide
Zirconium oxide
Crystalline

Viewing down the z-axis of Al_2O_3 and ZrO2



Hexagonal Al_2O_3

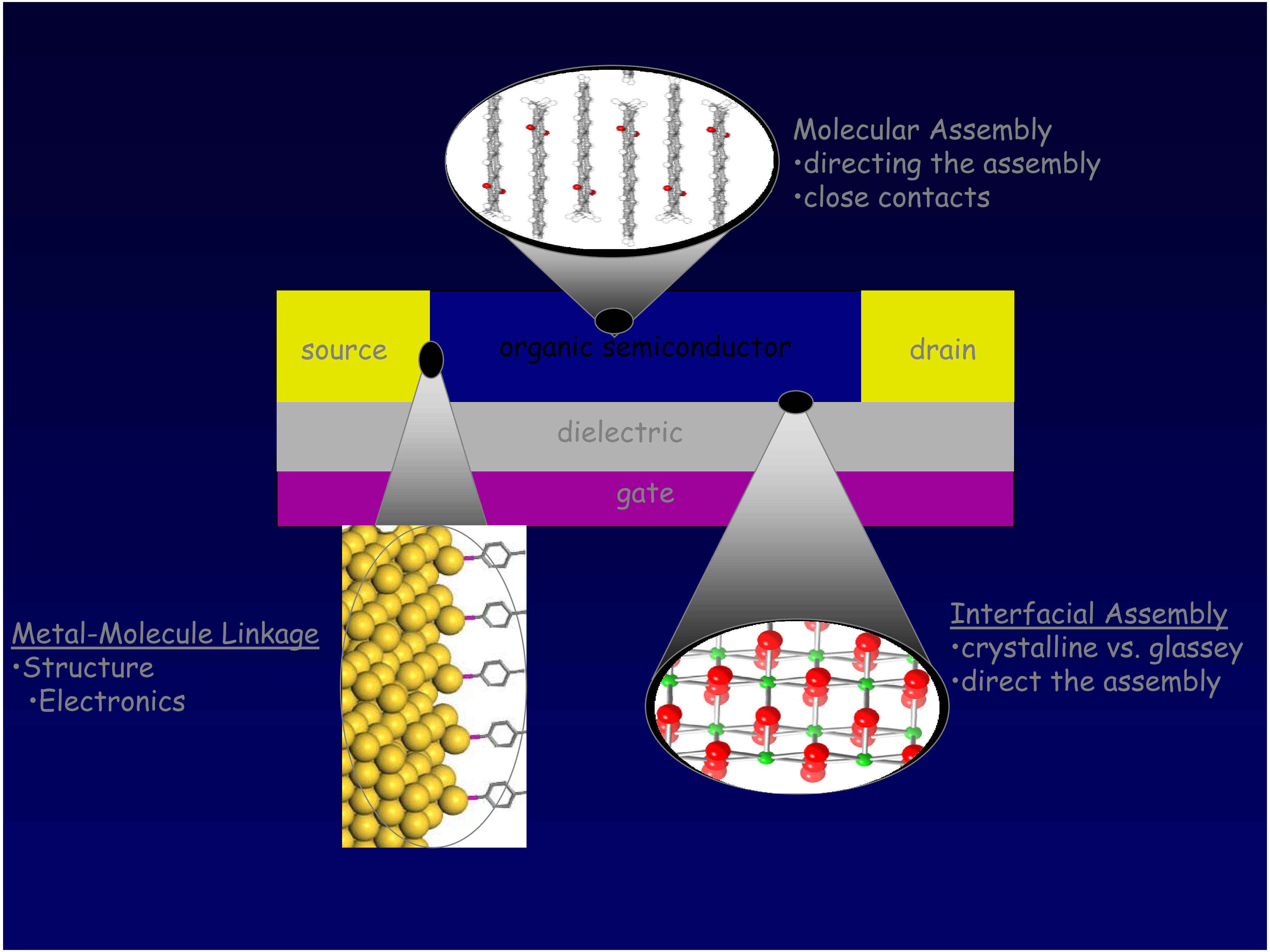
J. Appl. Phys. **1978**, *49*, 5823.



tetragonal ZrO_2

J. Appl. Cryst. **1995**, *28,* 206–208

George Tulevski, Qian Miao, Colin Nuckolls, Cherie Kagan (IBM)


Molecular Assembly
•directing the assembly
•close contacts
source
organic semiconductor
drain
dielectric
gate
Metal-Molecule Linkage
•Structure
•Electronics
Interfacial Assembly
•crystalline vs. glassey
•direct the assembly

Classic Example: Organosulfur, organoselenium

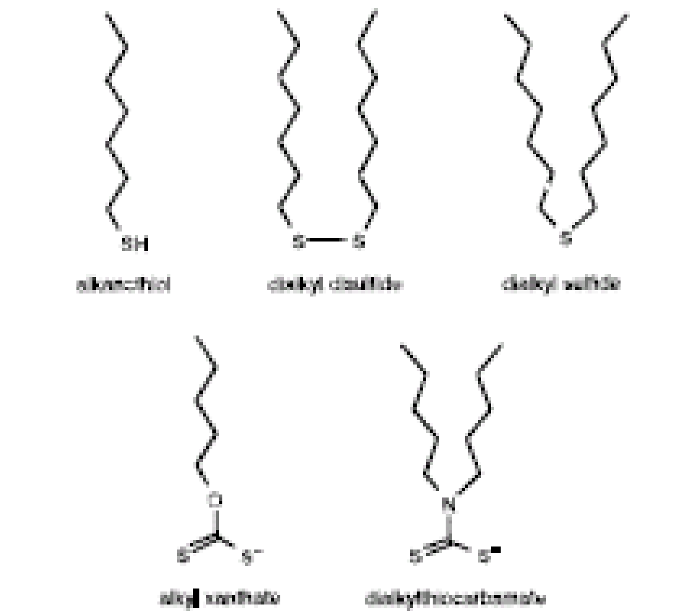


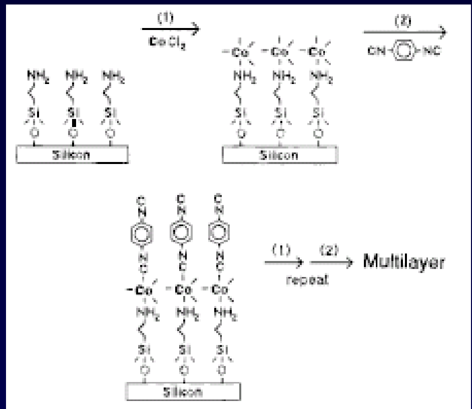
Figure 8. Surface-active organosulfur compounds that form monolayers on gold.

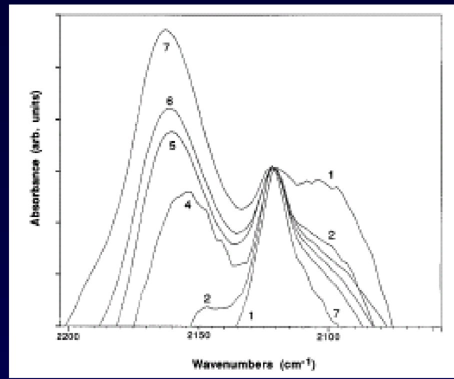
$RS\text{-}SR + Au_n^0 \longrightarrow RS^-Au^+\cdot Au_n^0$

$R\text{-}S0H + Au_n^0 \longrightarrow R\text{-}S^-Au^+\cdot Au_n^0 + ½\ H_2$

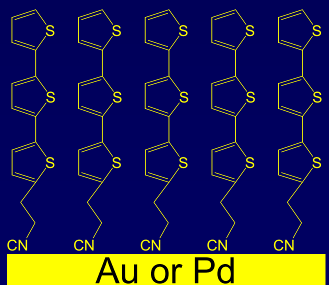
Nuzzo, R.G., Allara, D. L. J. Am. Chem. Soc. **105**, 4481 (1983)

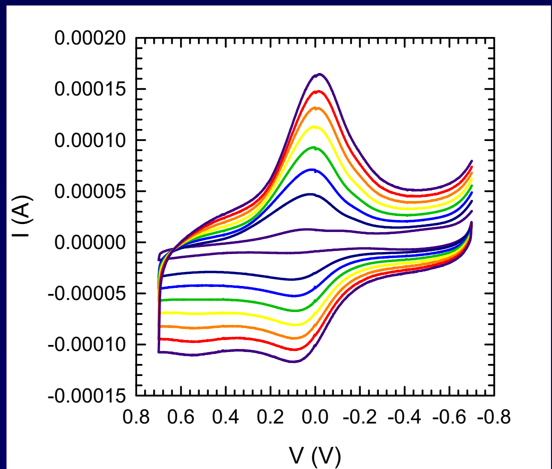
Other Head Group Chemistries for Self-Assembly on Metal Surfaces: Example Isocyanides

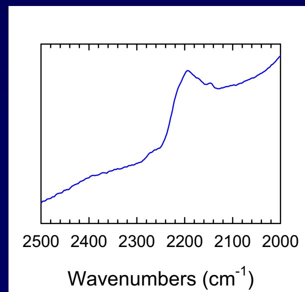


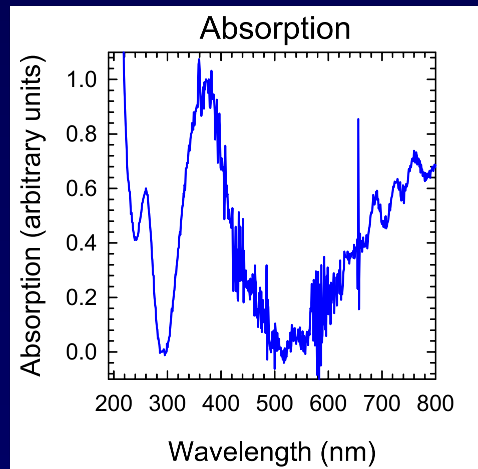


M. A. Ansell, E. B. Cogan, C. J. Page, *Langmuir* **16**, 1172 (2000).



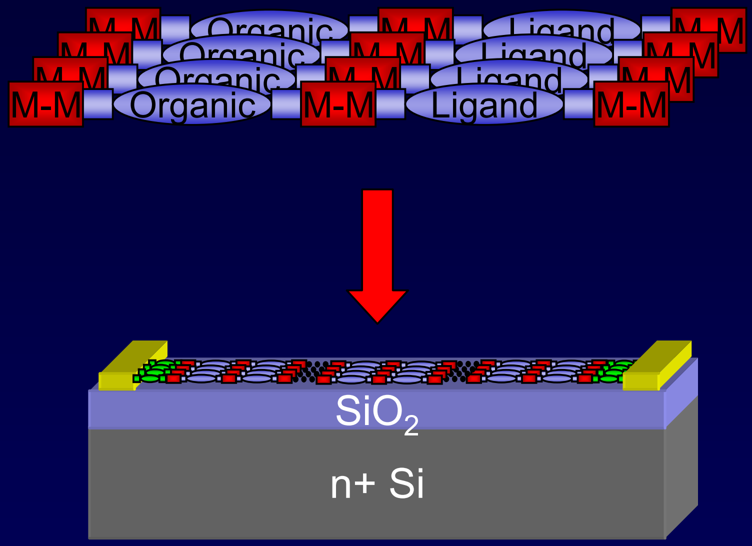


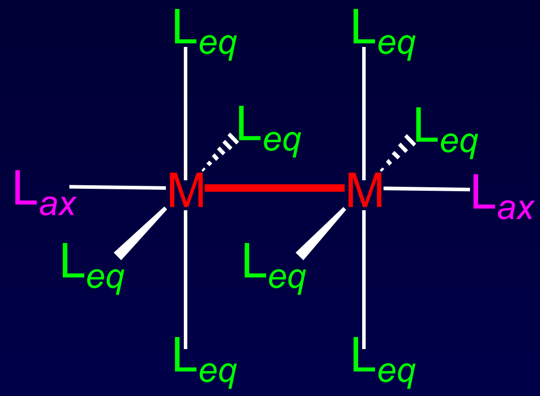




C. R. Kagan, A. Afzali, V. Sundar

Directed Assembly of Molecular Devices: Layer-by-Layer Growth of Metal-Metal Bonded Supramolecules





M = V, Nb, Cr, Mo, W, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag …

Ligands chosen to tailor:
- Electronic coupling between dimetal units
- Electrochemistry
- Solubility
- Structure ….

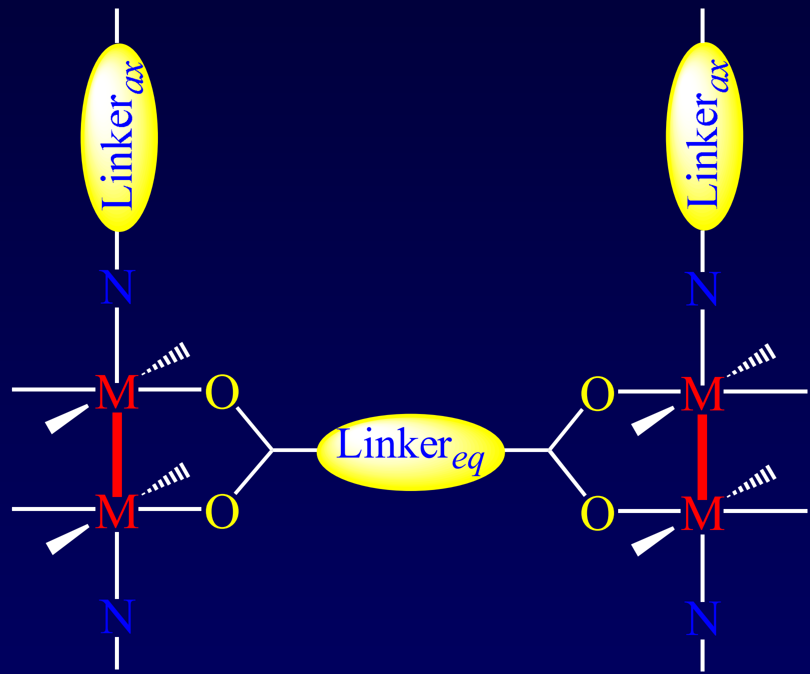
- Bridge channels > 3 nm
- Chemistry meet lithographic capabilities

Tailoring the Metal-Metal Bonded Supramolecule

- With equatorial linker

- With axial linker

- With equatorial and axial linkers

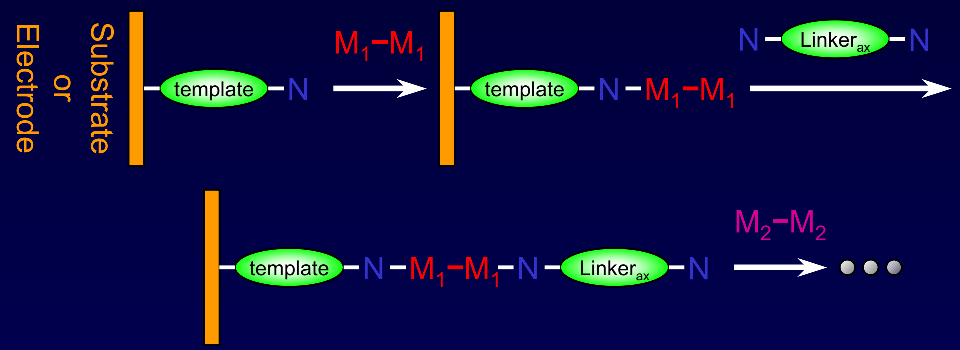


→ Supramolecules with a variety of crystal structures
Compounds previously studied in solution or single crystal form

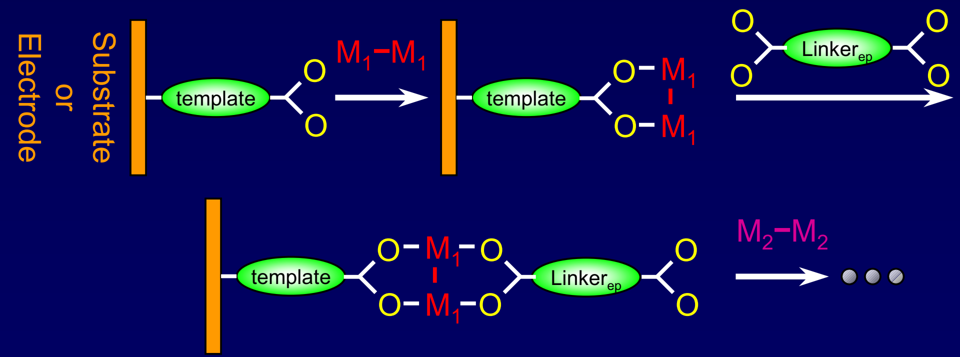
Metal-Metal Bonded Supramolecules

Assembling Devices:

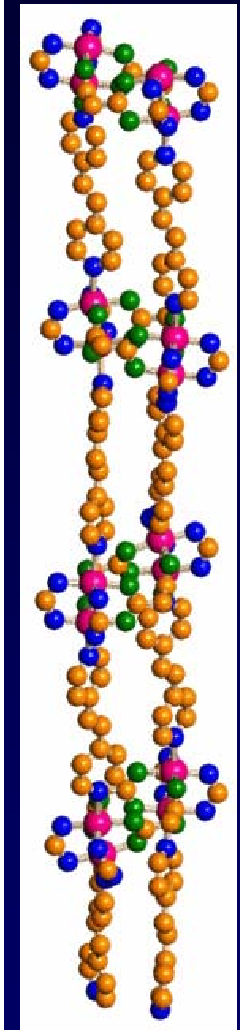
1 Link axially, functionalize equatorial positions

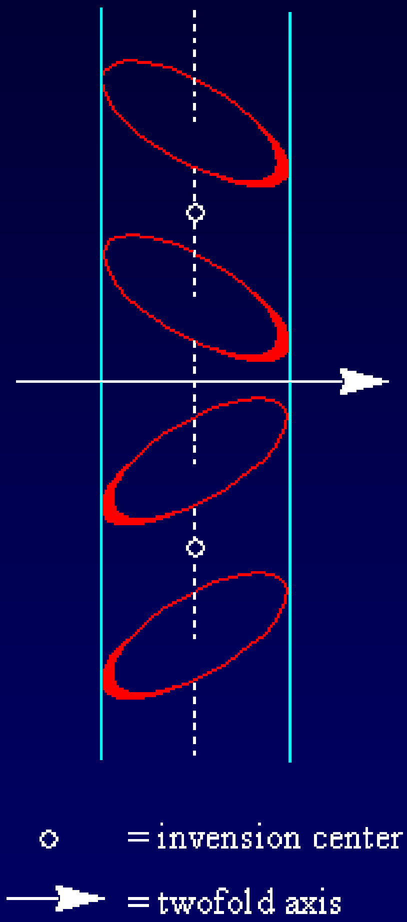


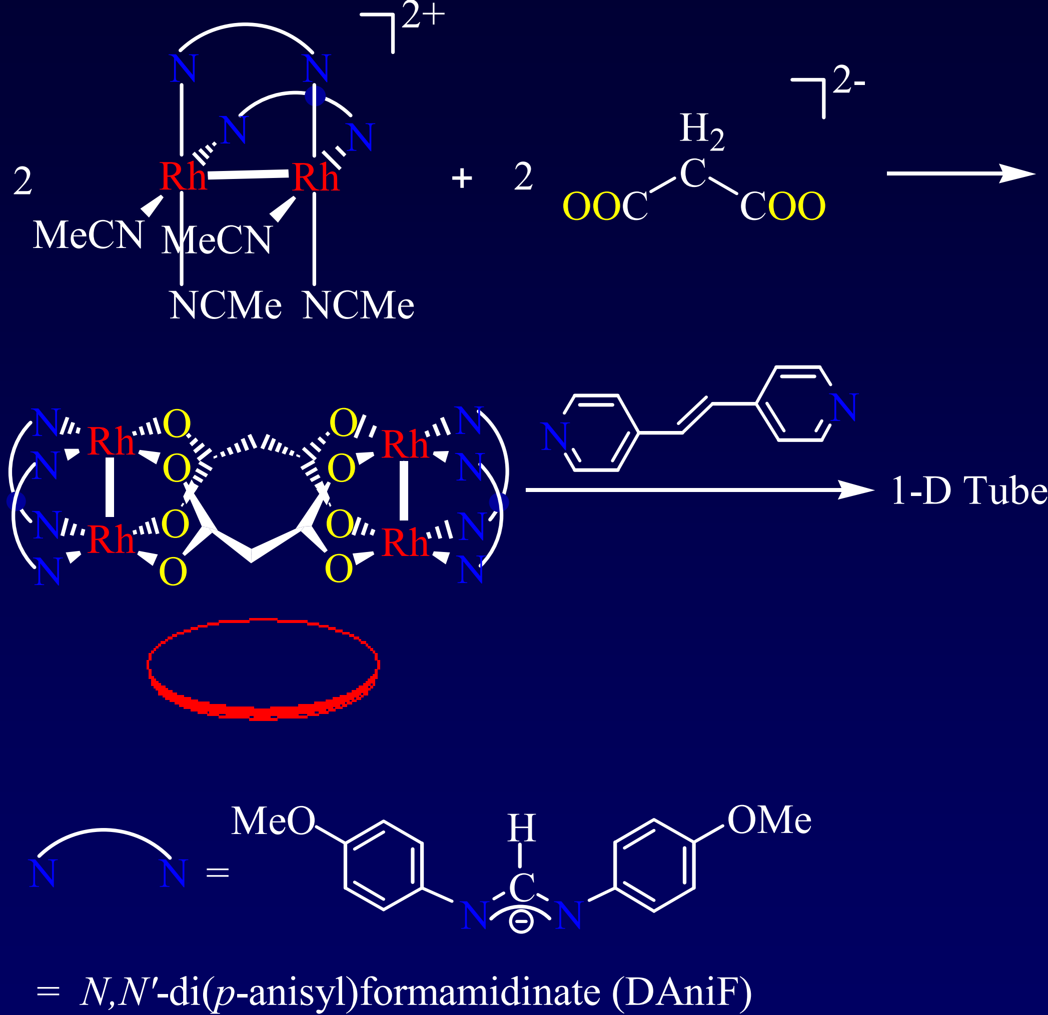
2 Link equitorially, functionalize axial positions



Molecular Tube

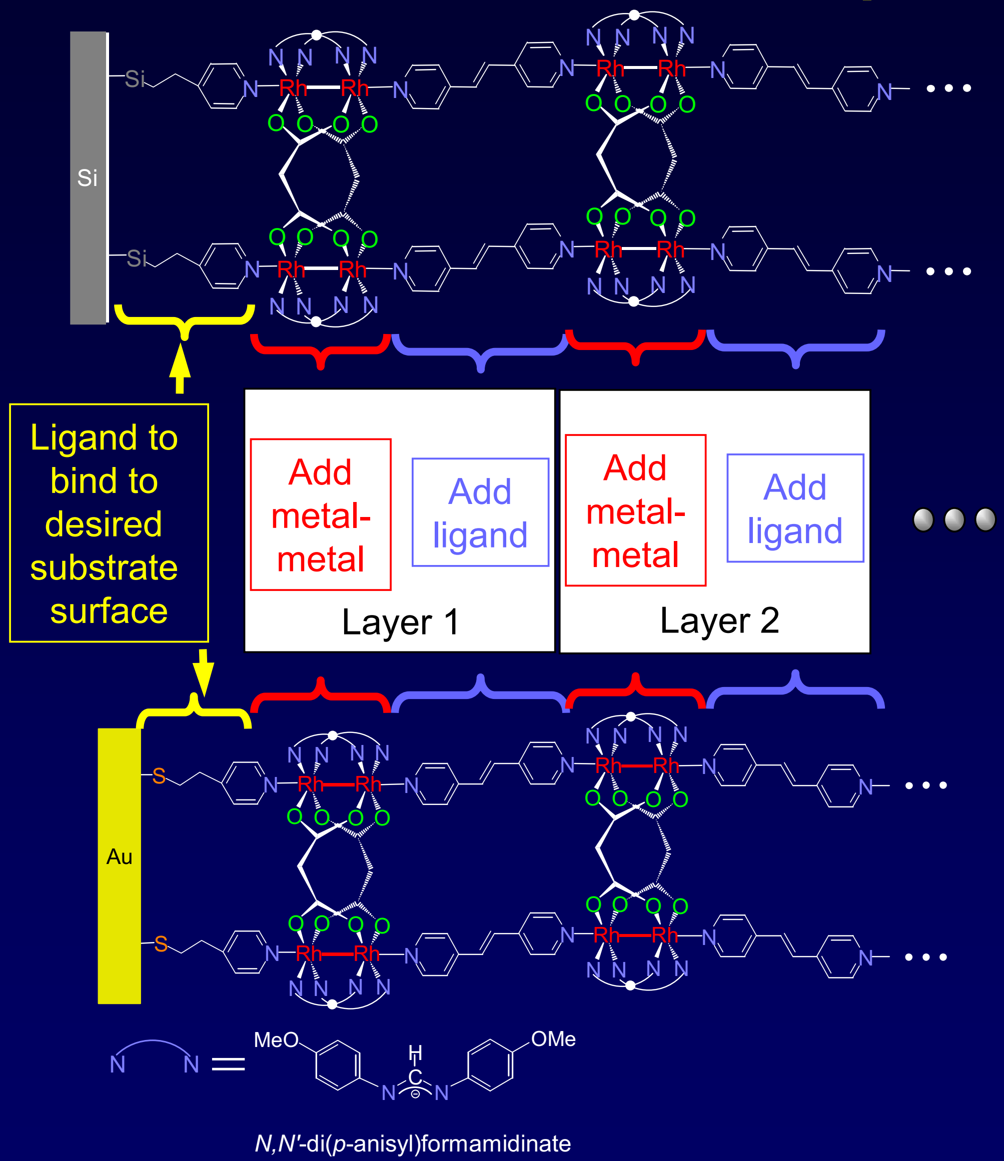






Cotton, Lin, Murillo *Chem. Commun.* **2001**, 11.

Layer-By-Layer Growth of Metal-Metal Bonded Compounds



Tailor head group of ligand
to bind to
particular substrate surface

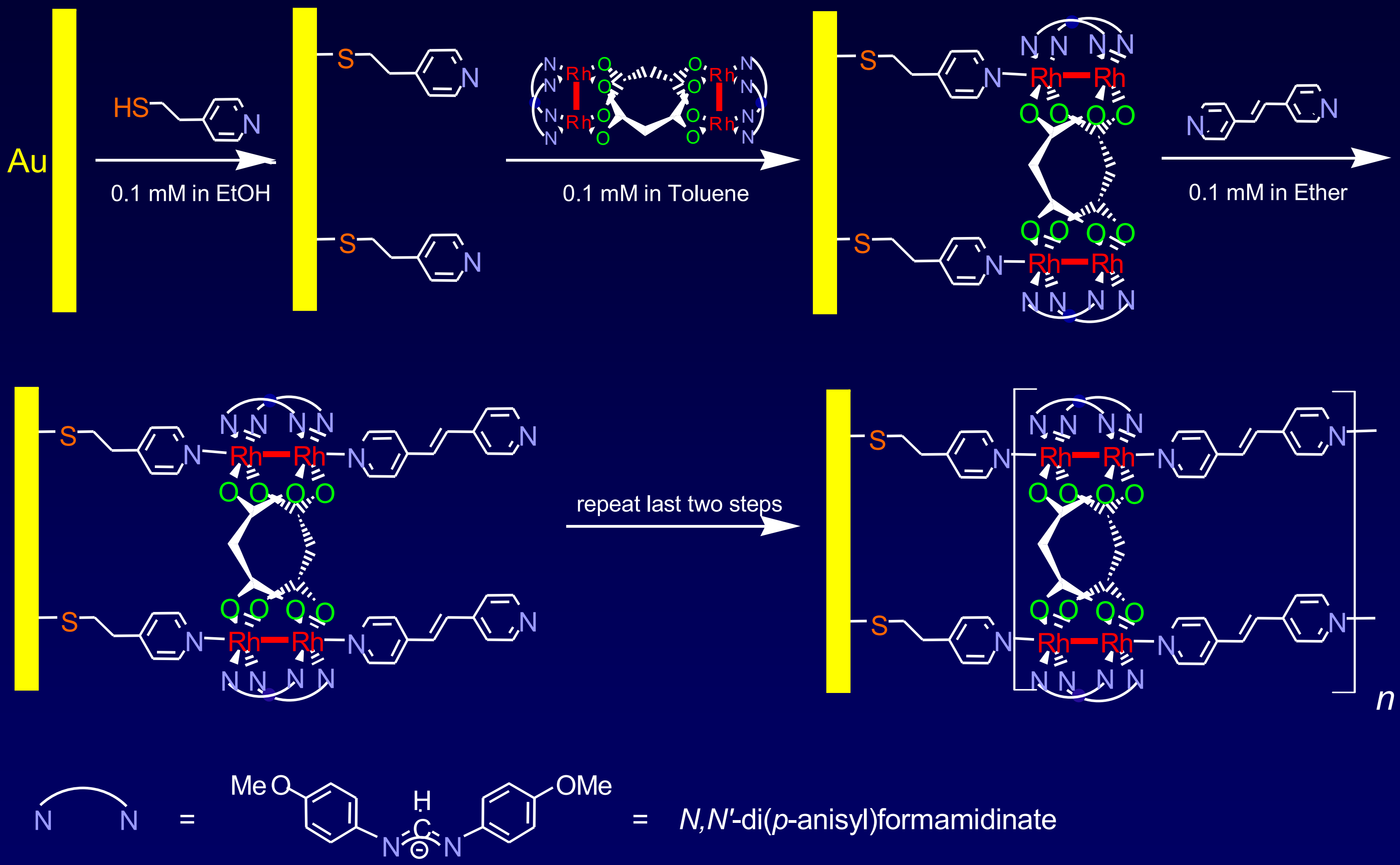
Tailor end group
to template
metal-metal bonded unit

Choose M-M bond

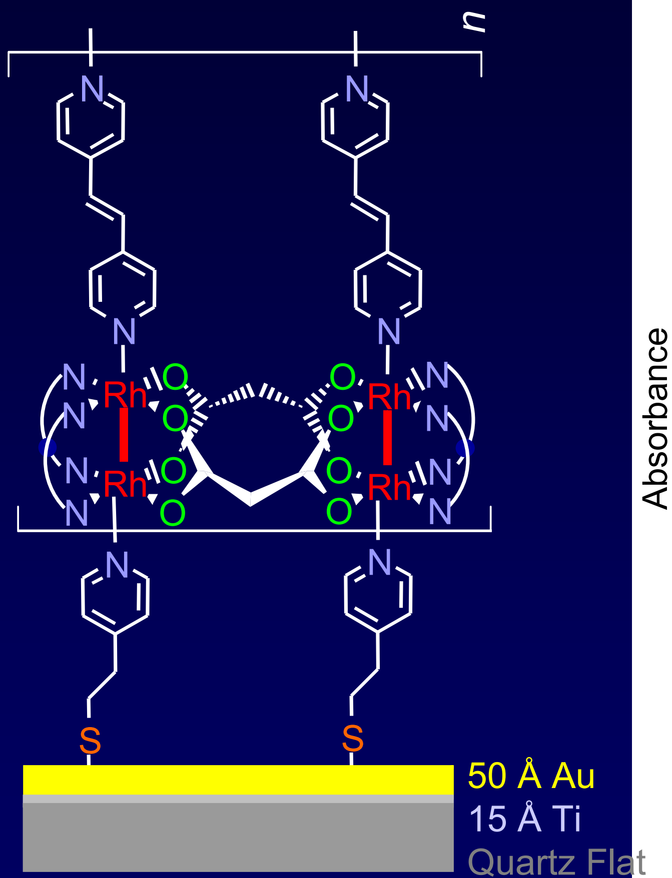
Choose ligand to bridge
M-M bonded units

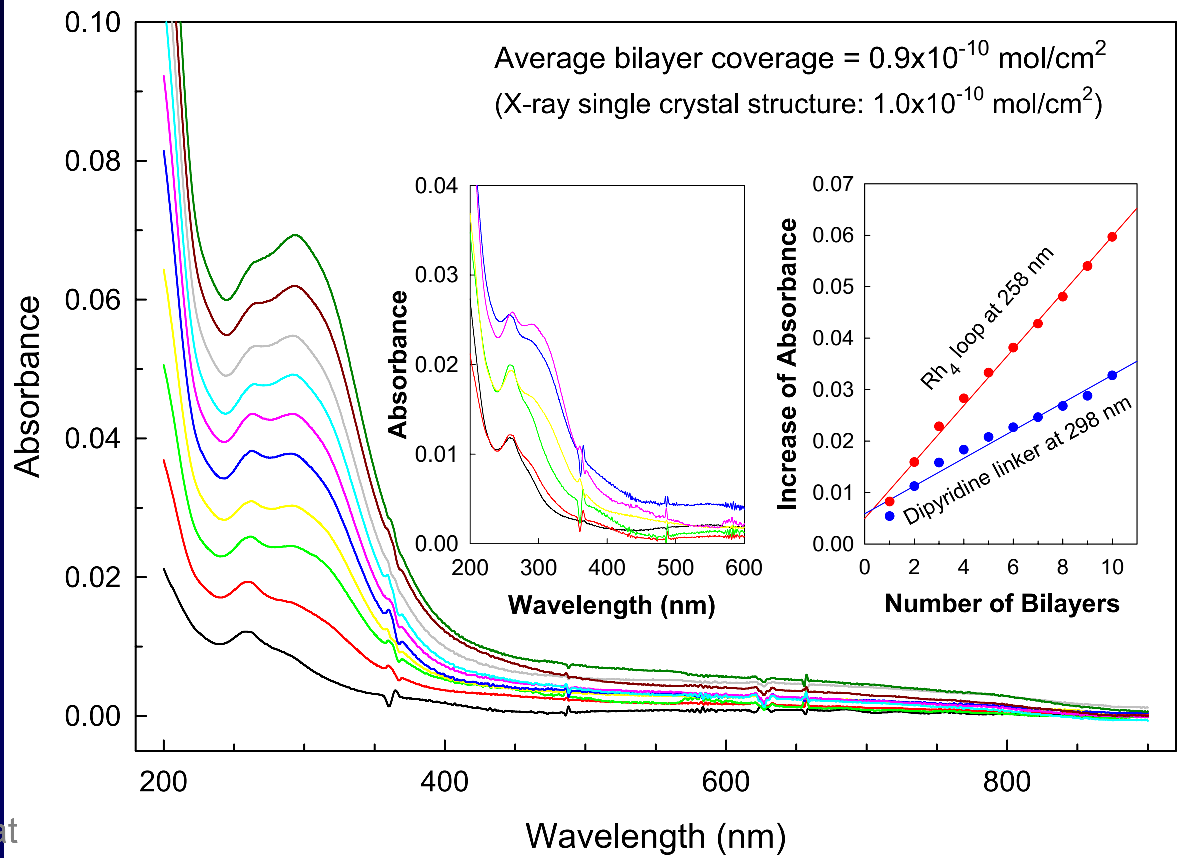
C. Lin, C. R. Kagan *JACS*, **125**, 336 (2003)

Synthetic Steps for Layer-By-Layer Growth

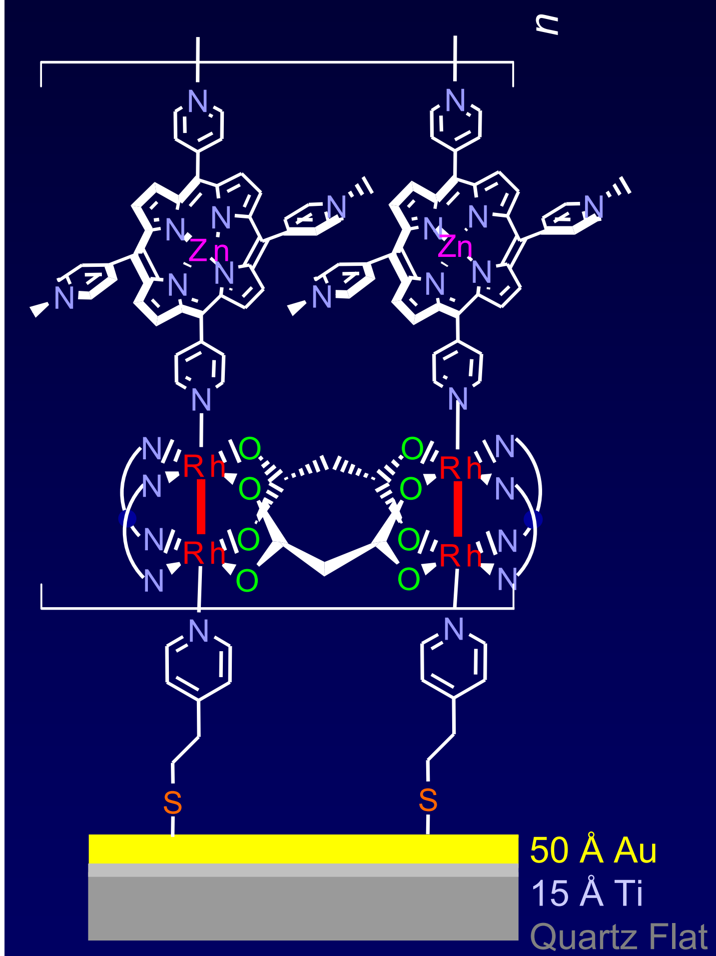


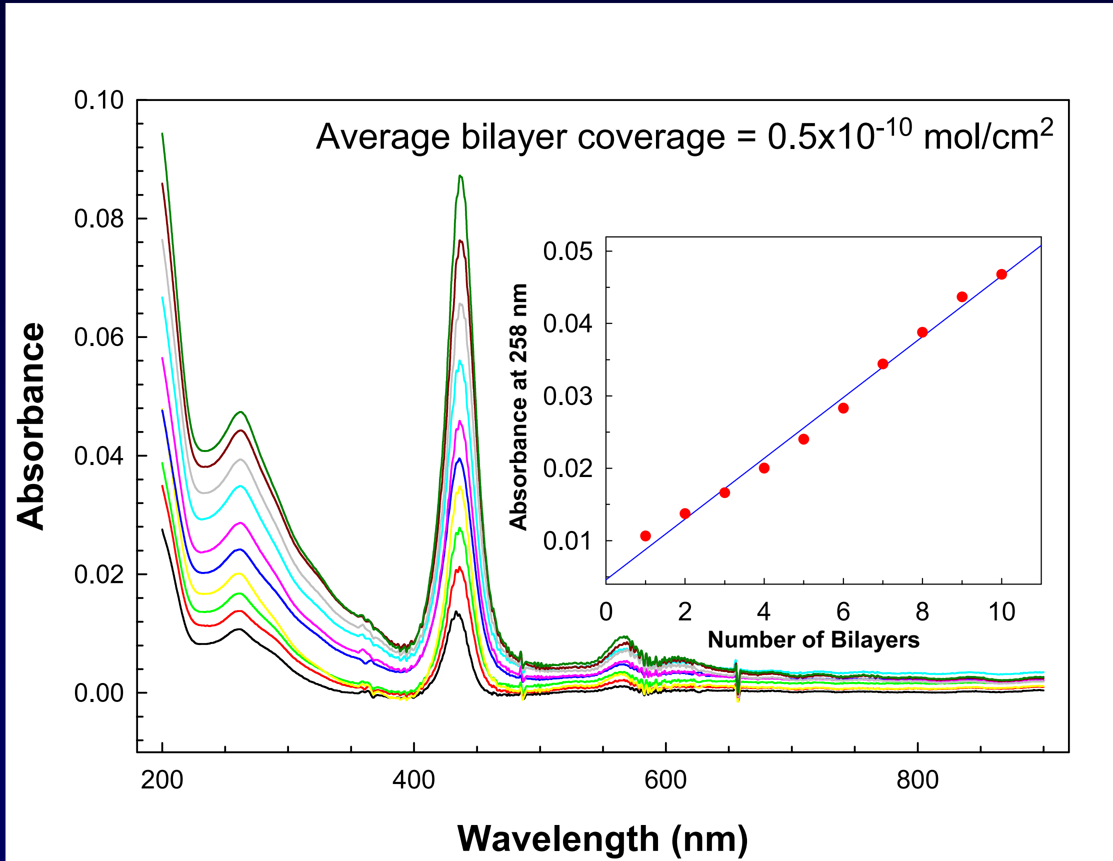
Monitor Layer-By-Layer Growth by UV-vis Absorption



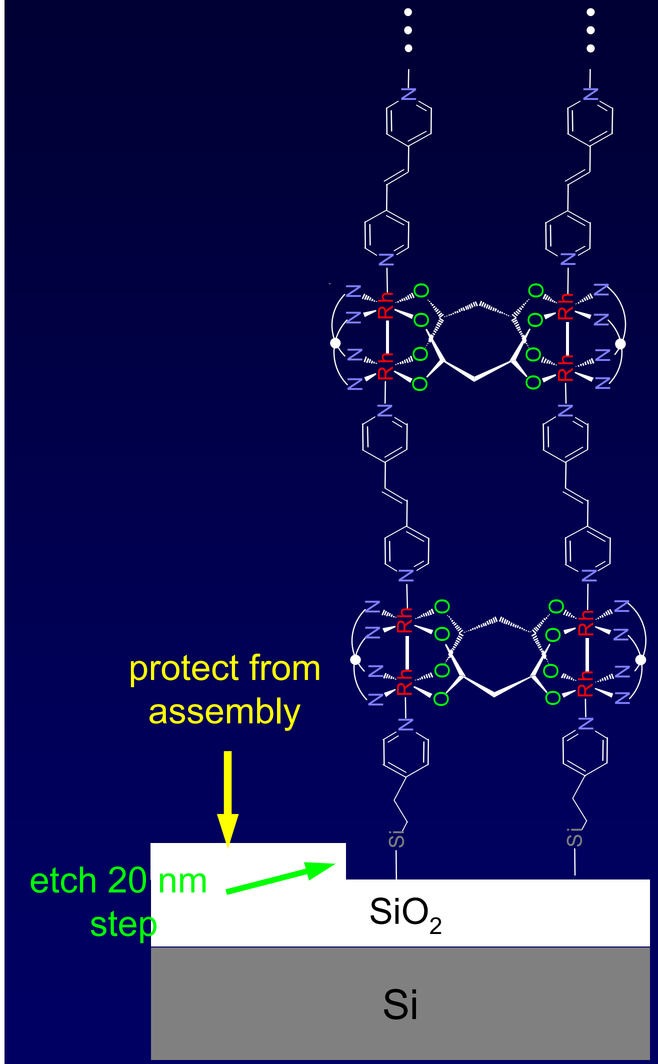


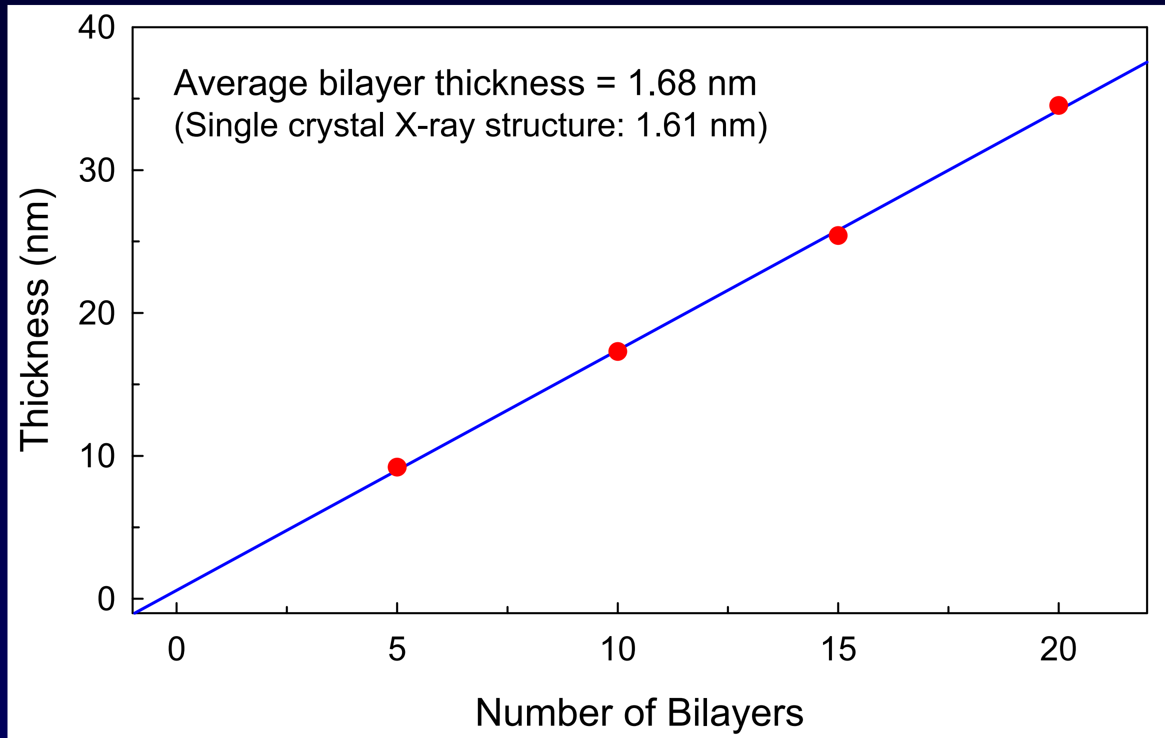
Monitor Layer-By-Layer Growth by UV-vis Absorption

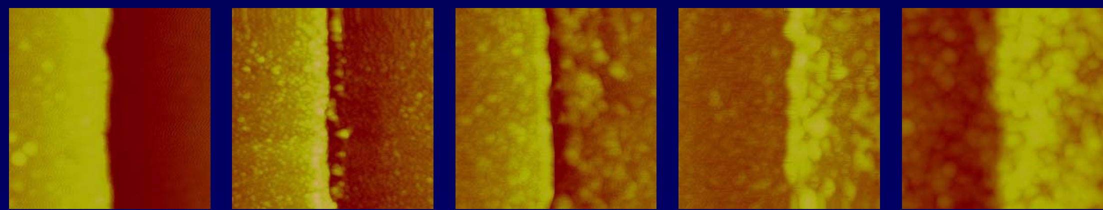




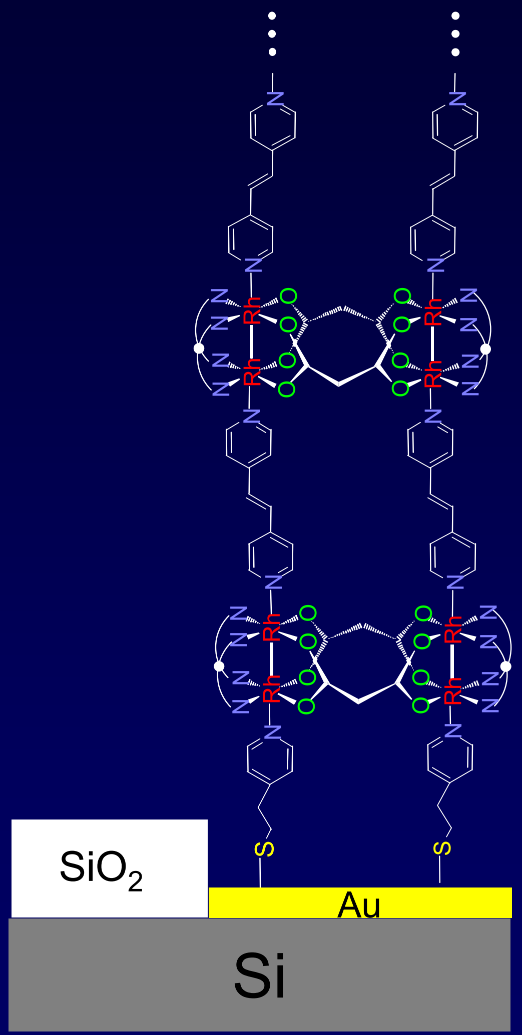
Monitor Layer-By-Layer Growth via AFM on SiO_2

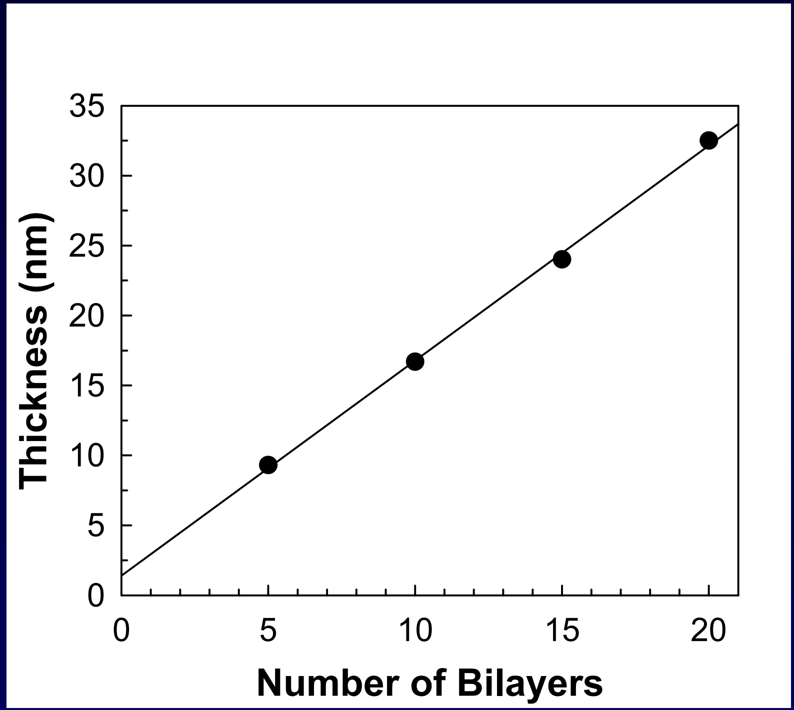




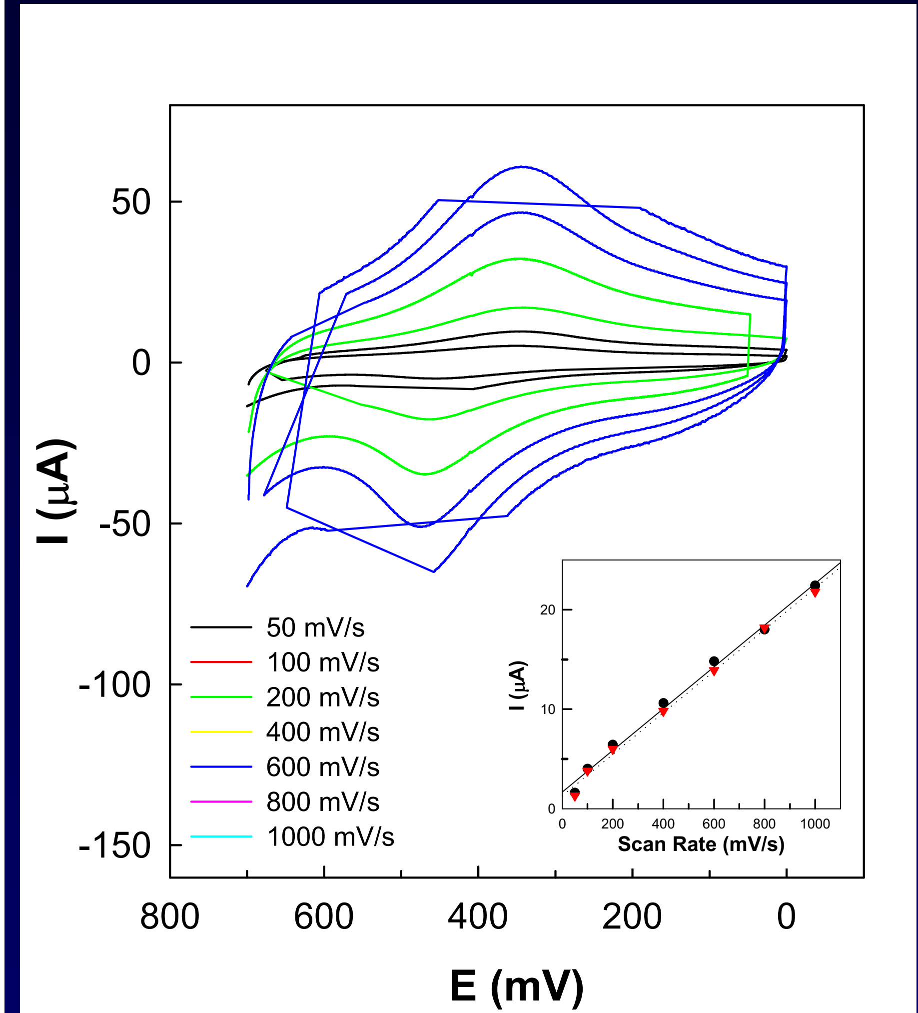


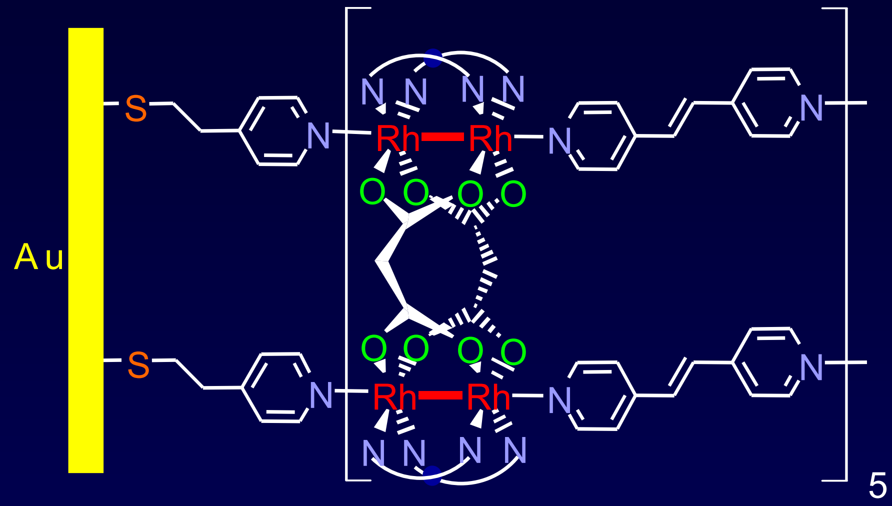
Monitor Layer-By-Layer Growth via AFM on Au





Electrochemistry of Metal-Metal Bonded Layers

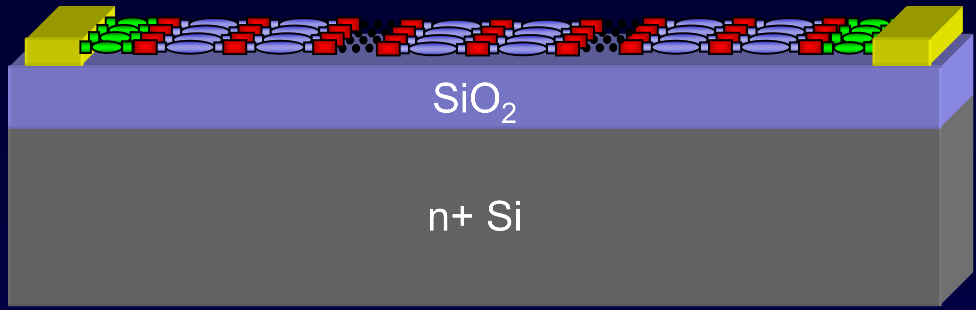


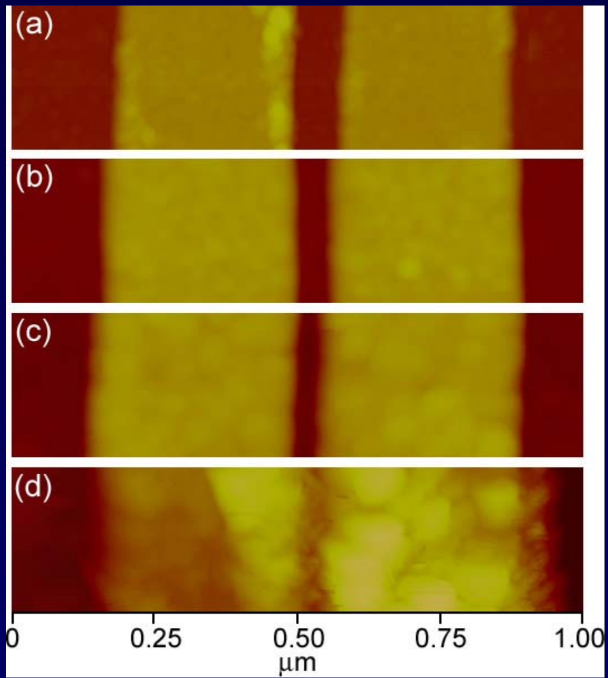


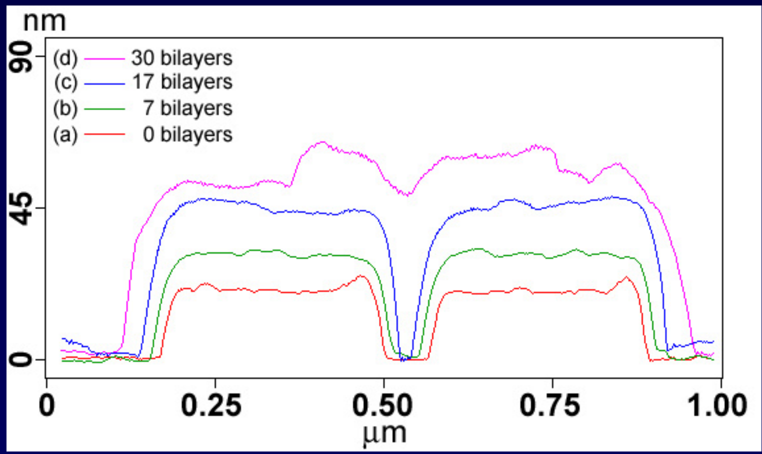
$$Rh_2^{4+} \underset{+\,e}{\overset{-\,e}{\rightleftharpoons}} Rh_2^{5+}$$

- $i_p \propto v$
- $E_p \neq f(v)$
- E^o = 406 mV *vs* Ag/AgCl in 1M NaCl

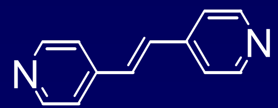
AFM images showing Layer-by-Layer Growth Across nm Scale Electrodes



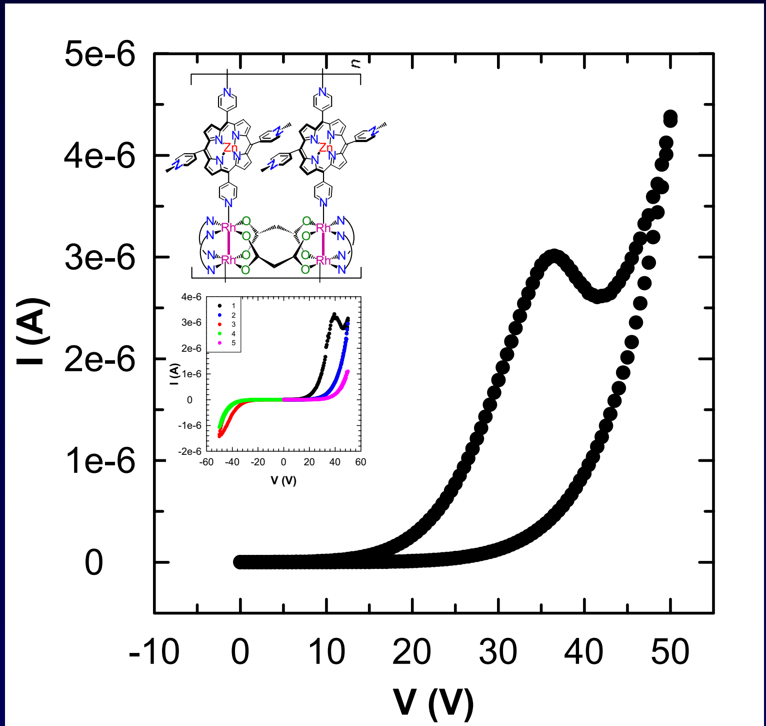


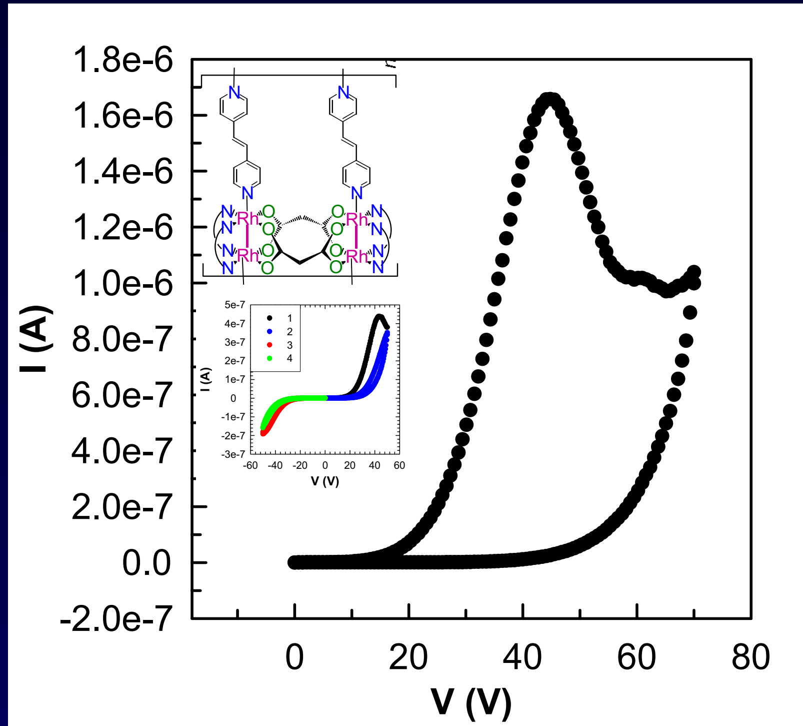


Axial Linker



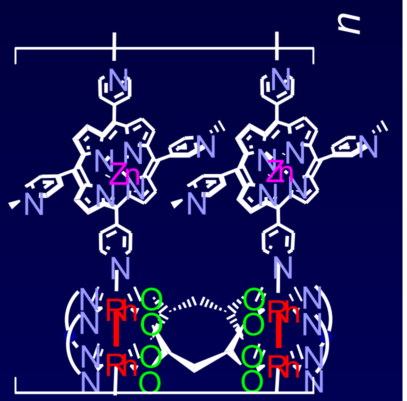
I-V Characteristics of Rh-Rh Supramolecules Grown Layer-by-Layer Across Device Channel

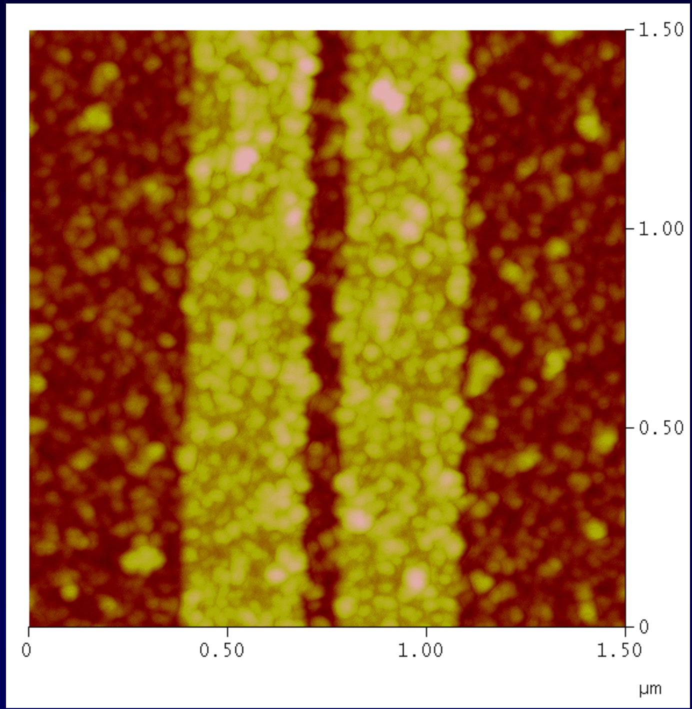


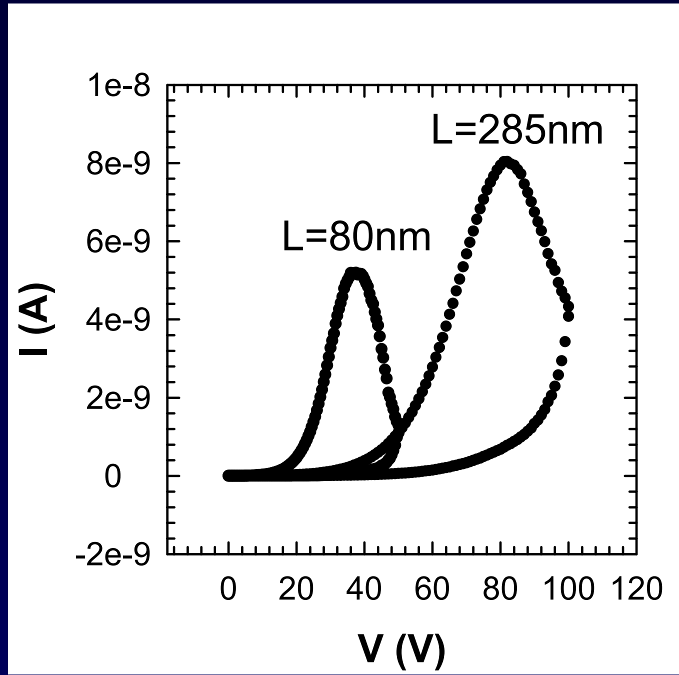


- Room Temperature
- Reproducible "Negative Differential Resistance"
  - Device-to-Device on Same Chip
  - Different Chip
  - Near Perfect Yield
- Not Reversible

Spin-coating Metal-Metal Bond Complex to Form Polycrystalline Thin Film

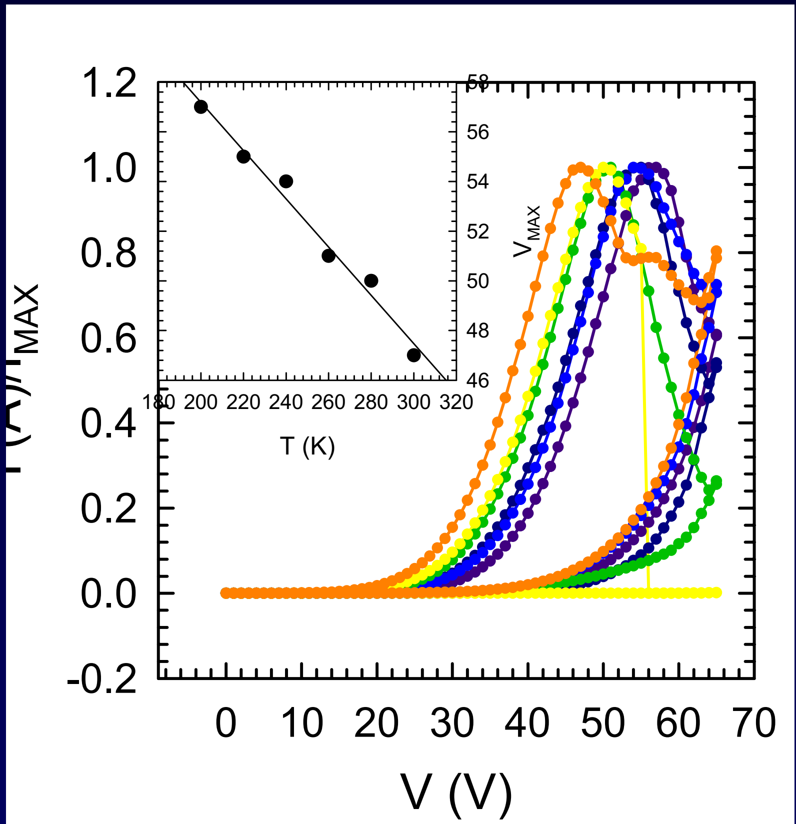




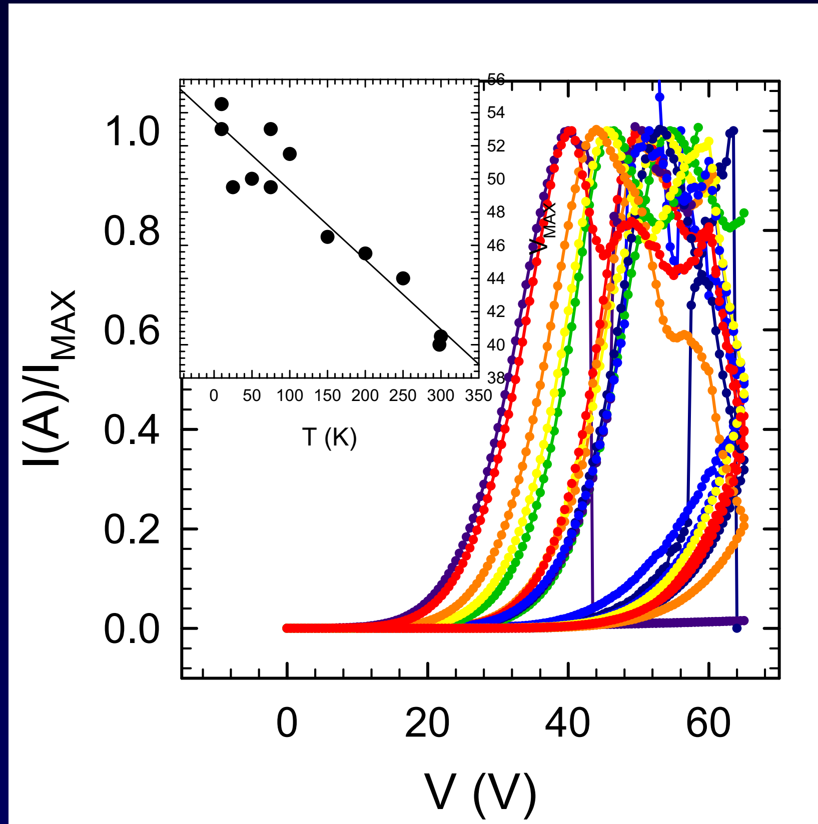


- compound assembles to form a polycrystalline thin film
- grain structure characteristic of underlying structural motif
- I-V characteristic show similar behavior
- peak potential increases with increasing channel length

Temperature Dependent I-V Characteristics
Rh-Rh Supramolecule with DipyridylEthylene Ligand



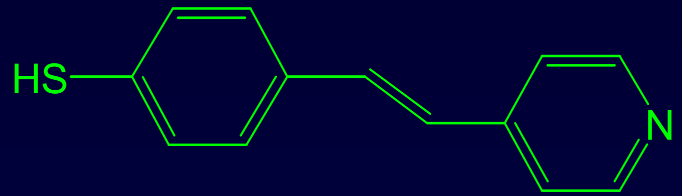
200-300K



5-300K

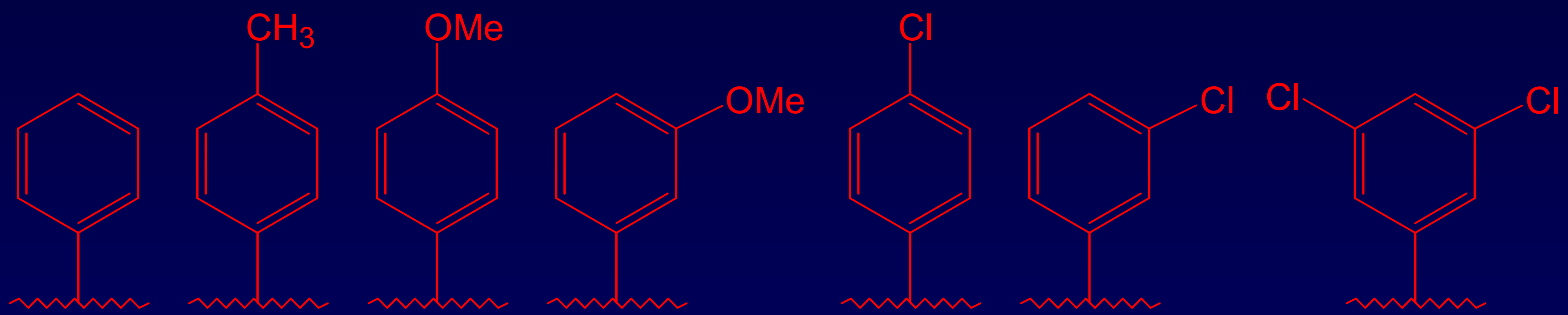
Chemical Manipulation : Examples

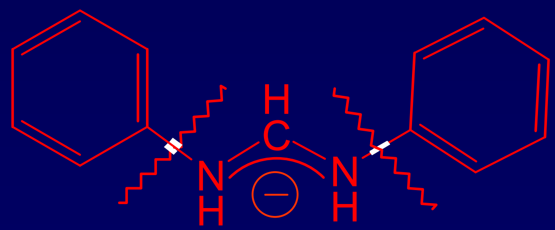
Surface Template – Molecule-Metal Contact



A. Afzali

Equitorial Ligands – “Switching” Potential, Receptors



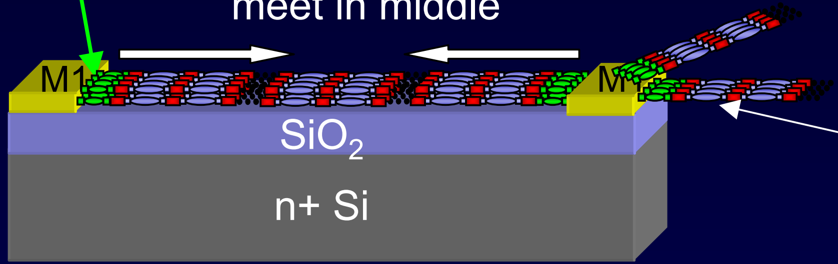


L. Vyklicky

Controlling Molecular Assembly through Device Geometry

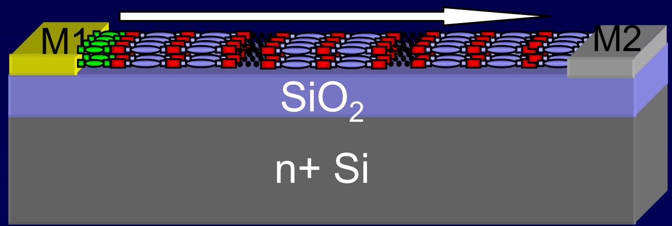
molecular template

step-wise assembly meet in middle



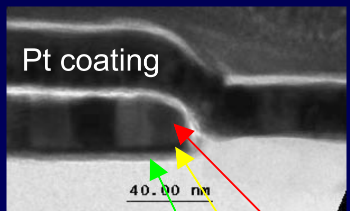
molecular material assembles everywhere off same metal surface

step-wise assembly from one-side to the other

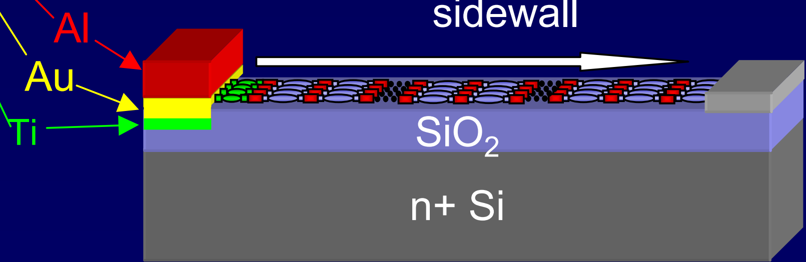


different metal electrodes

a start



limit assembly to electrode sidewall



embedded electrodes
hide adhesion layer
limit molecular assembly

control charge flow in device

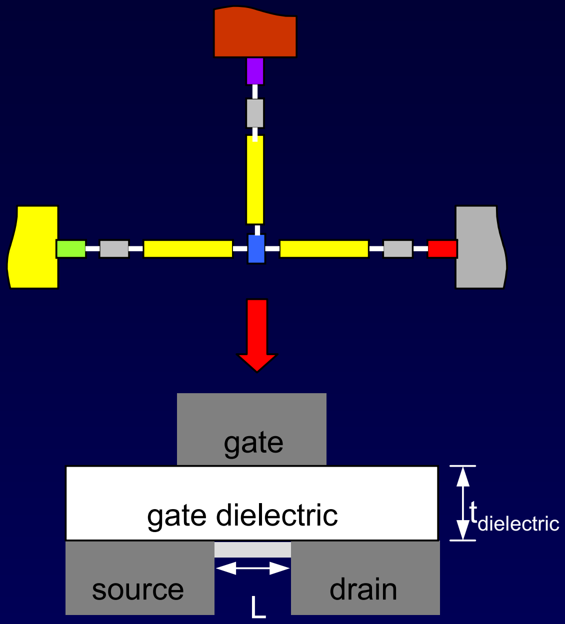
The Physics of Molecular Devices

Cherie R. Kagan

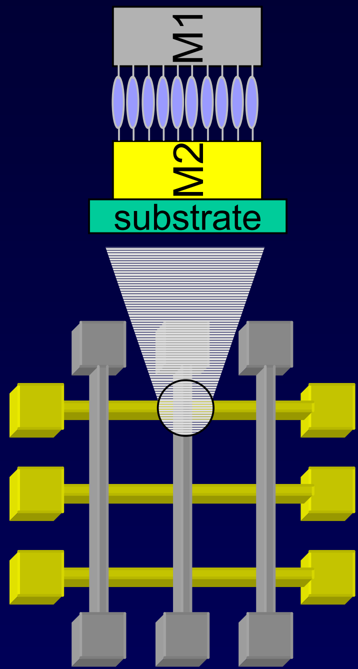
IBM T. J. Watson Research Center
Yorktown Heights, NY

Molecular Electronics, Memory, Sensors

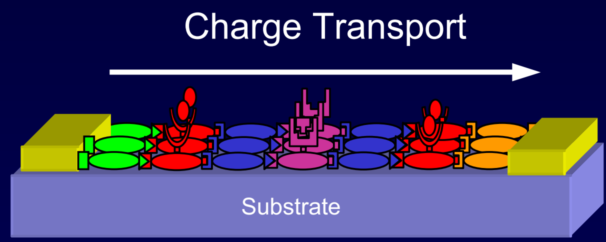
Transistors



Memory



Sensor

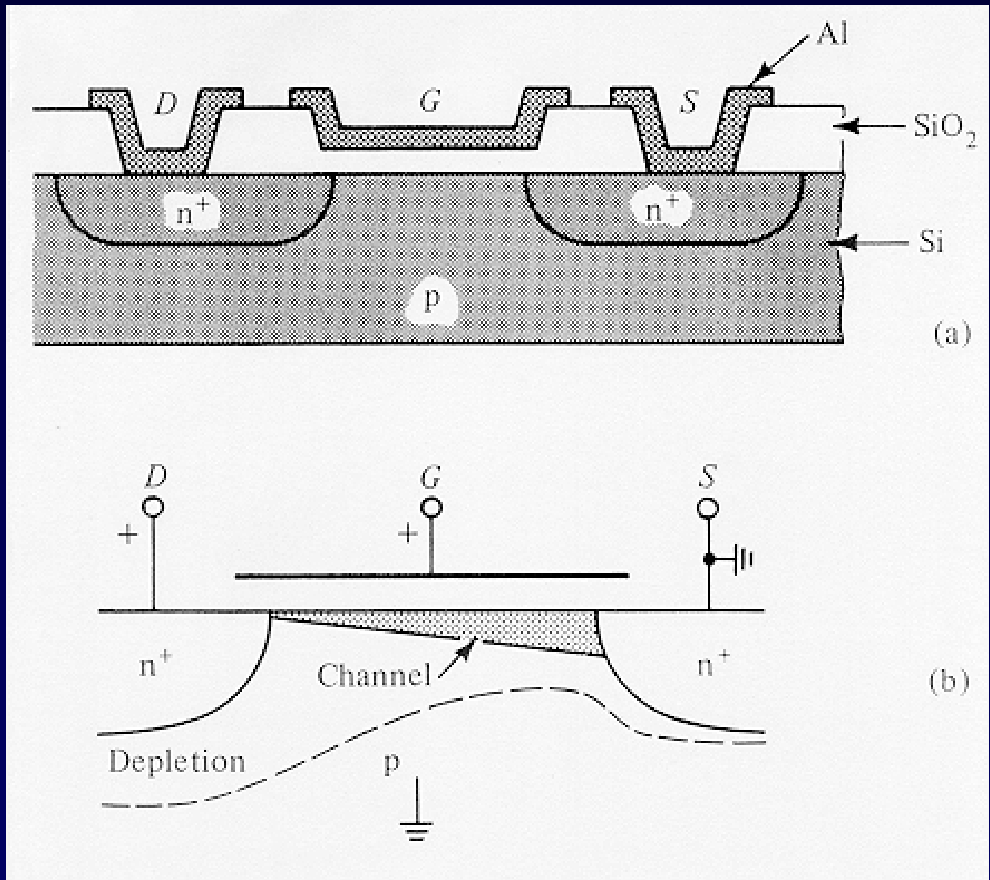


Molecular Electronics, Memory, and Sensors
Opportunity for Solid State Chemistry and Physics

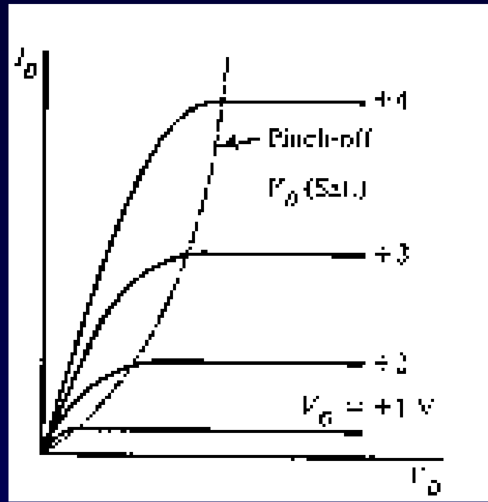
Understand:

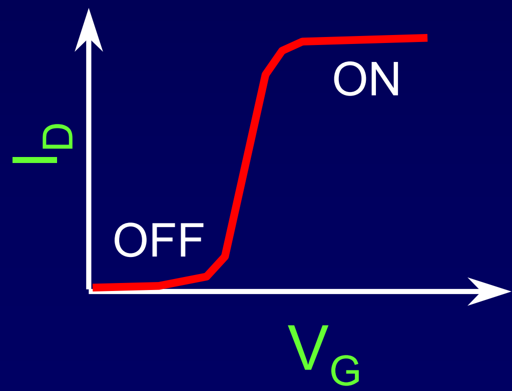
- Molecular design, assembly, and function
- Device Test Structures
- Use Chemistry to Build Devices

Metal-Insulator-Semiconductor Field Effect Transistor (MISFET)

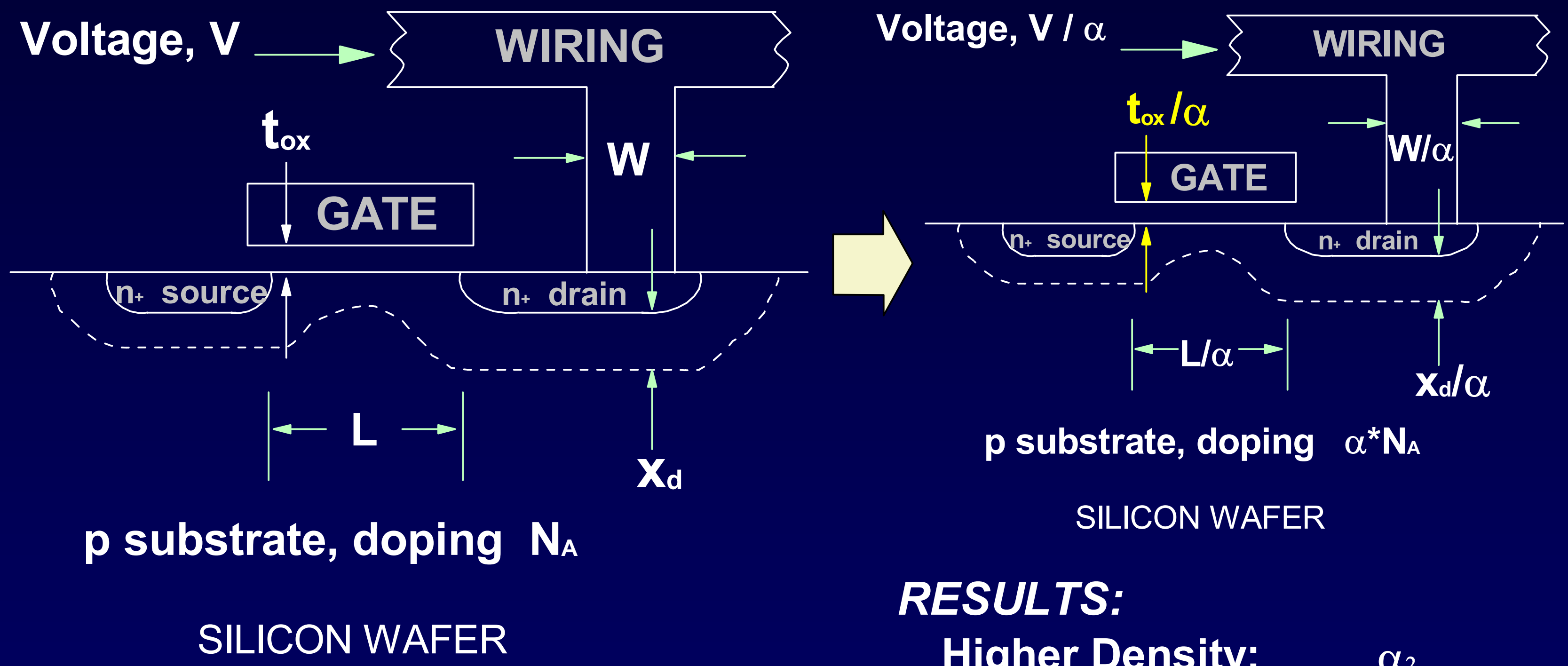


Cross section and schematic illustration of a MOS transistor.





Transistor Scaling (Dennard Scaling)



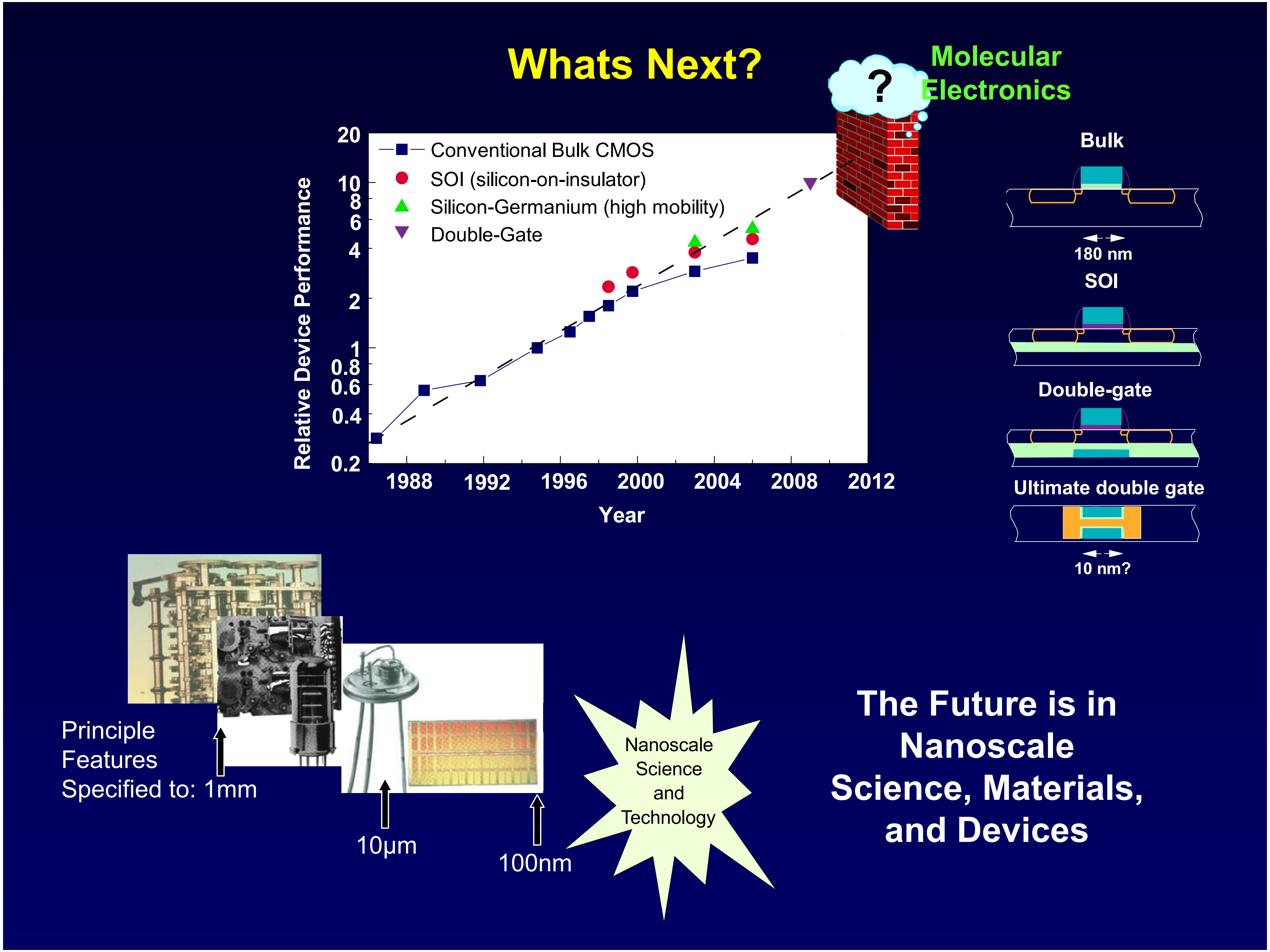
RESULTS:

Higher Density: α^2

Higher Speed: α

Lower Power: per circuit $1/\alpha^2$

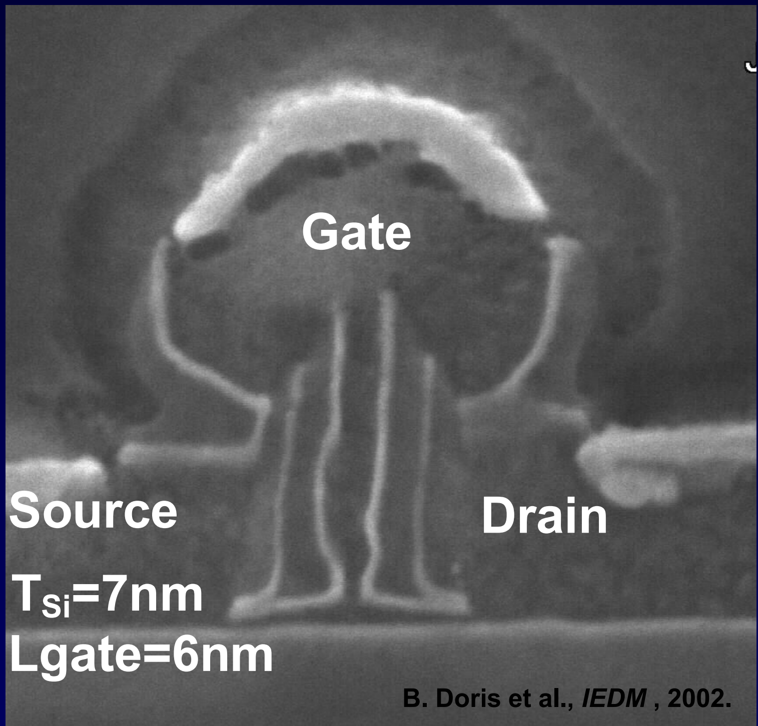
Power Density: **Constant**



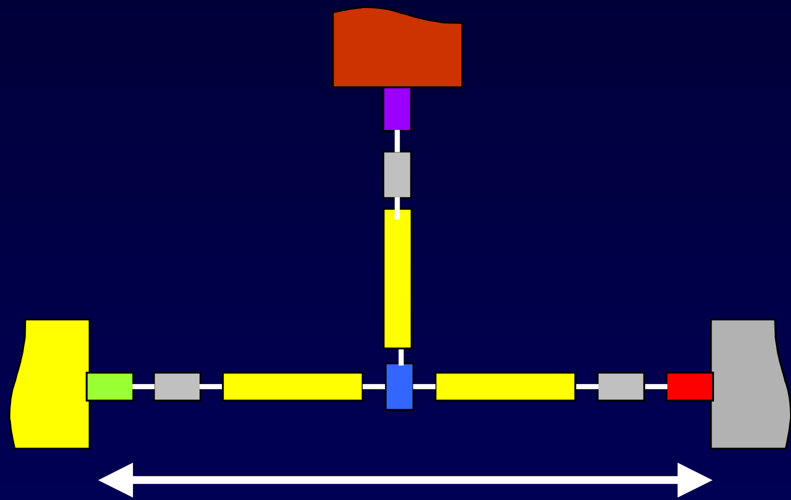
Whats Next?
?
Molecular Electronics
Relative Device Performance
20
10
8
6
4
2
1
0.8
0.6
0.4
0.2
1988
1992
1996
2000
2004
2008
2012
Year
Conventional Bulk CMOS
SOI (silicon-on-insulator)
Silicon-Germanium (high mobility)
Double-Gate
Bulk
180 nm
SOI
Double-gate
Ultimate double gate
10 nm?
Principle Features Specified to: 1mm
10µm
100nm
Nanoscale Science and Technology
The Future is in Nanoscale Science, Materials, and Devices

Its Not Only in Size, But Cost and Functionality

Si FET



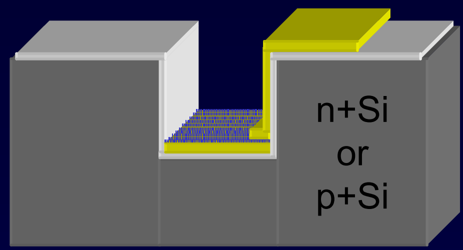
Molecular Device



L >2.5 – 3 nm

- Silicon and Molecular Devices are governed by electrostatics and eventually limited by tunneling
  - difficult to be much smaller than 2 - 3 nm

Colleagues



SAMFET:

Ali Afzali
Richard Martel
Lynne Gignac
Paul Solomon
Alex Schrott
Bruce Ek

Contributions From:

ASTL, Ying Zhang, CSS (Nina Ruiz), T. Domenicucci, Chun Lin
Frank Meyer zu Heringdorf, Mike Prikas, Dave Medeiros,
Vincent Derycke, Harry Hovel, Paul Andry, James Vishiconti

Special Thanks: Ruud Tromp, David Frank, Norton Lang, Phaedon Avouris,
Philip Wong

Self-Assembled Monolayer FETs?

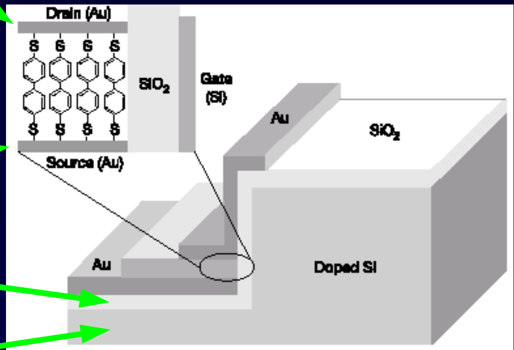
verbally amended SiO_2 thickness on <u>sidewall</u> from 30 to 3-6 nm

Drain by shadow evaporation using trench wall

Source by collimated evaporation

30 nm SiO_2

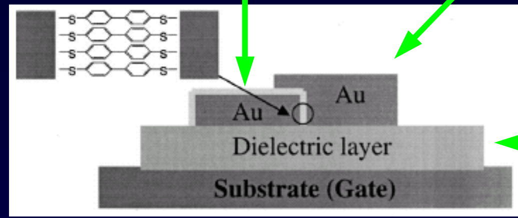
Trench anisotropically etched into (110) n+ Si



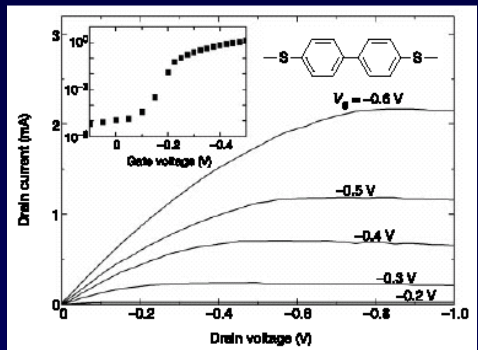
Source 150 Å Au

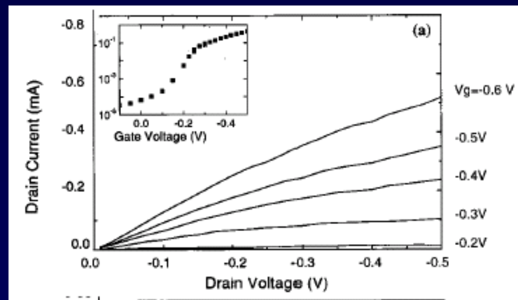
Drain by low angle evaporation

30 nm SiO_2



Reported transconductance ~ 10 mA/V
Wow, that's better than Si Fets!





Cartoon:

- What do the structures really look like?
- Do dithiols form ordered/oriented monolayers?
- Can Au be deposited on the trench bottom without coating the sidewalls?

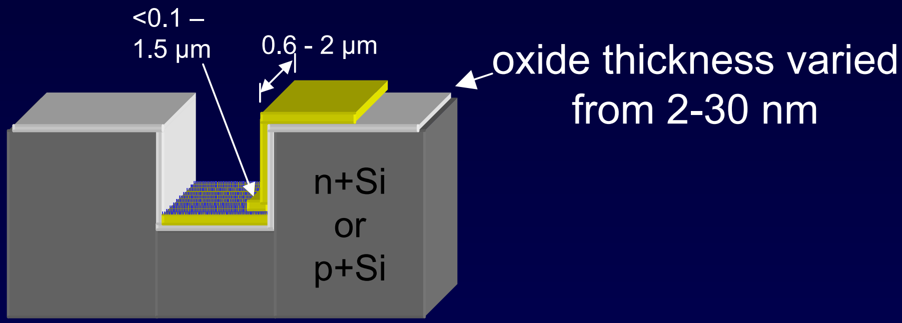
Device Mysteries:

- $L << t_{dielectric\ layer}$
    - Gate field penetrate channel?
    - Long channel behavior?
- At 0 V_G, the device is OFF ?
- Subthreshold slope better than kT/q?

Device Structures - Trenches

Cross-section:

Channel dimensions depend
on which set of structures are chosen
as defined by mask sets



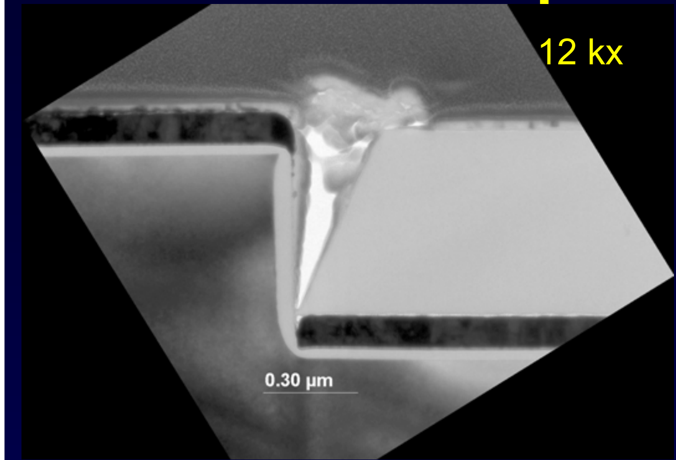
Two approaches:

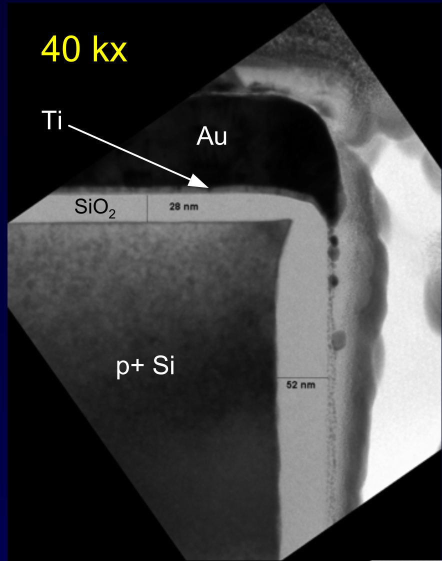
1. RIE using (100) p+ Si
   (note difficult to RIE vertical
   sidewalls in n+ Si, too much
   lateral etching)

2. Wet chemical etch into (110) n+ Si
   (note can't wet etch into p+ Si)

C. R. Kagan, A. Afzali, R. Martel, L. Gignac, P. Solomon, B. Ek, *Nanoletters*, **3**, 119 (2003).

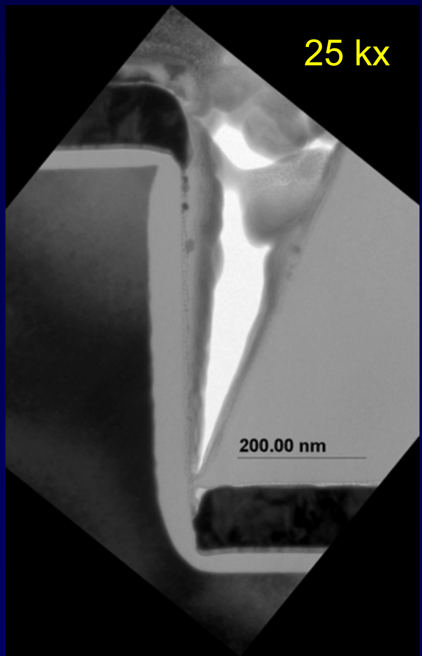
TEM Images of RIE Trench with Bottom Electrode Deposited By Collimated Source

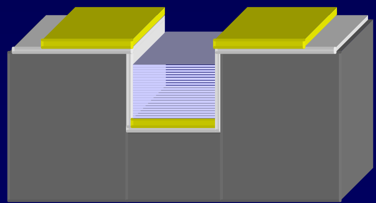




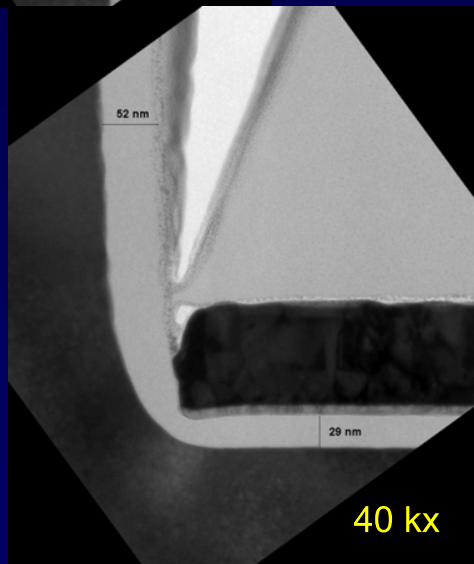
Collimation :
In large part, it is good but, there are particulates on the sidewall

RIE (100)
Sidewall ~1.8x thicker Than bottom and top surface



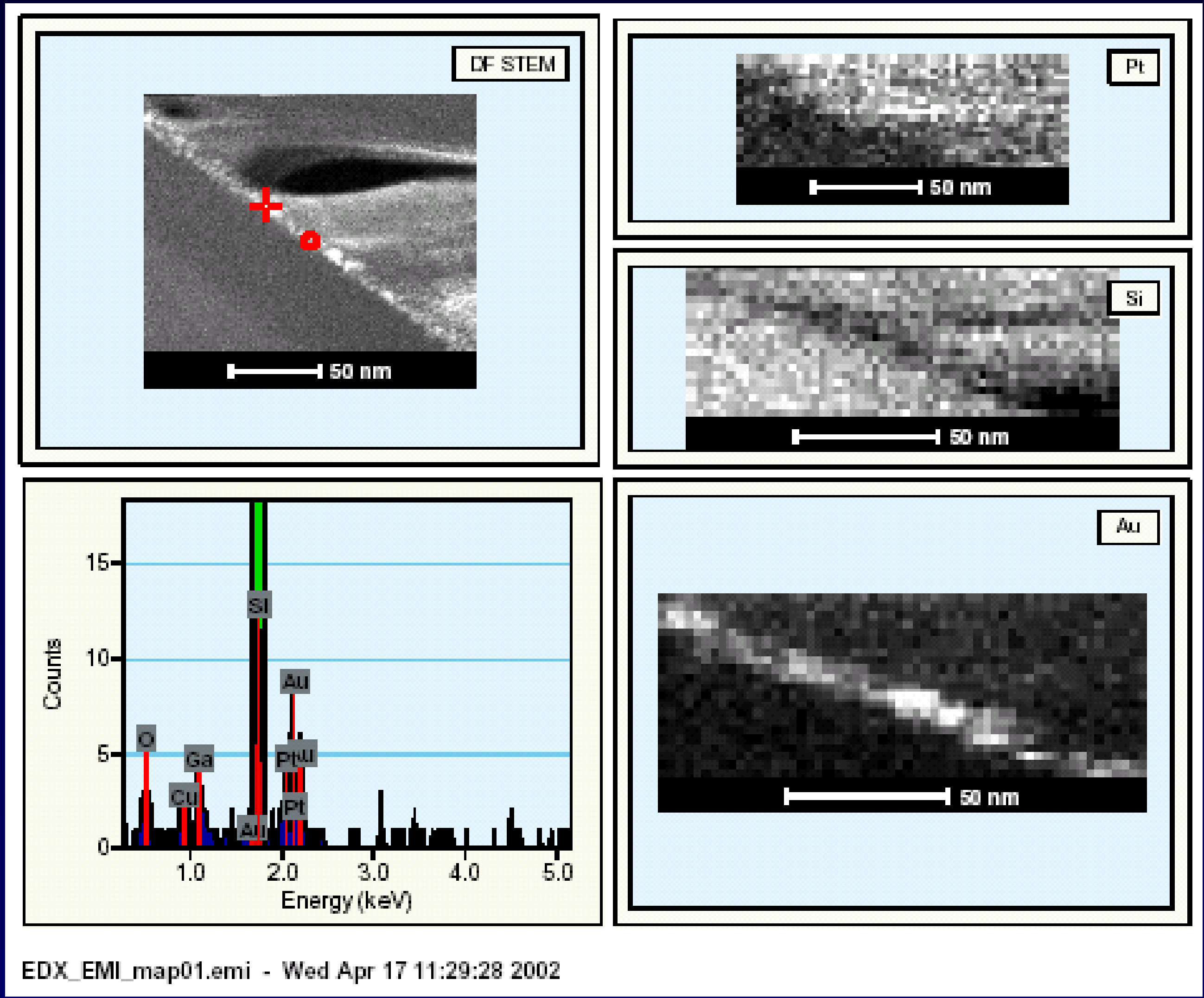


Cartoon



D. B. Kao, J. P. McVittie, W. D. Nix, K. C. Saraswat. *IEEE Trans. Elect. Dev.* **34**, 1008-1017 (1987).

EDS Data of Gold Electrode in RIE Trenches

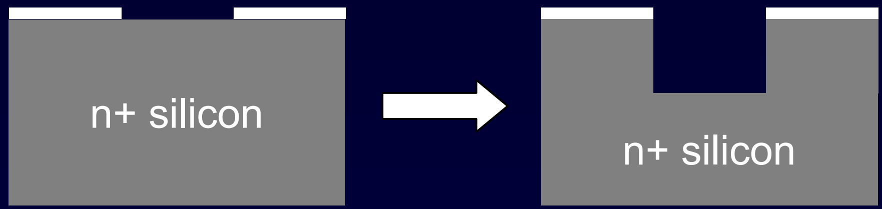


Pt is used to FIB the structure

Sidewall is rotated from 12 to 4'oclock in images

Au is on sidewall although not continuous

(110) Trenches: KOH Anisotropic Etch

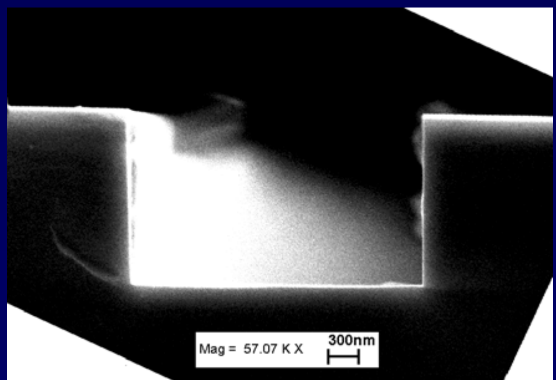


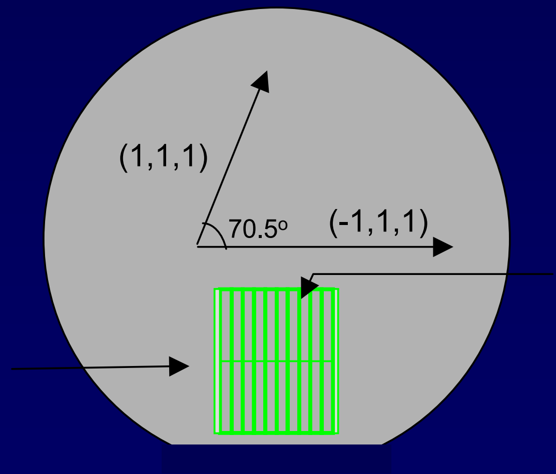
Alignment within +/- 0.1° necessary
- wafer flat cut accurate to +/- 0.5°
- Two stage process: alignment pattern first be etched to accurately locate {-1,1,1}

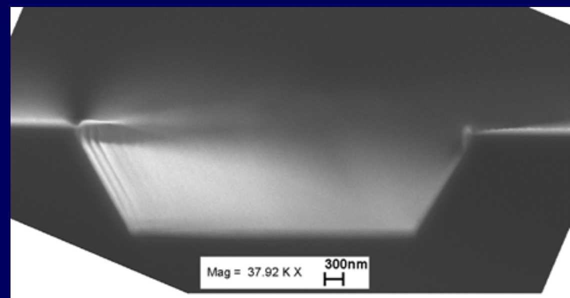
Small misalignment produces:
- Lower aspect ratio (h/L)
- Non-vertical sidewalls

Additional requirements for high aspect ratio and finish:
- High KOH concentration = 44% (isopropanol added to improve surface finish)
- Rate and finish strongly dependent on:
  - Temperature of bath
  - Agitation (avoid bubble formation at Si surface)

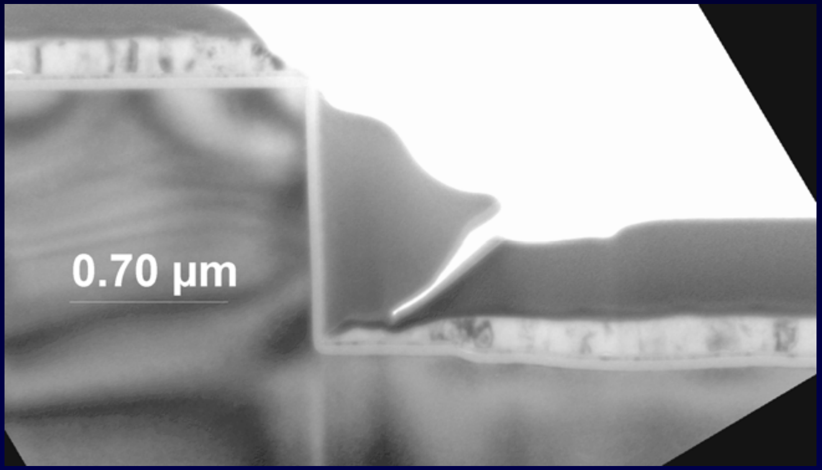
Alignment of mask with the {-1,1,1} plane is critical

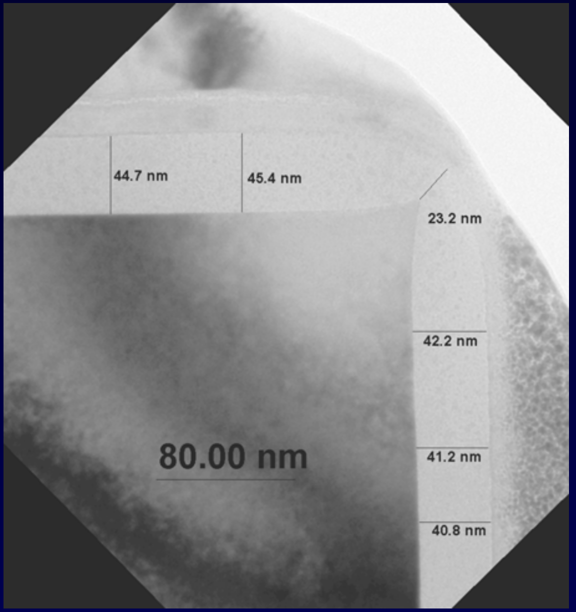


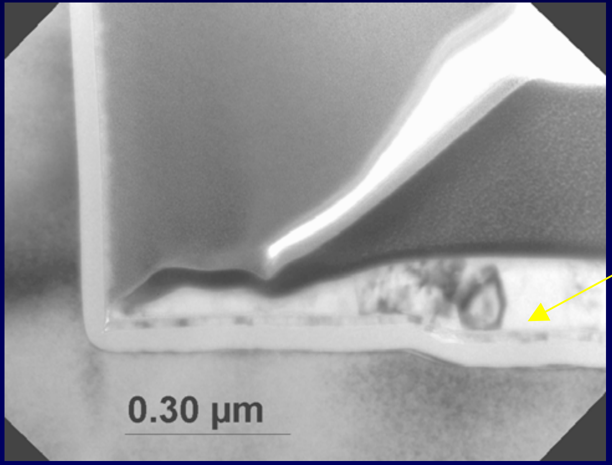




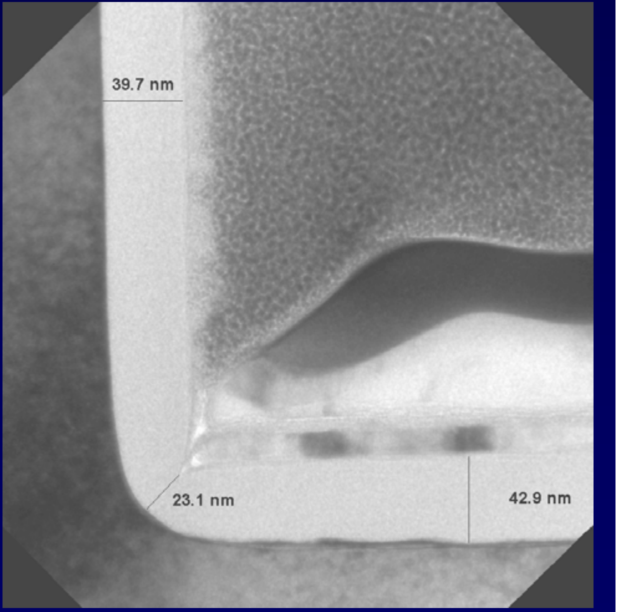
(110) Trench After Oxidation







Roughness in trench bottom

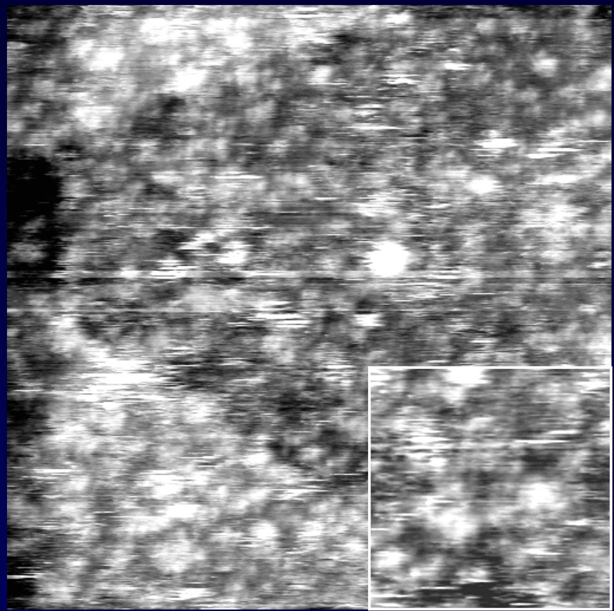


Aim: 30 nm oxidation, always greater in n+ Si than on n, p, or p+ Si

Conclusion: t_{oxide}(sidewall) ~ t_{oxide}(top/bottom)

STM of 1,1’-biphenyl-4,4’-dithiol and hexanethiol Assembled on Flame-Annealed Au/Mica

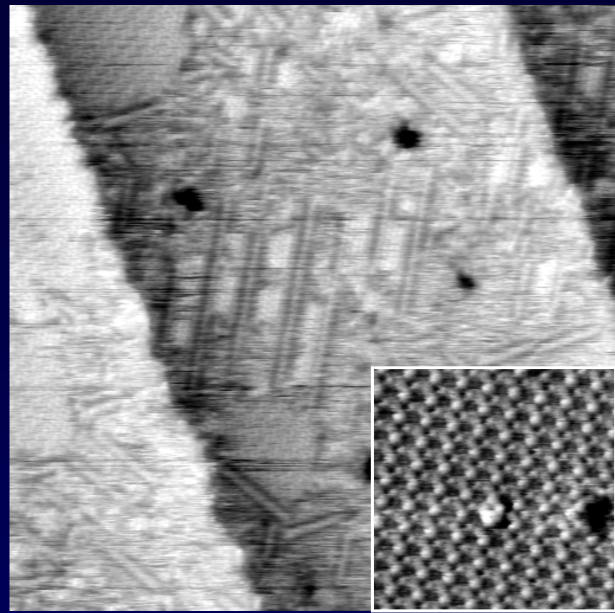
1,1’-biphenyl-4,4’-dithiol



5 nm

60 nm

hexanethiol

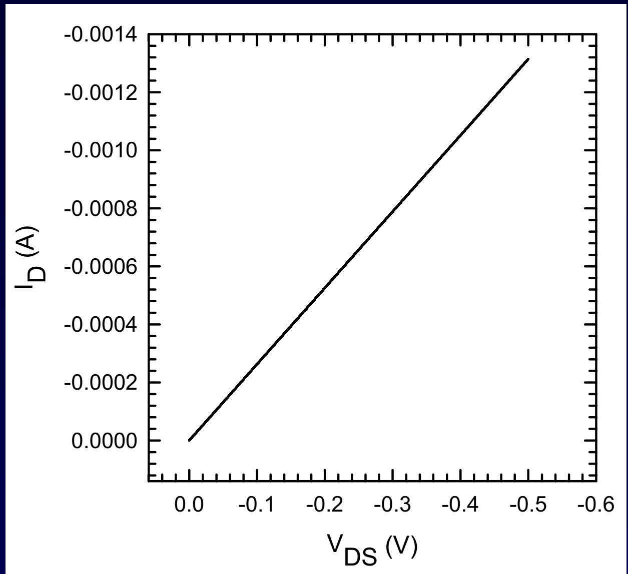


10 nm

50 nm

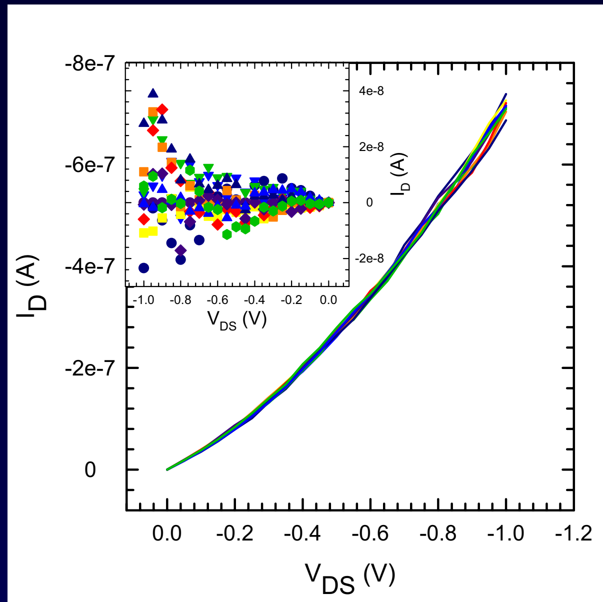
- biphenyldithiol bound to surface, but not well-ordered
- disorder in dithiols consistent with literature
- disorder in biphenylthiols consistent with literature

Trench Structure with 1,1'-biphenyl-4,4'-dithiol



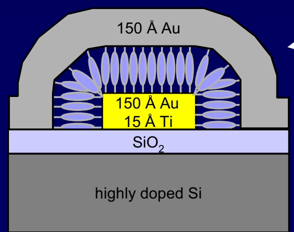
"Monolayer"

characteristics of hundreds of devices
in the trench structure
and thousands in the planar structure



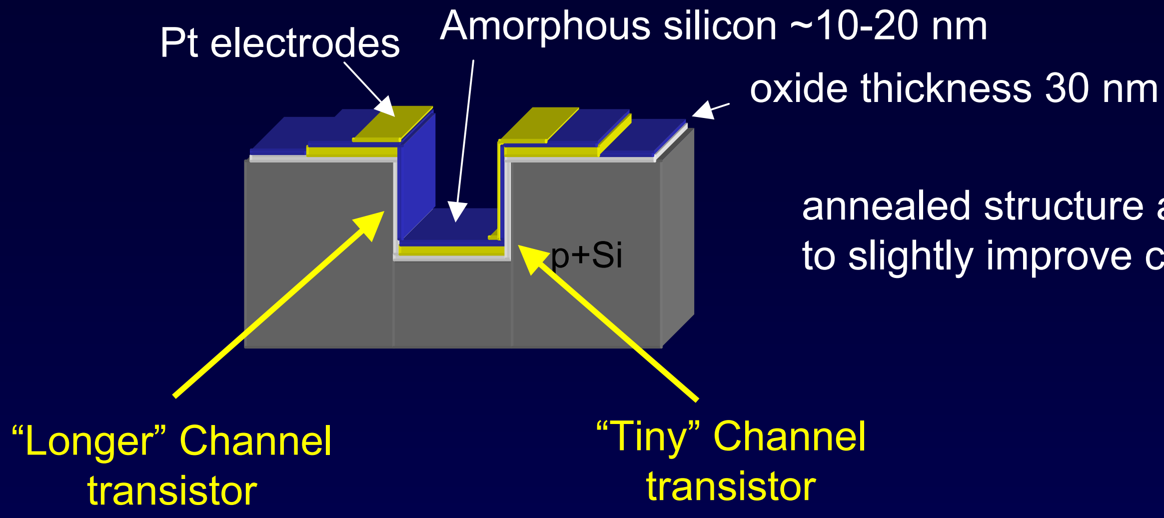
"Multilayer"

representative of ~1% of devices
solution for assembly allowed
to dry on surface

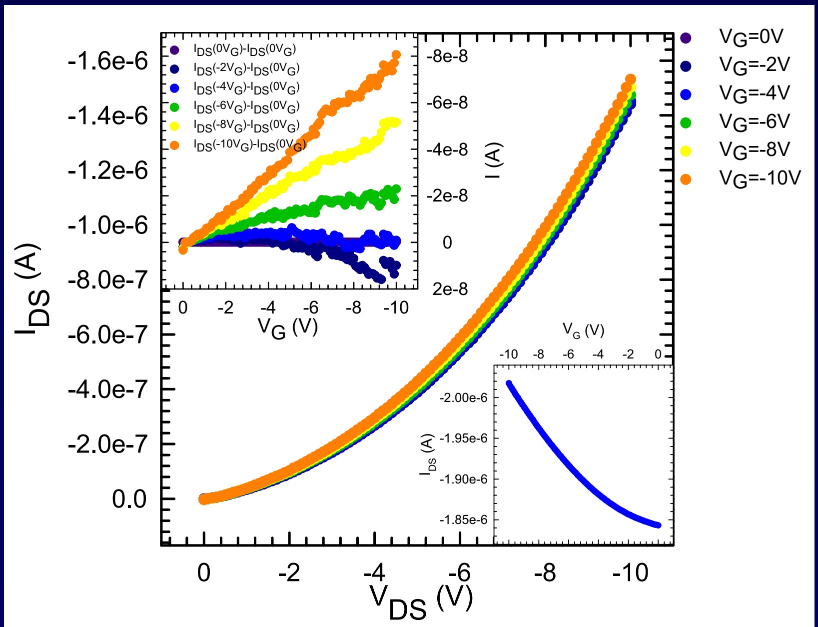


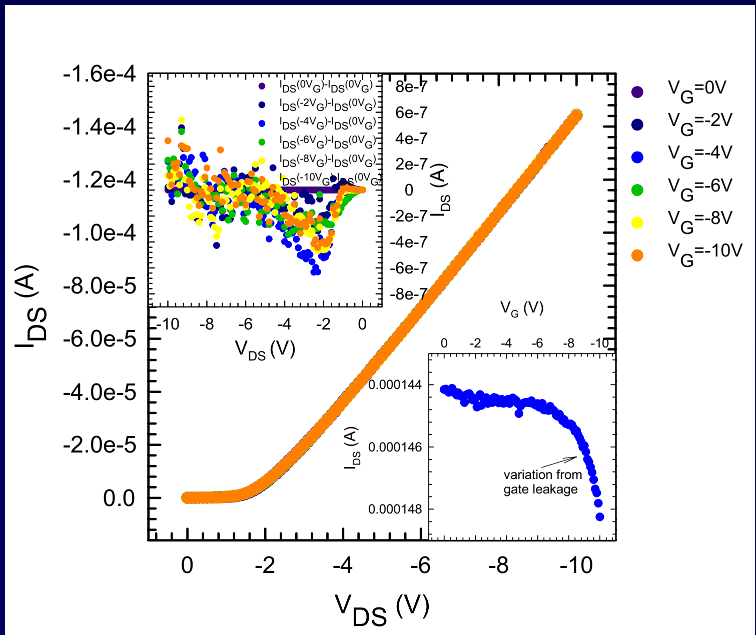
- Devices do not turn OFF
- No observed gate effect

Trench Structure with an Amorphous Silicon Channel
The Sanity Check

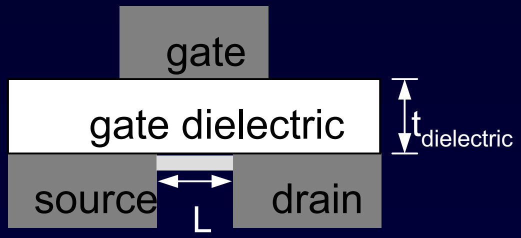


annealed structure at 200 °C in N_2 to slightly improve contacts

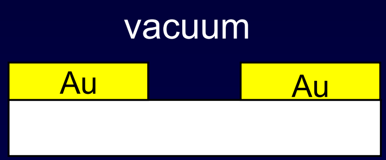




Key Requirements for Molecular Devices: The Off State

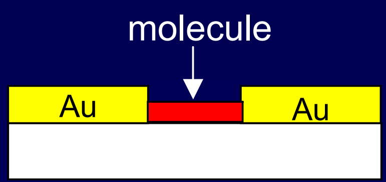


How small can L be?



ϕ_{Au} ~ 5 eV
assuming **no** barrier lowering

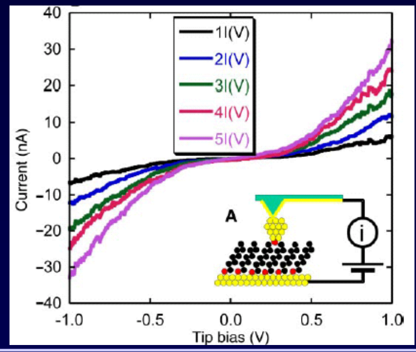
For L = 1.2 nm, device area = 8×10^6 Å^2
At 0.5V $I_{tunneling}$ ~ 5 nA



$I_{tunneling}$ higher

- If E_{HOMO}-E_{LUMO} ~ 4 eV, E_F-E_{HOMO} ~ 0.98 eV
  I increase by ~ 4.5×10^6
- hybridization typically creates finite density of molecular states at E_F [Lang, PRB (2001)]
- lowering of the workfunction of the metal electrodes

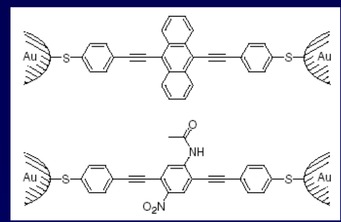
Conductive Probe AFM



At 0.5 V
I ~ 1 nA

[Lindsay group]

Break Junction Measurements



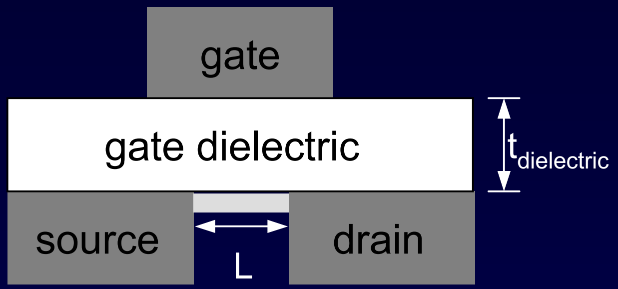
At 0.5 V
25- 200 nA

[Reichert et. al. PRL (2002)]
[Reed, Science (1997)]

- **Design molecules ≳ 2-3 nm long**
- **Tunnel barriers to tune coupling between molecule and electrode**

Scaled to device dimensions
I ~ mA

Key Requirements for Molecular FETs: Gate Modulation of the Conductance



In Si MOSFETs,
$L \gtrsim 1.5\ t_{dielectric}$

to attain a gate field
not dominated
by the drain field

as described by Poisson's
equation

Scaling to Molecular Dimensions

$t_{dielectric} \lesssim L$

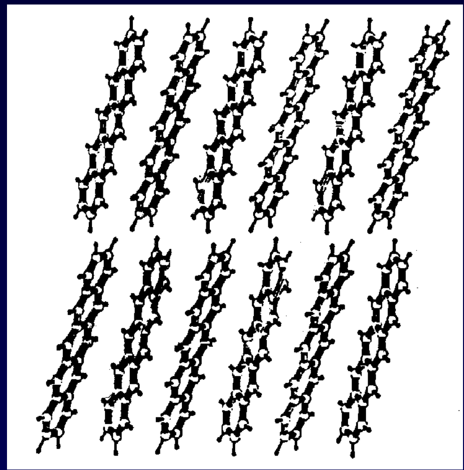
yet $t_{dielectric}$ cannot be leaky

even for an anisotropic molecule,
the component of the drain field in
the direction of the gate field
may dominate

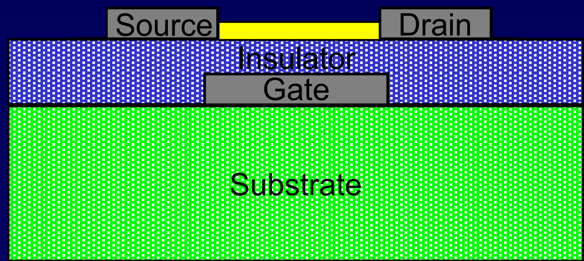
Many mechanisms for molecular switching may be envisioned but the device electrostatics must work

Organic Thin Film Transistors

Intermolecular Charge Transport

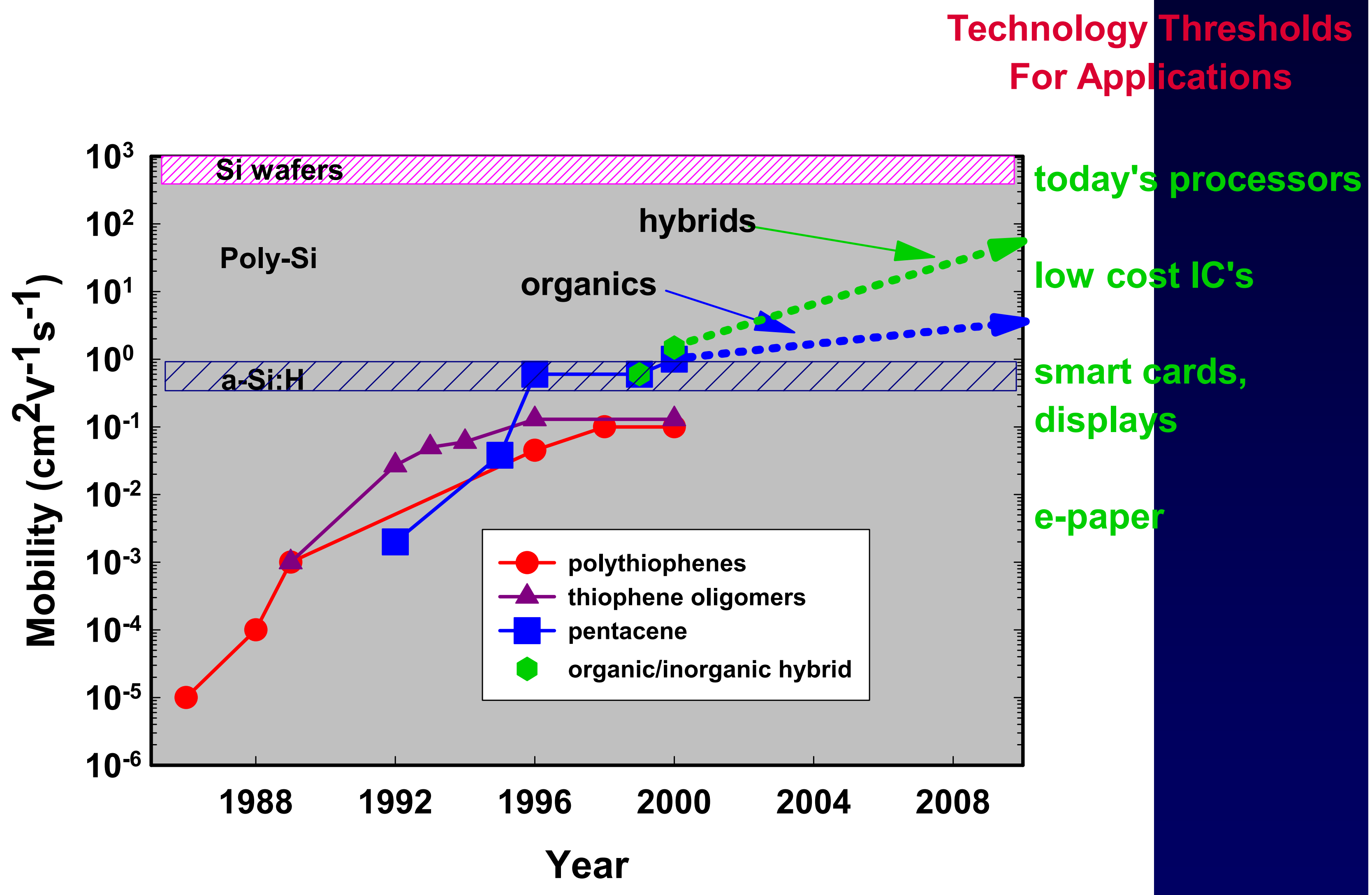


Collective property of molecules



Channel Lengths ~ μm

Organic Semiconductor Performance Trends



Where New Materials May Impact Technology

Head-mounted Display

IBM Watchpad

Palm Pilot

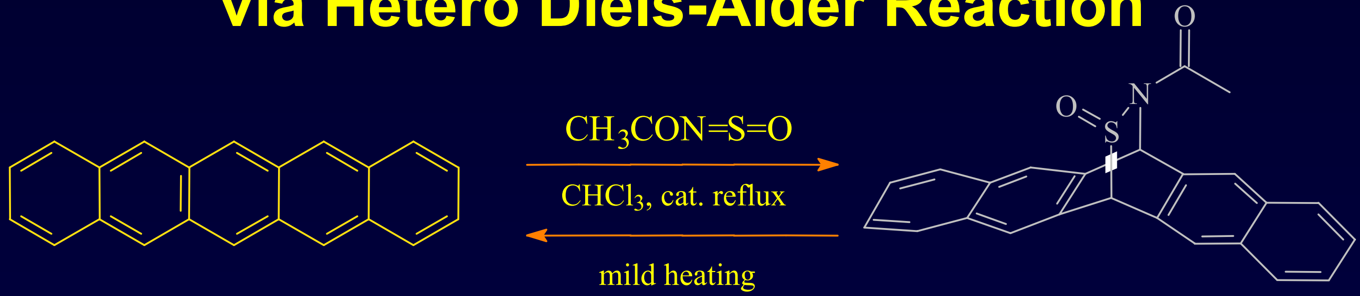
IBM ThinkPad

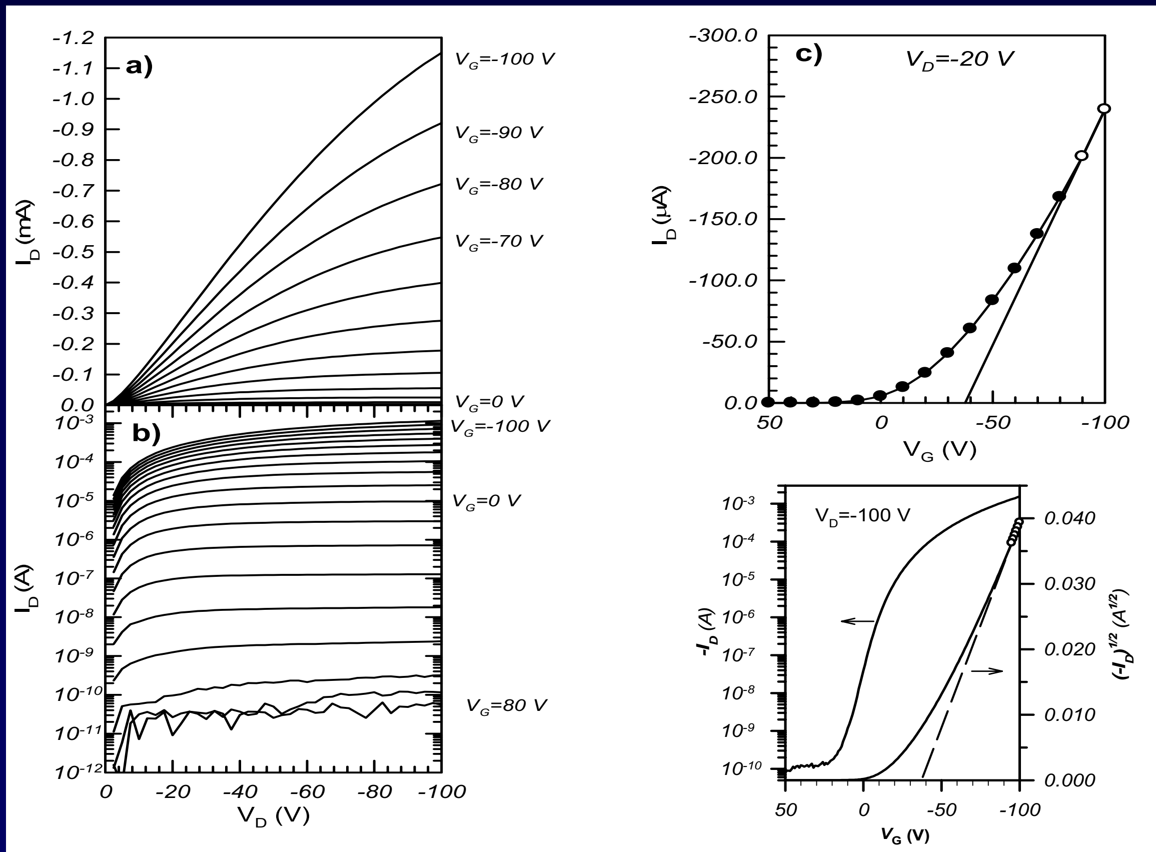
RFID Tags

Smartcards

Electronic Newspaper
R. Steinbugler, IBM

Synthesis of a Pentacene precursor via Hetero Diels-Alder Reaction



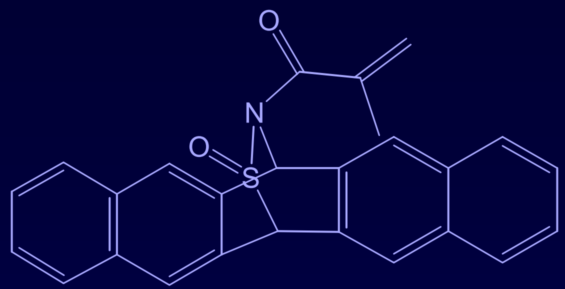


μ_{sat} ~ 0.5 cm^2/V-sec

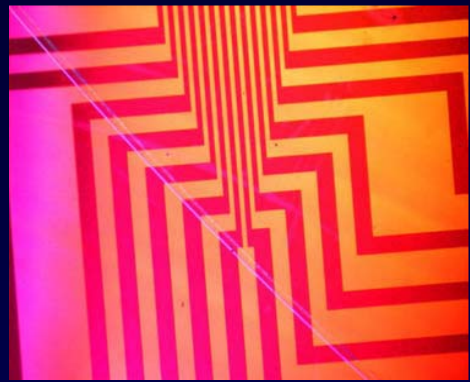
I_{ON}/I_{OFF} ~10^7

A. Afzali, C. D. Dimitrakopoulos, T. L. Breen, JACS **124**, 8812 (2002).

Device Stability of Photoimageable Pentacene Precursor

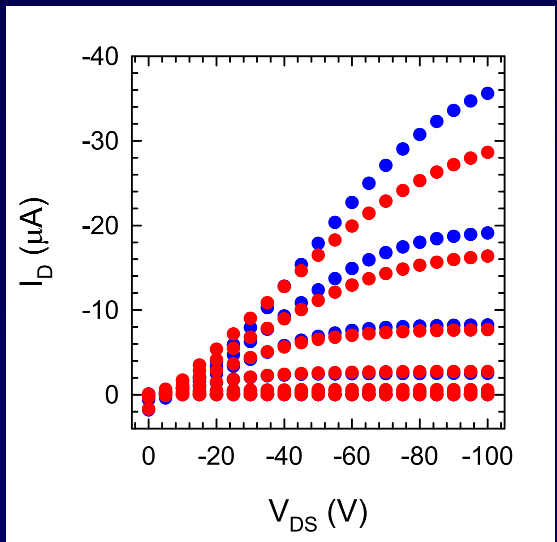


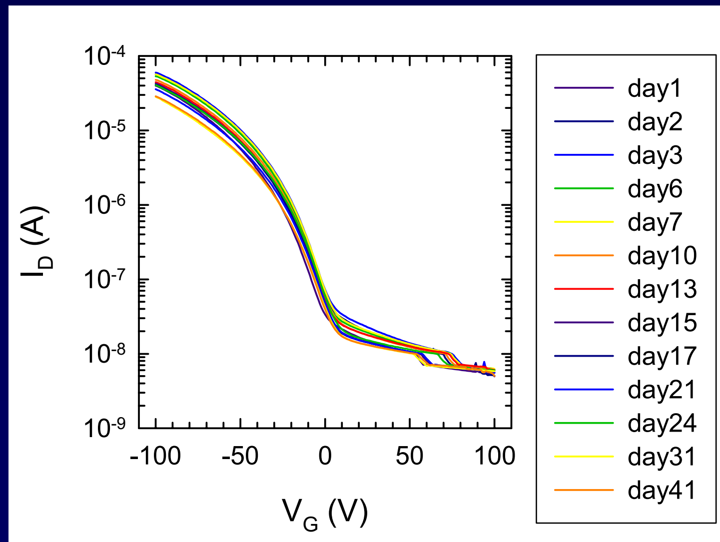
N-sulfinylmethylacrylamide pentacene adduct



Photoimageable precursor

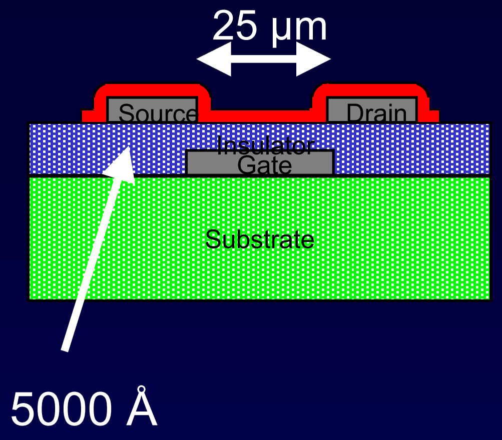
A. Afzali, C. D. Dimitrakopoulos, T. O. Graham, Adv. Mat. (in press).

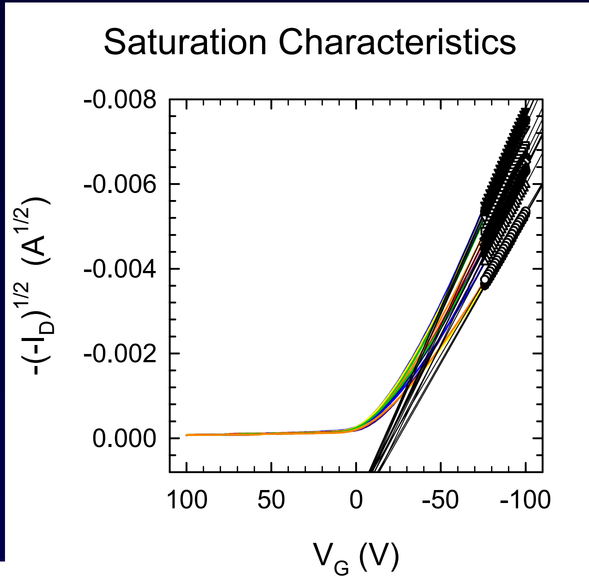


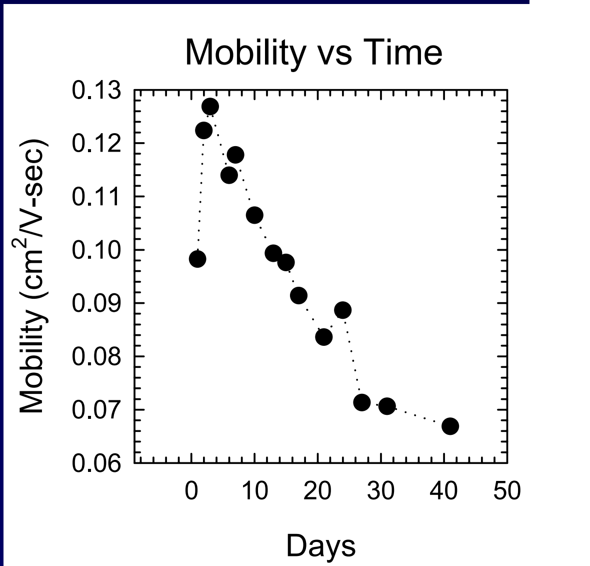


Device measured and stored in ambient

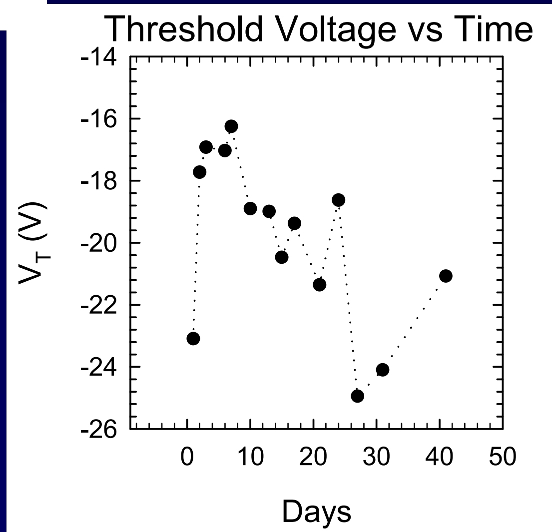
Important Device Characteristics Beyond Mobility and On-Off Ratio





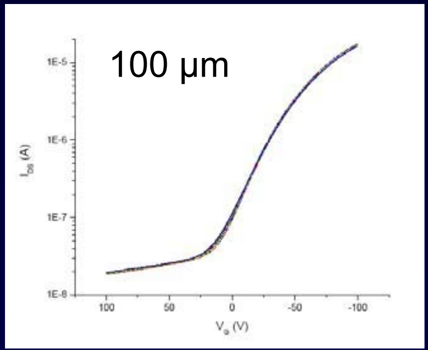


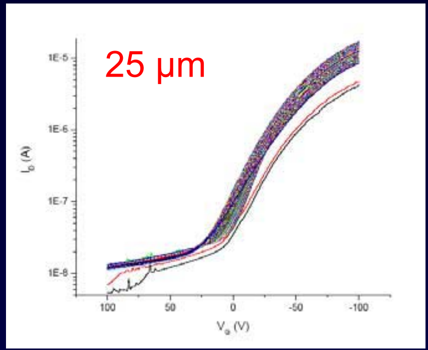
Mobility varies +/- 30%

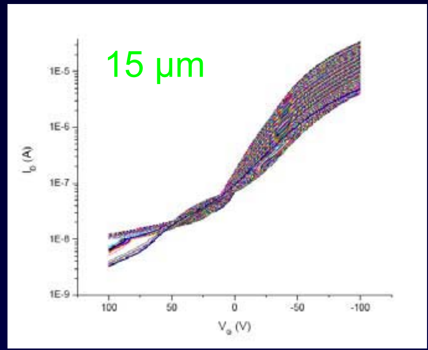


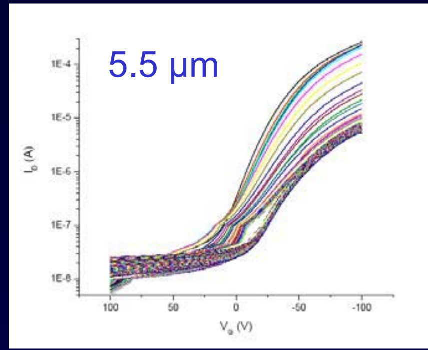
C. R. Kagan, A. Afzali, T. O. Graham

Cycling Devices
Channel Length Dependent Stability



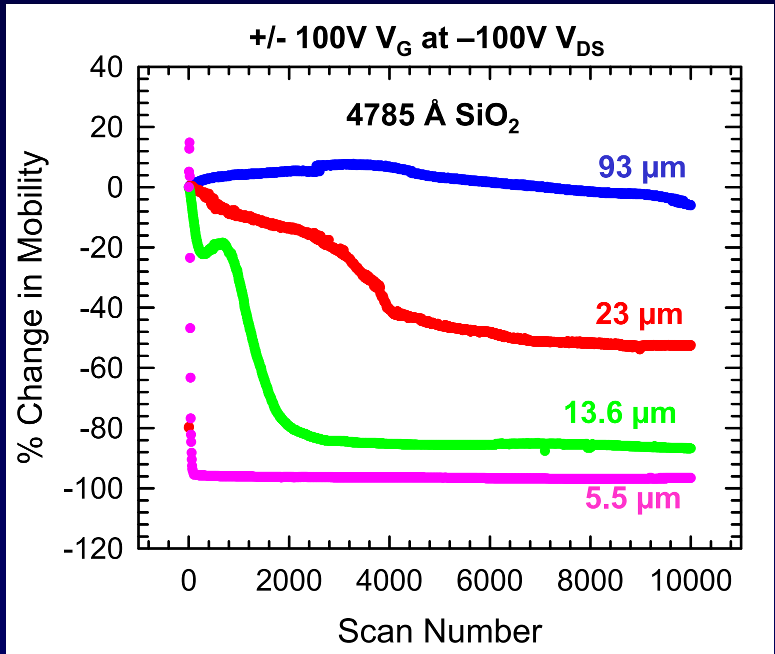






Cycle Devices 10001x

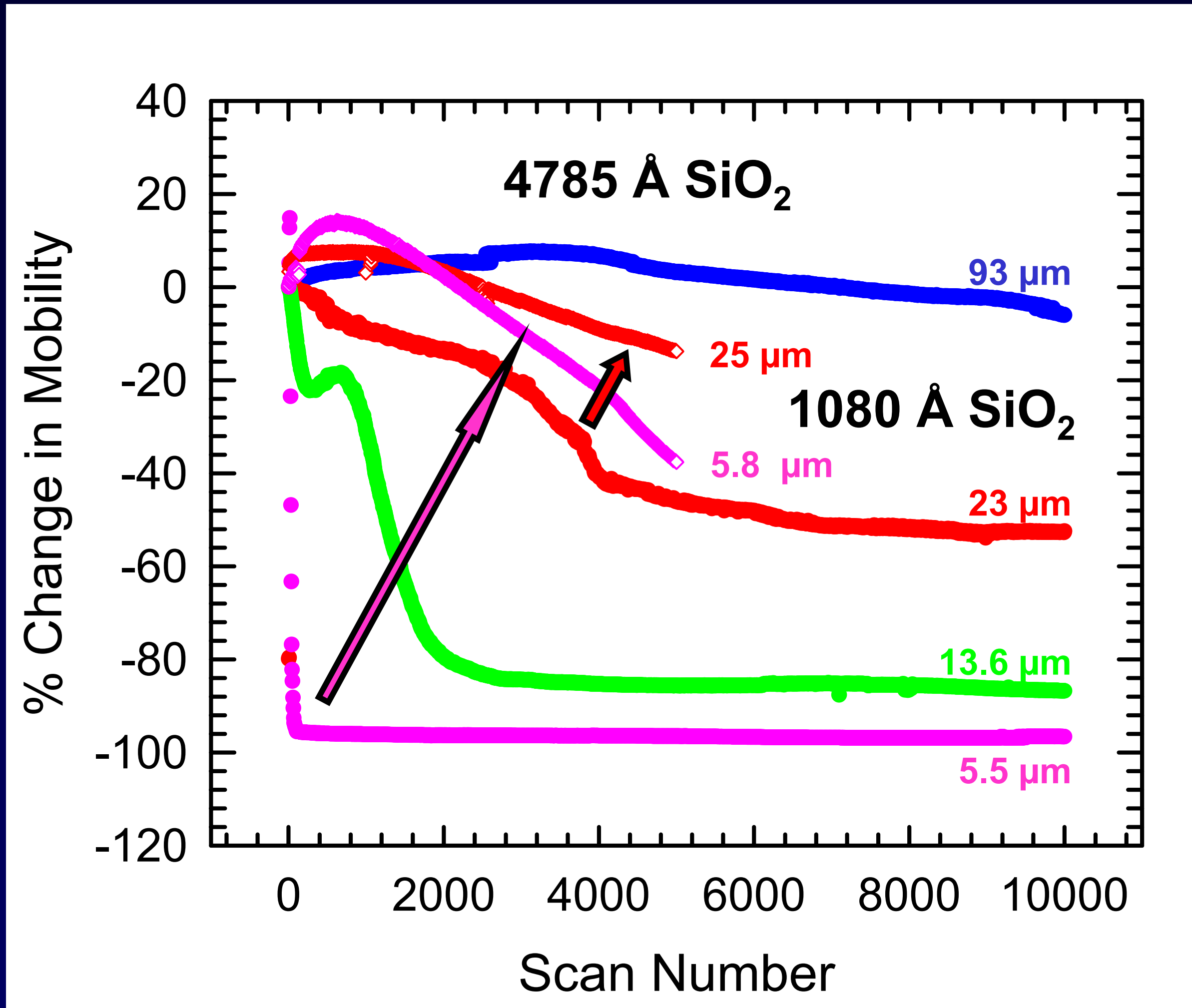
V_G -/+ 100V @ -100 V_{DS}



Mobility drops dramatically with decreasing channel length

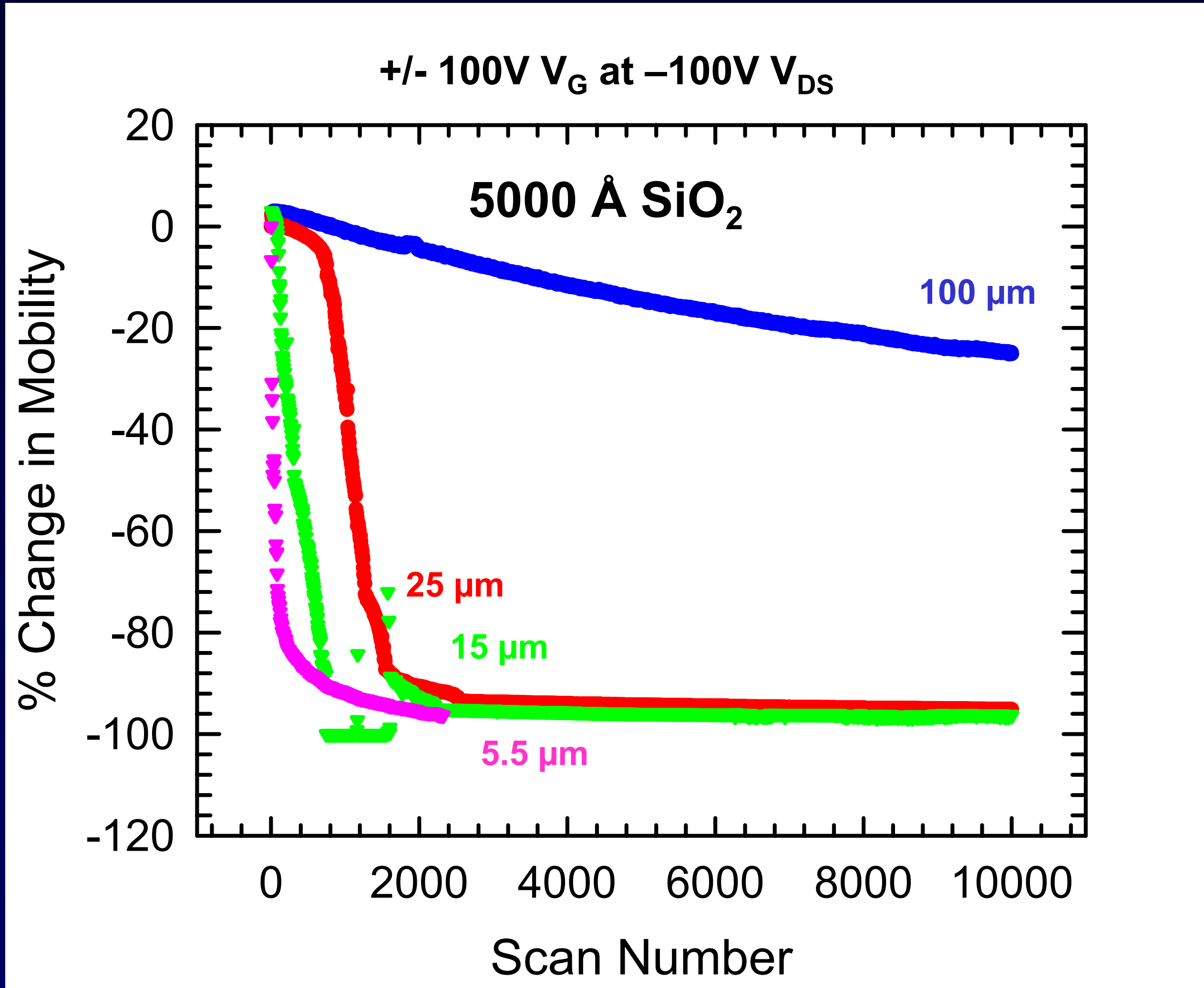
Mobility varies between ~0.015-0.06 cm^2/V-sec in these devices

Oxide Thickness Dependence of Carrier Mobility



Fields not perfectly scaled, but lower V reduces decay in device mobility

Vacuum Evaporated Pentacene

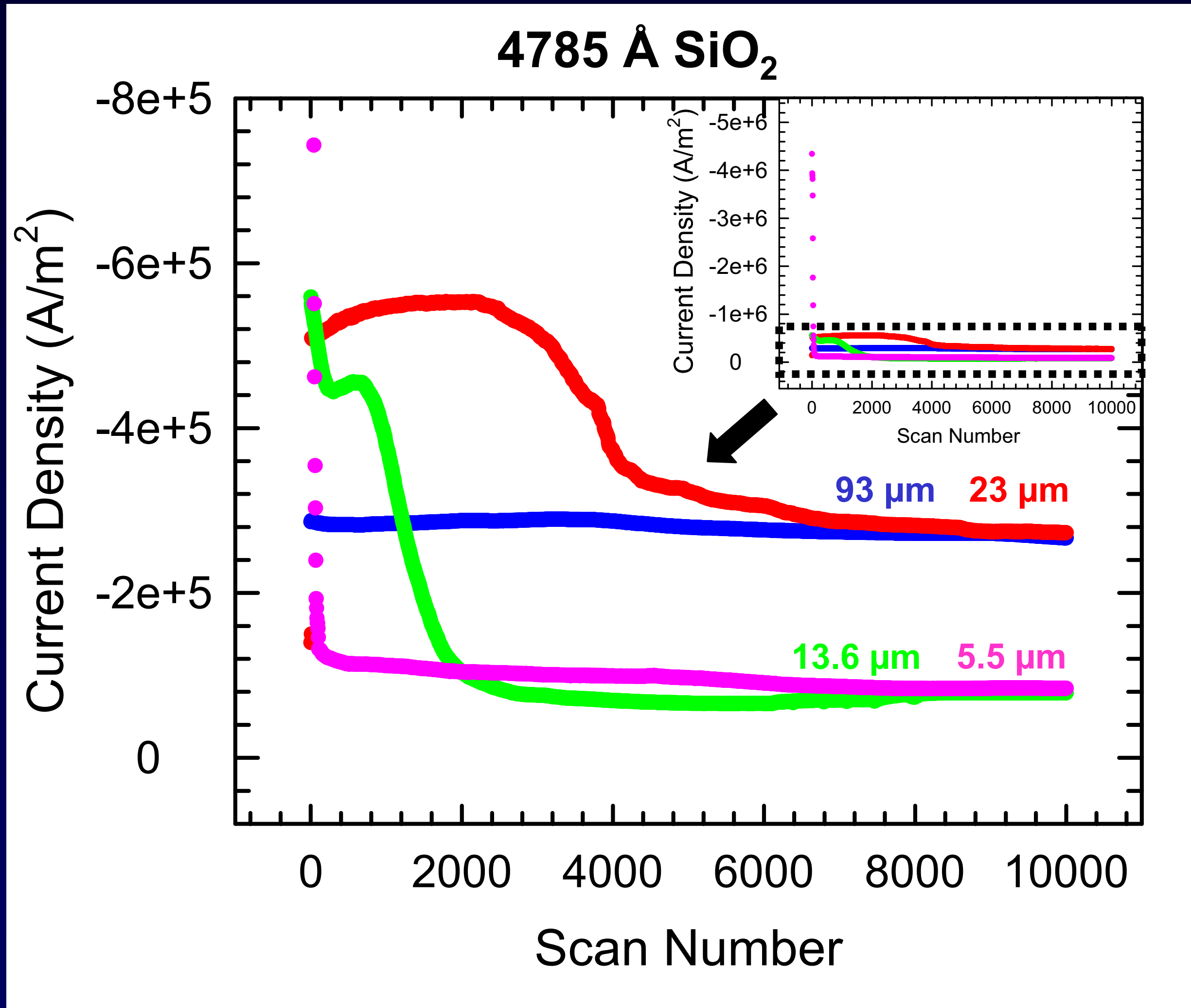


Mobility of solution deposited films 0.015-0.06 cm^2/V-sec

Mobility of vacuum deposited film 0.6 cm^2/V-sec

Vacuum deposited film less stable – power density limitation of evaporated film or chemical stability/morphology of soluble precursor

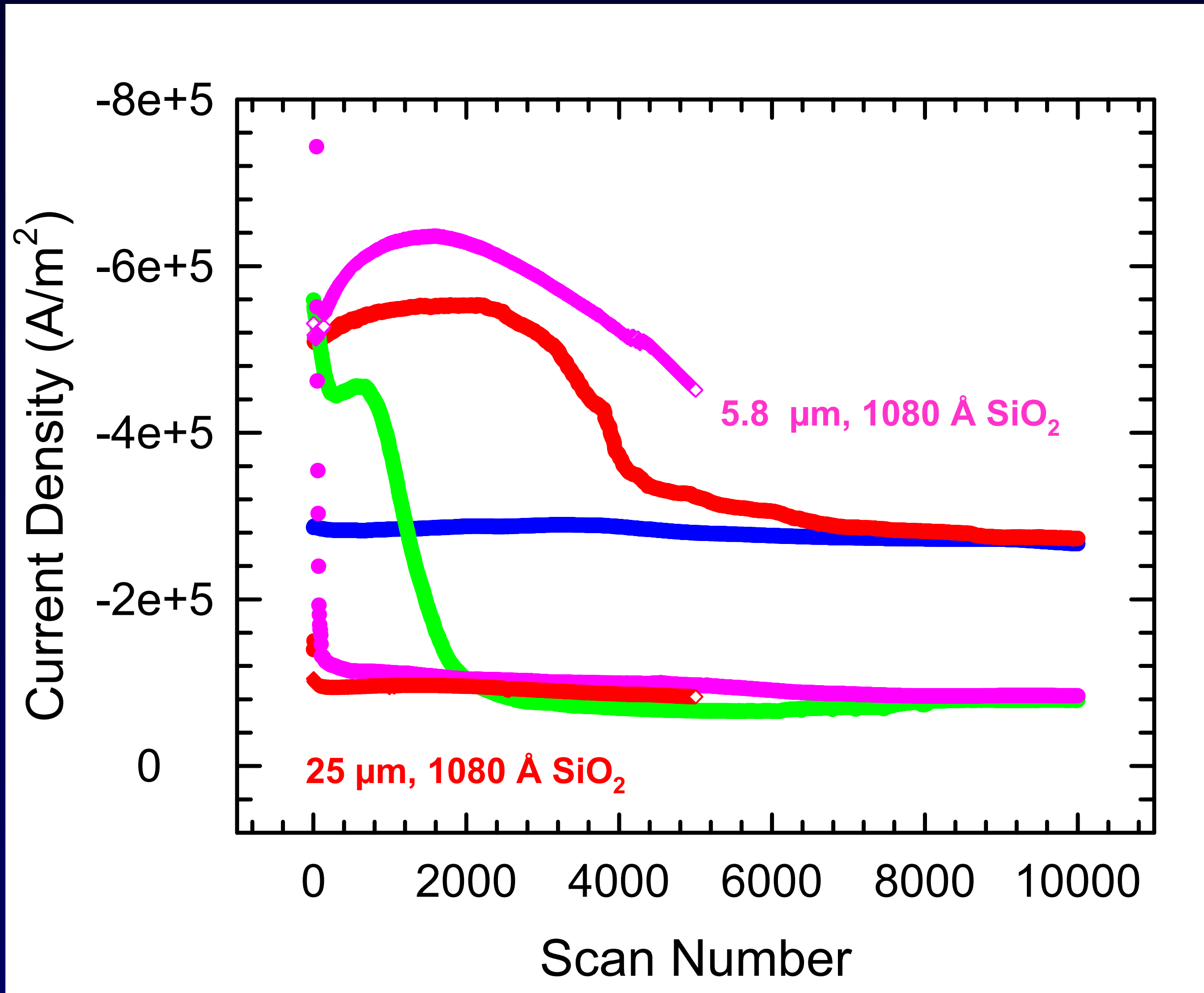
Channel Length Dependent Current Density



At same voltages (various source-drain fields), higher current densities not maintained

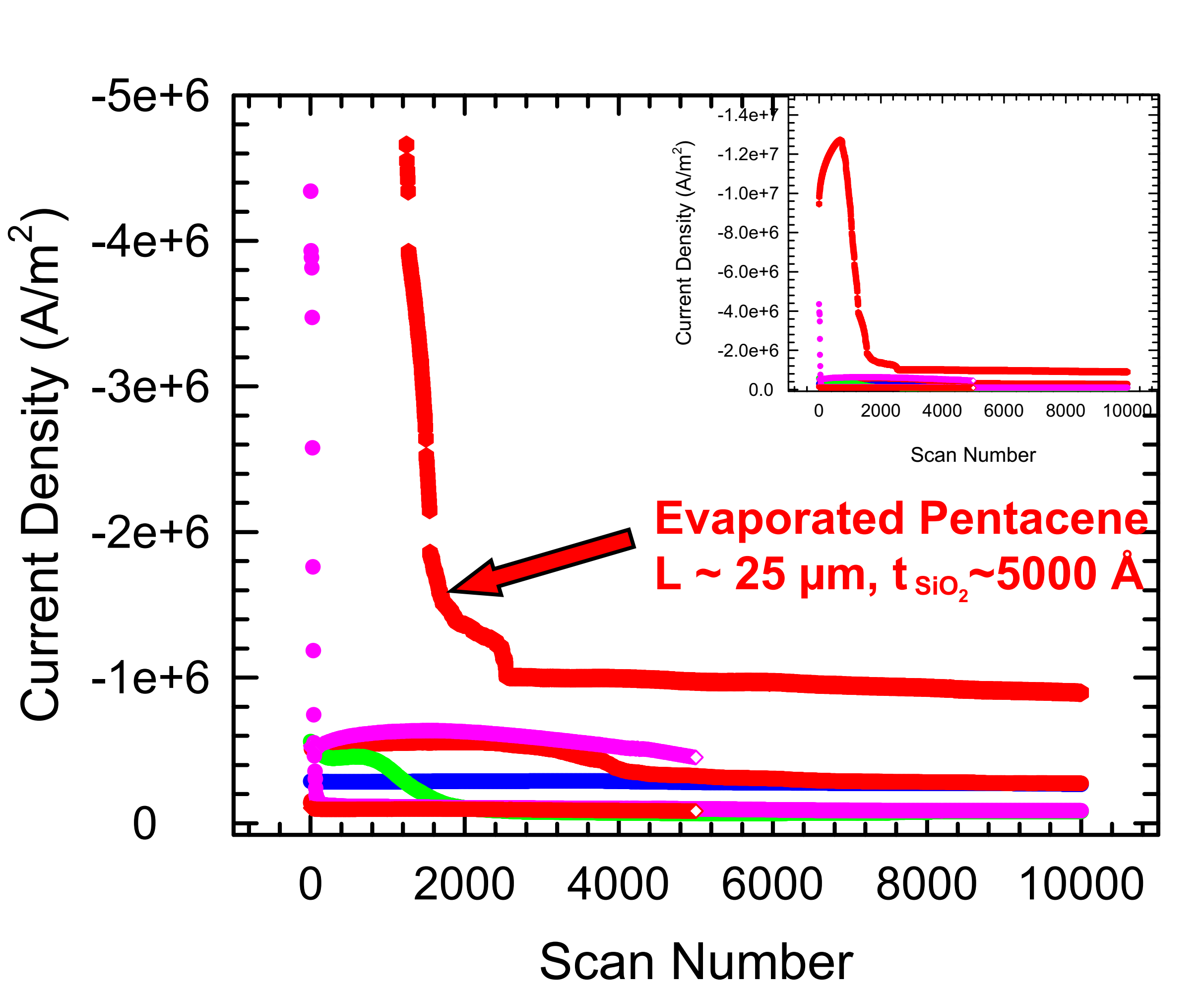
As number of scans increased current density drops and plateaus

Oxide Thickness Dependence of Current Density



At lower voltages, source-drain fields, device can maintain a higher current density suggests stability is limited by power density and scaling devices may be used to achieve desired current densities

Solution versus Vacuum Evaporated Pentacene Achievable Current Density



Evaporated film current density drops more dramatically, but plateaus at high level