



the  
**abdus salam**  
international centre for theoretical physics

ICTP 40th Anniversary

SMR 1564 - 35

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

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**SEMICONDUCTORS; DEVICES**

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

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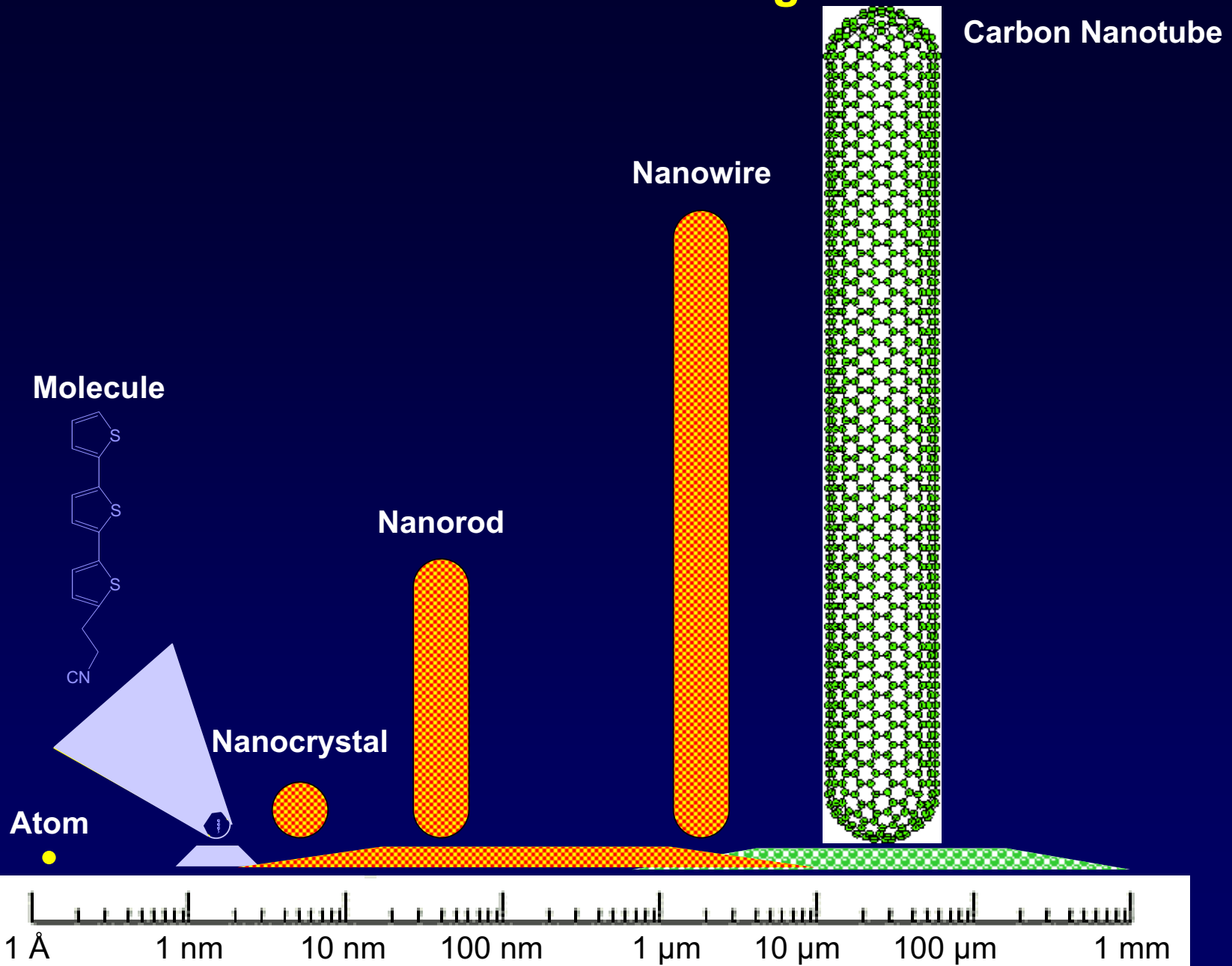
*These are preliminary lecture notes, intended only for distribution to participants.*

# **Making Electrical Contact to Molecules**

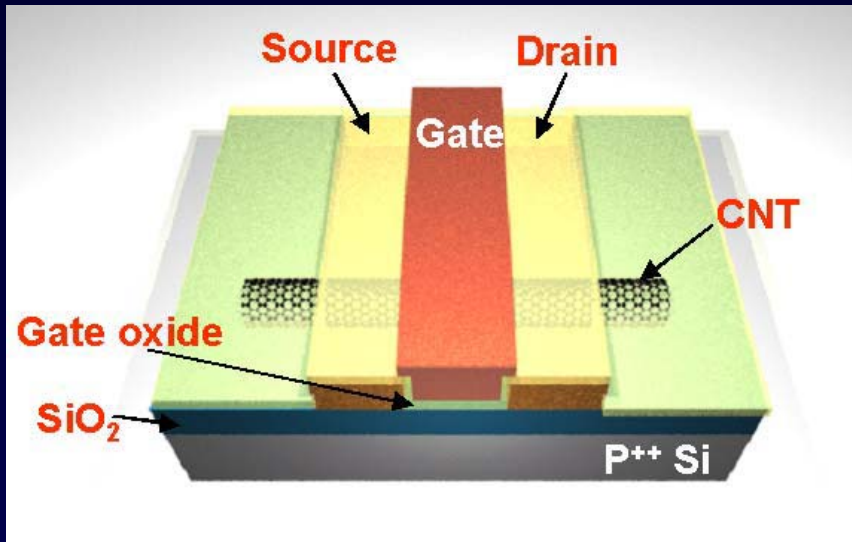
**Cherie R. Kagan**

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

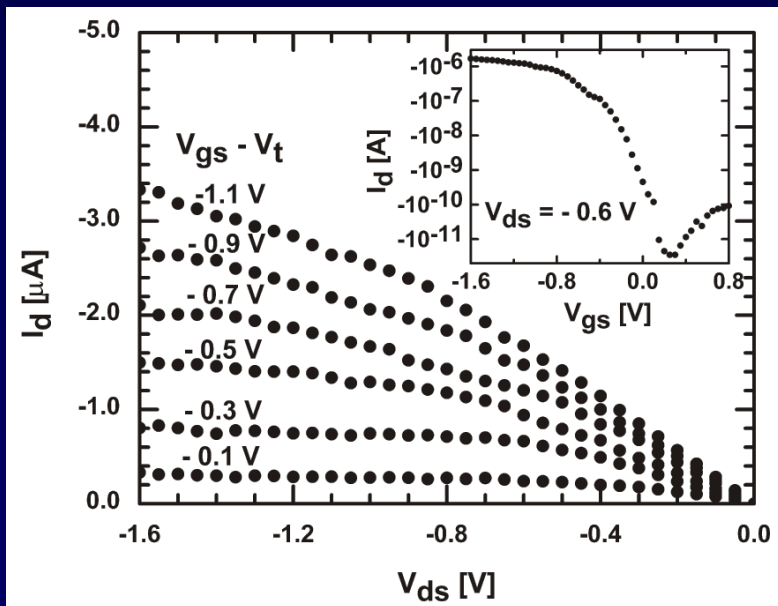
# On The Size of Things



# Carbon Nanotube Transistor



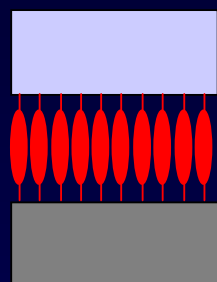
- Channel Length is 300 nm
- Oxide fabricated on top of CNT



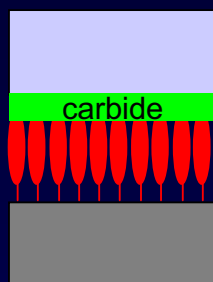
S.J. Wind, J. Appenzeller, R. Martel, and Ph. Avouris, *Appl. Phys. Lett.* **80** 3817 (2002).

# Challenges in Fabricating Molecular Junctions Vertical Structures

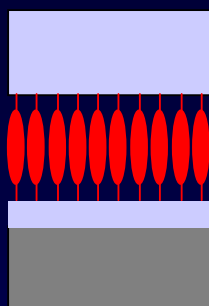
## Local Challenges



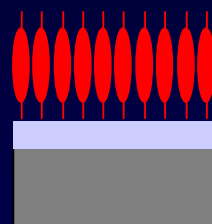
Idealized Structure



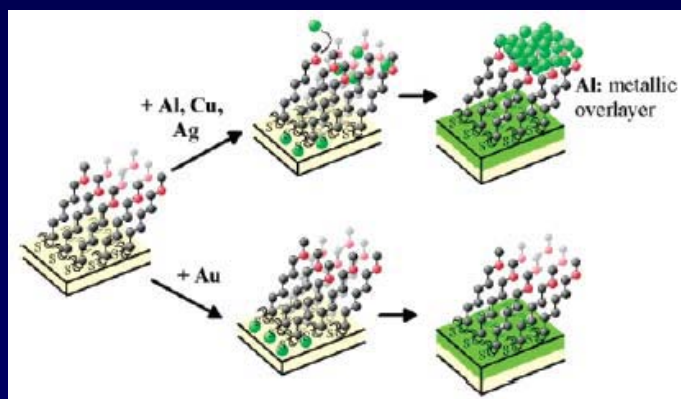
Reactive Metal (Ti)



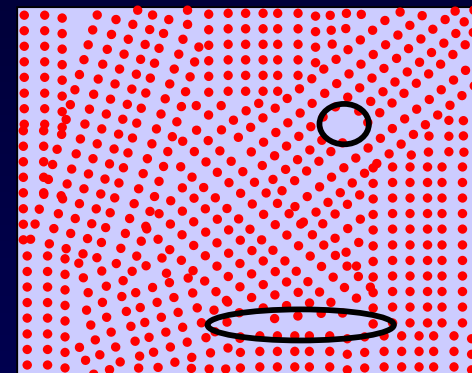
Middle of the road Metal  
Al, Cu, Ag



Unreactive Metal (Au)



## Global Challenges

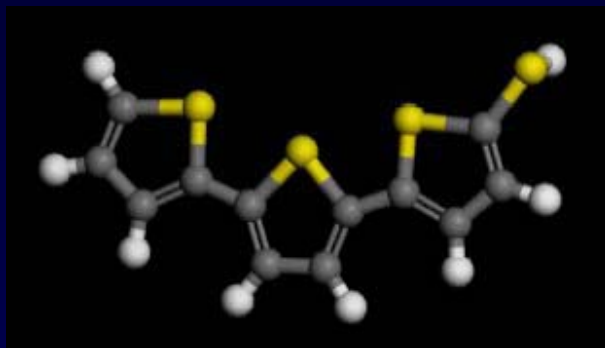


Metal penetration through defects in monolayers

- domain boundaries
- voids

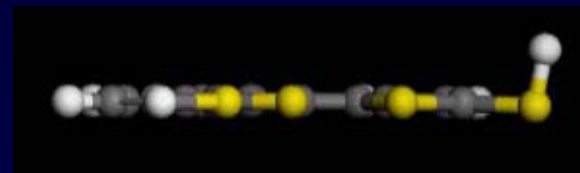
A. V. Walker, T. B. Tighe, O. M. Cabarcos, M. D. Reinard, B. C. Haynie, S. Uppili, N. Winograd, D. L. Allara, *J. Am. Chem. Soc.* **126**, 3954 (2004).

# Challenges in Fabricating Molecular Junctions: Lateral Geometry



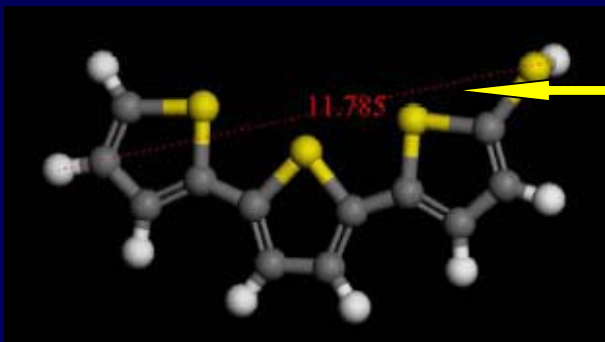
$\alpha$ -terthiophene thiol

rotated 



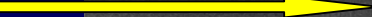
molecule's planarity provides:  
good  $\pi$ -overlap, conductivity  
rigidity, reducing solubility

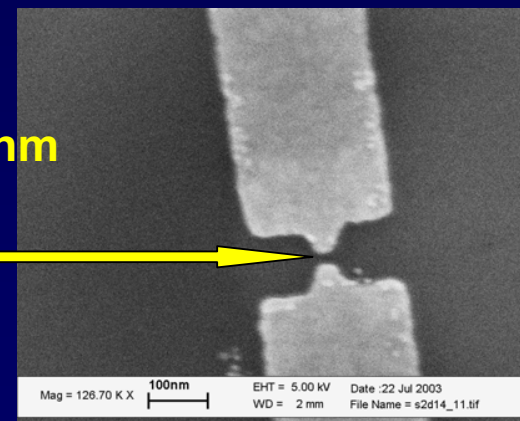
 distance



Limits length of molecule

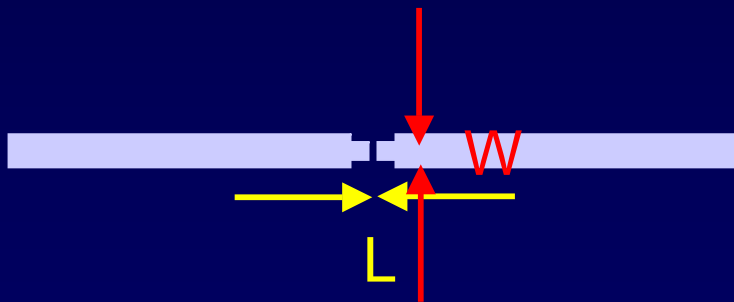
 ~1.2 nm

 ~17 nm



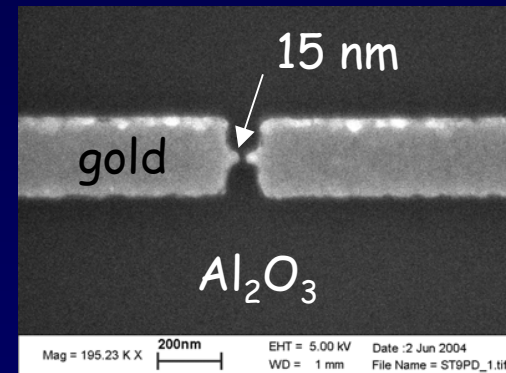
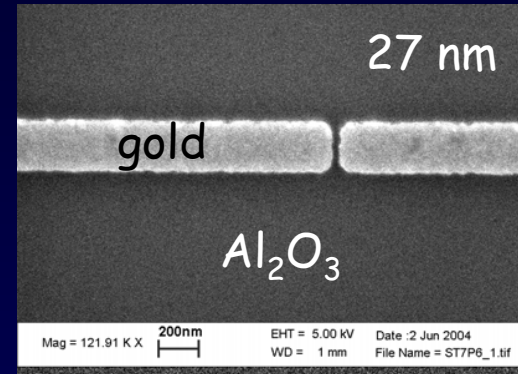
# Limitations of e-beam Lithography

Design



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

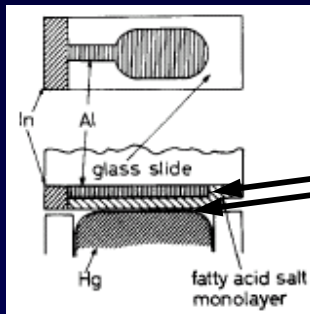
Product



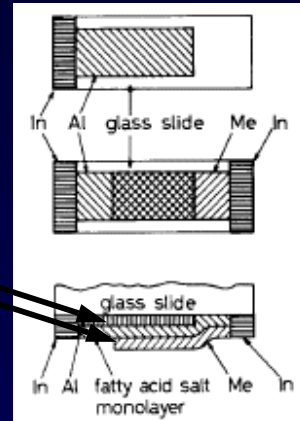
# First Examples of Transport Measurements in Molecular Junctions

## Kuhn – 1971

### Tunneling through Fatty Acids



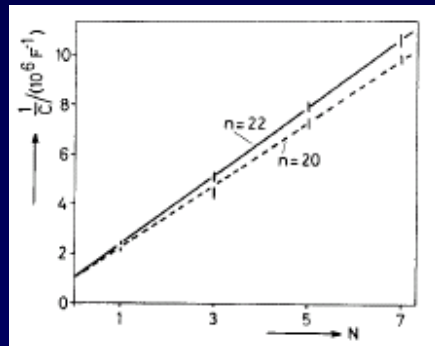
native  
oxide layer



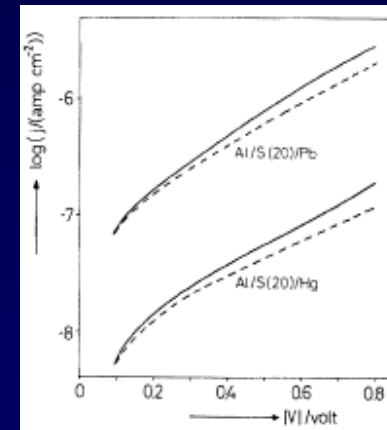
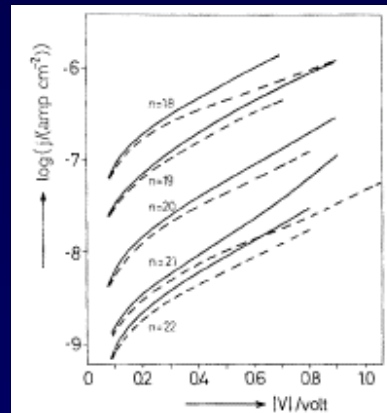
Fatty acids:  $\text{CH}_3(\text{CH}_2)_n\text{COOH}$

Metal Salts, example:  
 $[\text{CH}_3(\text{CH}_2)_n\text{COOH}]_2\text{Cd}$

Metal: Pb, Al, Ag, Au



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



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

(for small voltages  $V$ ),

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

(for large voltages  $V$ ),

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

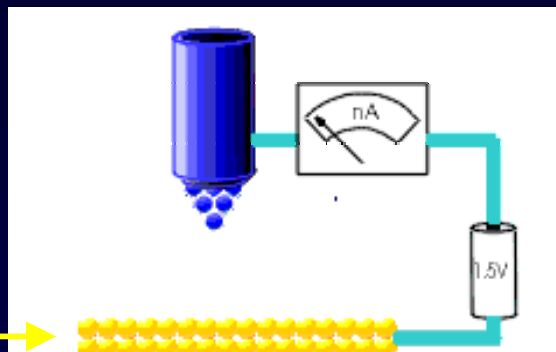
B. Mann, H. Kuhn, *J. Appl. Phys.* **42**, 4398 (1971).

# Scanning Tunneling Microscopy of Molecular Assemblies

Map density of states

Not measure of  
molecular conductance

Metal

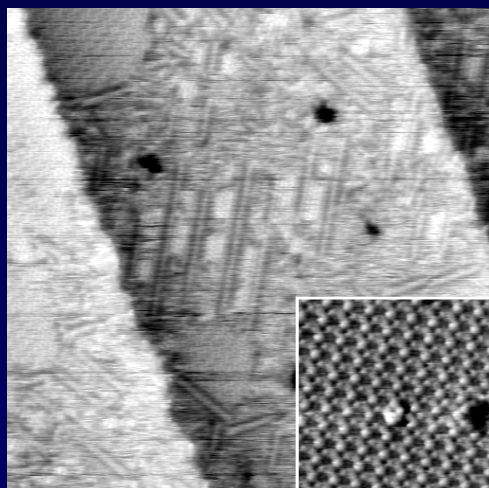


$$d_{\text{tip-sample}} \leq 10 \text{ \AA}$$

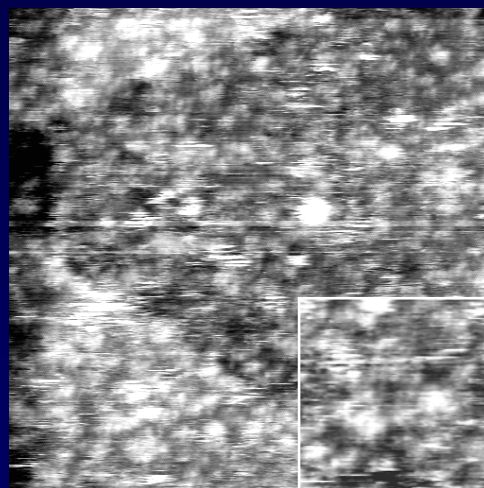
$$I \propto \exp\left(\frac{2\sqrt{2m\Phi\hbar}}{d}\right)$$

## Ordered versus Dis-ordered Assembly

hexanethiol



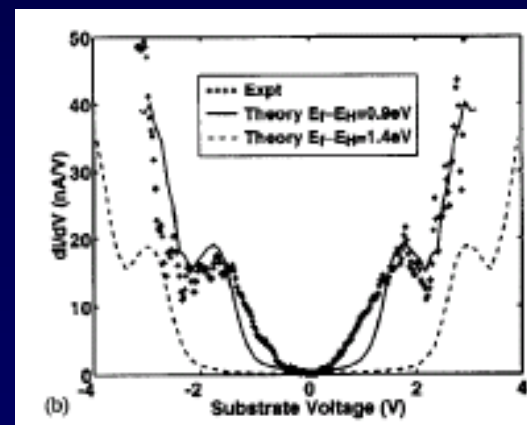
1,1'-biphenyl-4,4'-dithiol



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

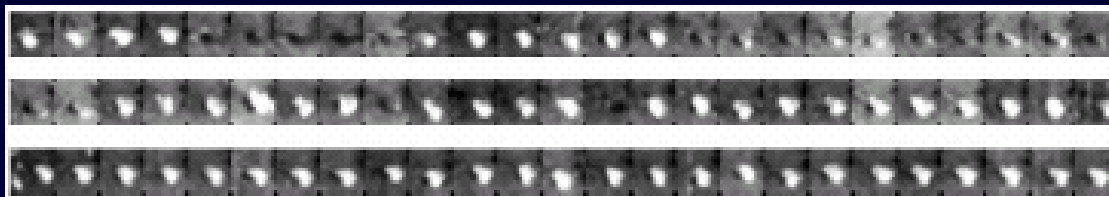
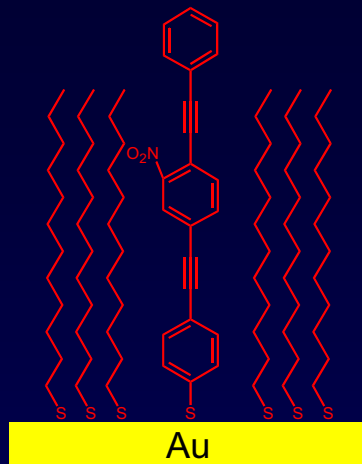
## Spectroscopy

$\alpha,\alpha'$ -xylyl dithiol



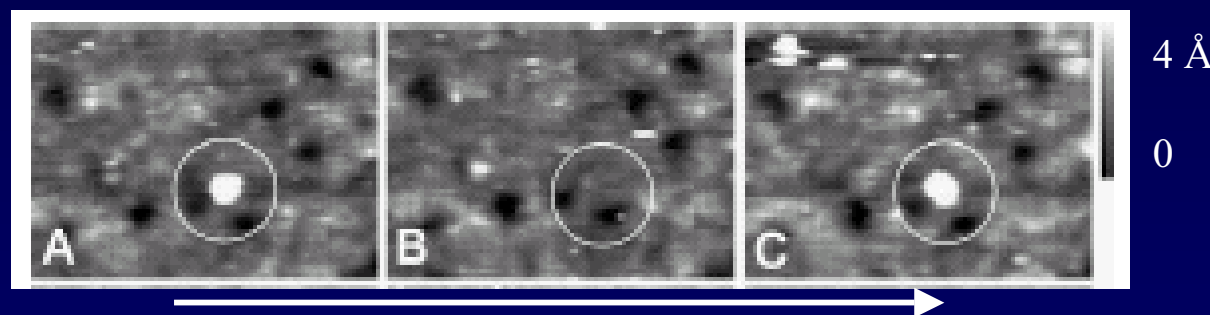
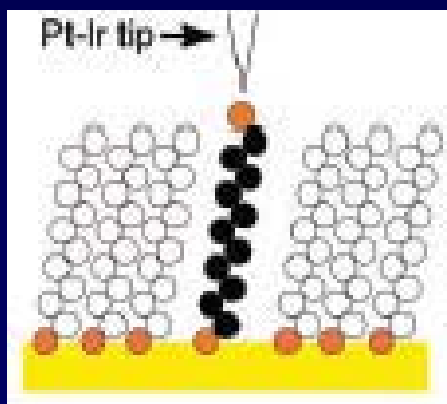
W. Tian, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, C. P. Kubiak, *J. Chem. Phys.* **109**, 2874 (1998).

# 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).

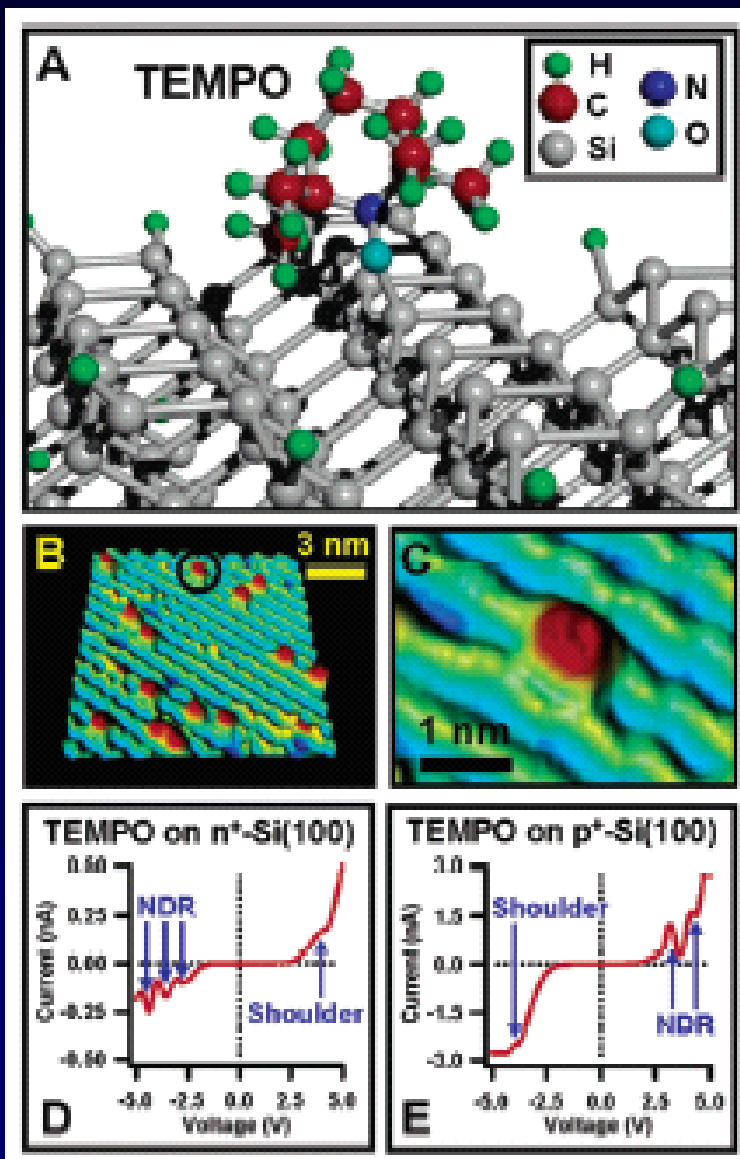


Time

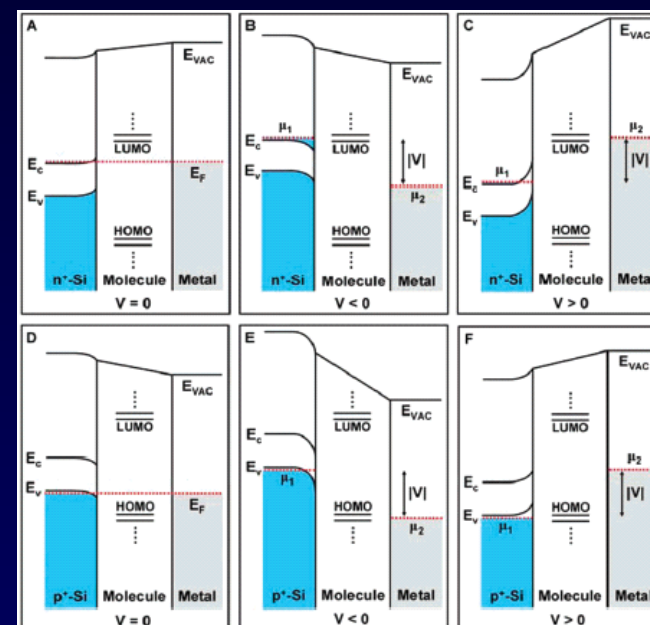
G. K. Ramachandran, T. J. Hopson, A. M. Rawlett, L. A. Nagahara, A. Primak, S. M. Lindsay, *Science* **300**, 1413 (2003).

Stochastic switching – arise from Au-S bond breaking?

# STM Measurements of Molecules on Si

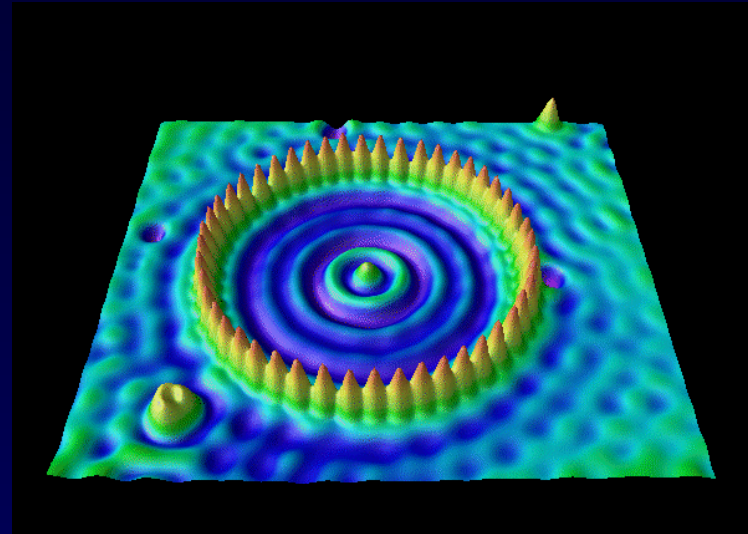
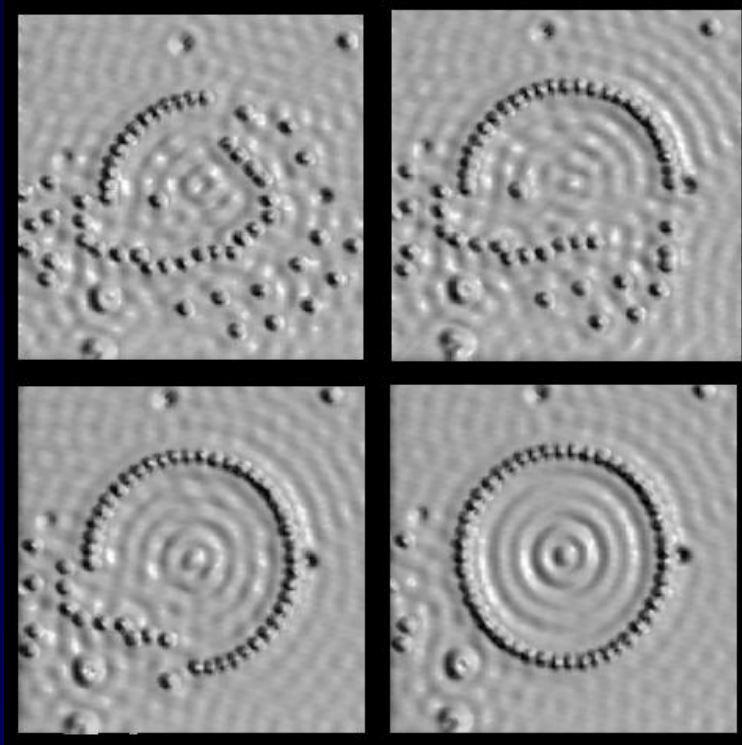


- NDR when molecular levels cross Si band edge
- Shoulder when molecular levels cross metal Fermi level



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

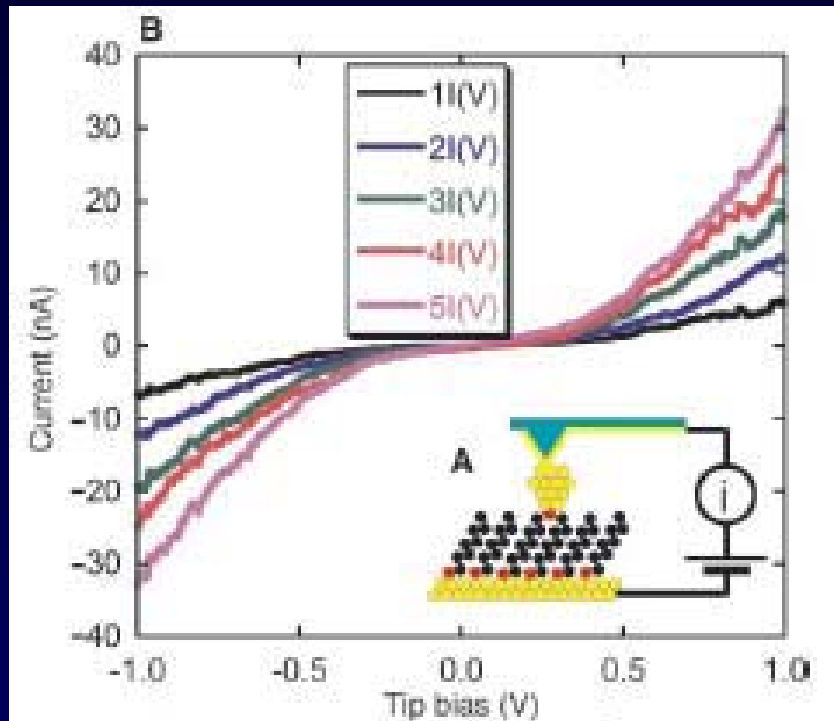
# Scanning Tunneling Microscopy of Atoms



**Fe adatoms on Cu (111)**

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

# Conductive Probe AFM

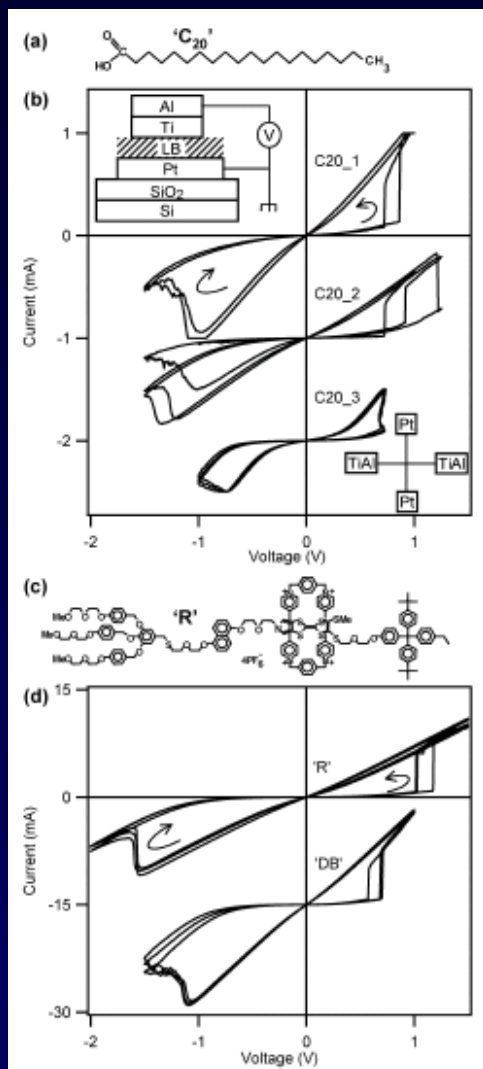


Two-physical contacts  
allows measurements  
of conductance

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

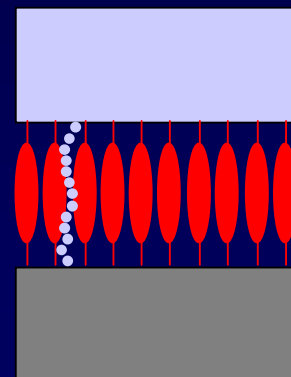
X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, S. M. Lindsay, *Science* **294**, 571 (2001).

# Metal-Molecule-Metal Sandwiches/Crossbars



I-V characteristics are independent of the molecular chemistry

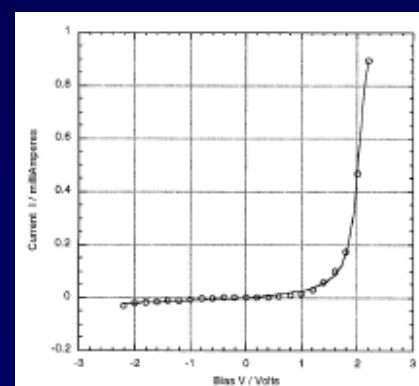
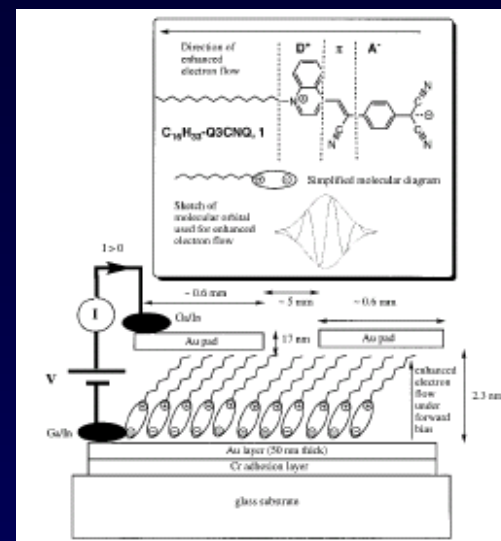
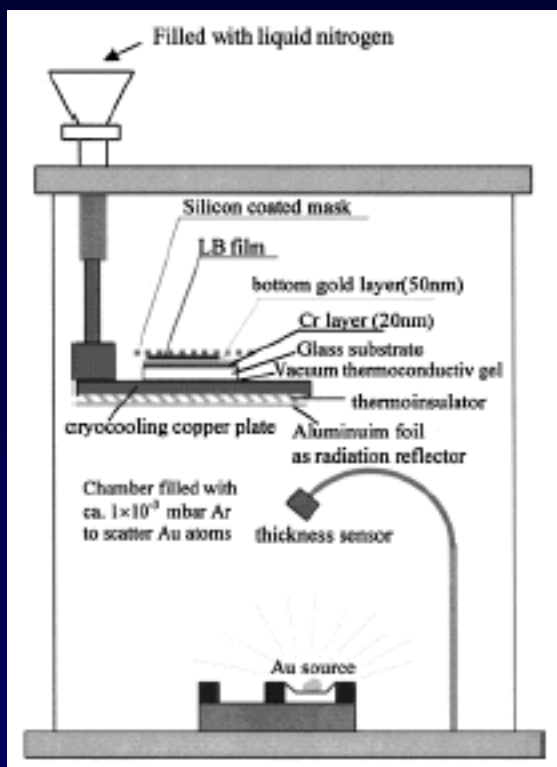
Metal filament formation?  
Known to give similar characteristics even in thin organic and oxide films for ~40 years



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).

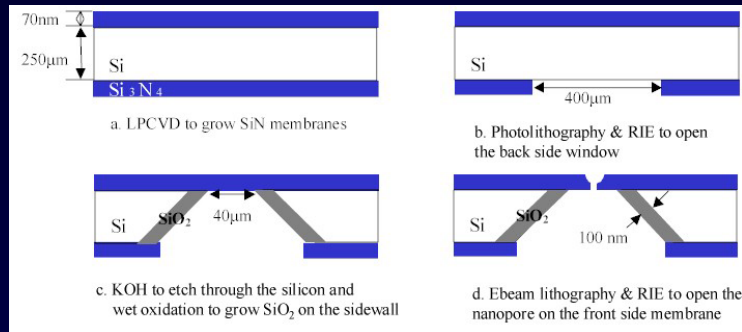
# Cold-Gold Evaporation: Metal-Molecule-Metal Rectifying Junctions

Langmuir-Blodgett monolayer of  
hexadecylquinolinium tricyanoquinodimethanide

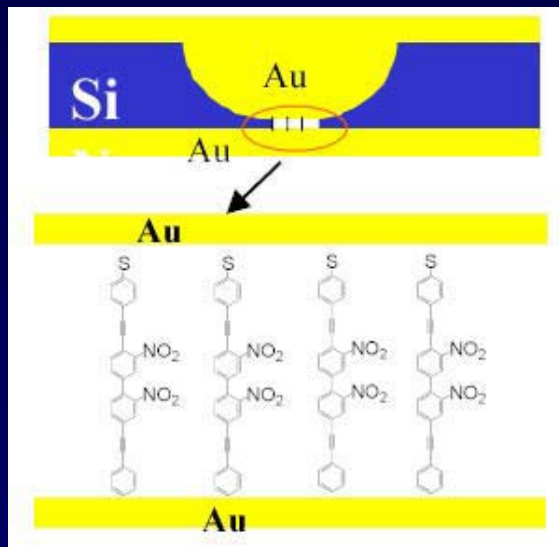


R. M. Metzger, T. Xu, I. R. Peterson, *J. Chem. Phys. B* **105**, 7280 (2001).

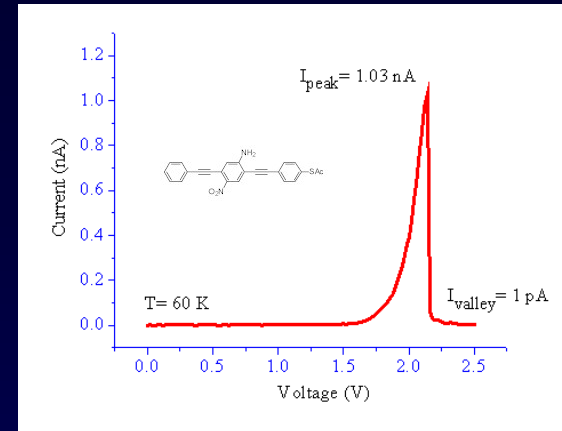
# Nanopore Geometry



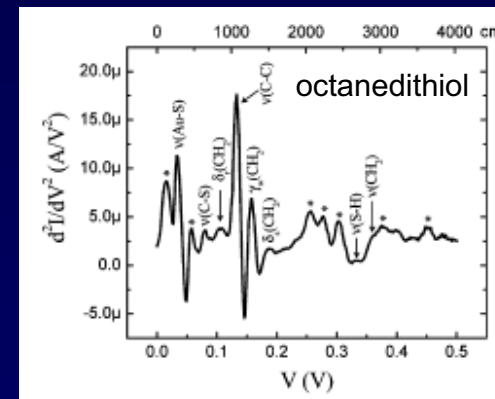
M. A. Reed, Yale University



Decrease probed area to small  $\sim 30$  nm dimension to reduce the probability of defects



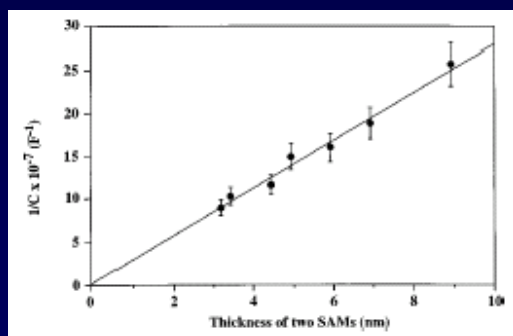
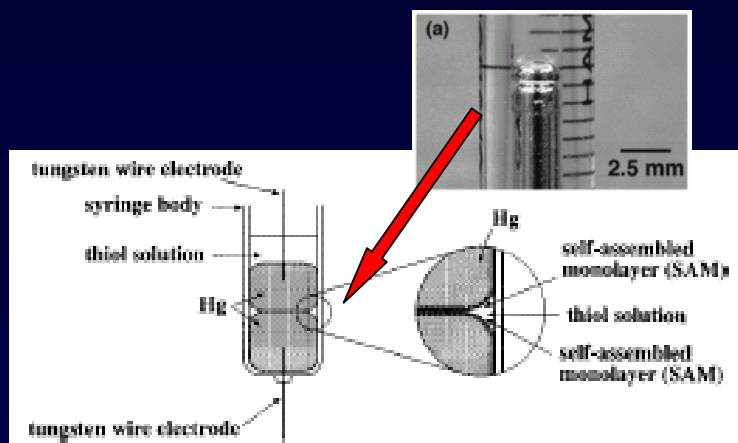
J. Chen, M. A. Reed, A. M. Rawlett, J. M. Tour, *Science* **286**, 1550 (1999).



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

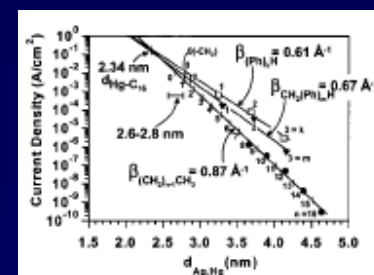
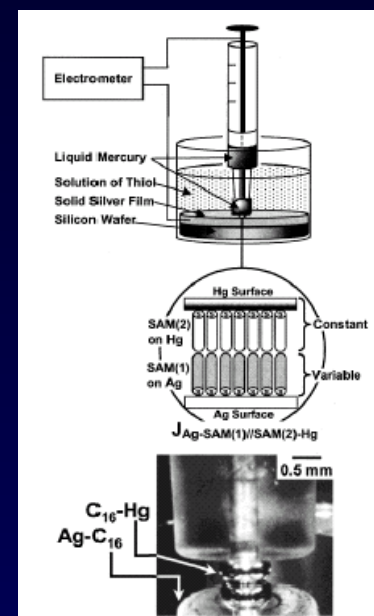
# Using Hg as an Electrode

## 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



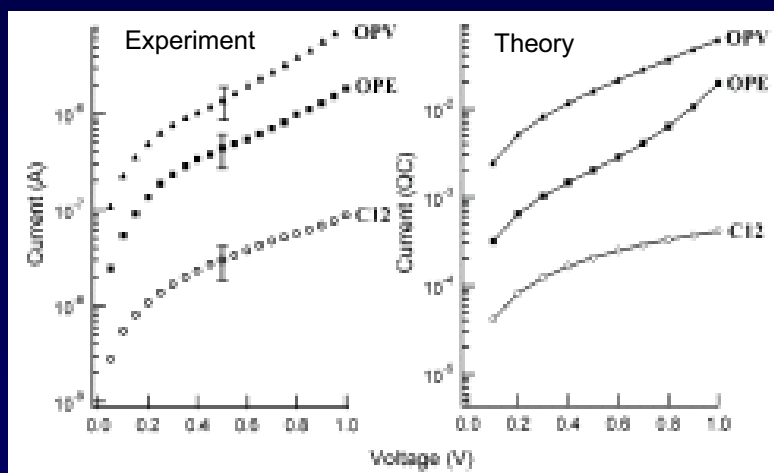
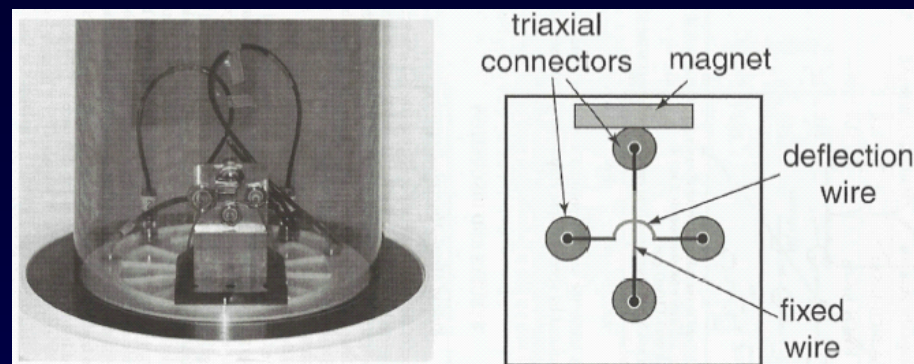
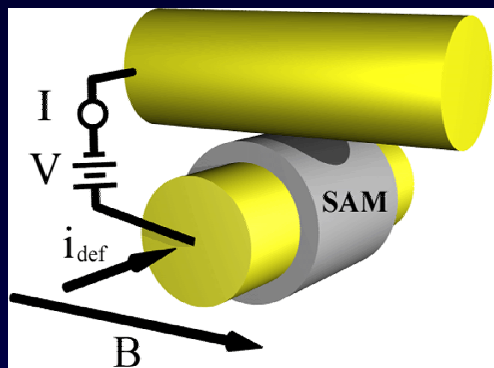
$$I \approx I_0 [e^{-\beta(1)d_{SAM(1)}}] [e^{-\beta(2)d_{SAM(2)}}]$$

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

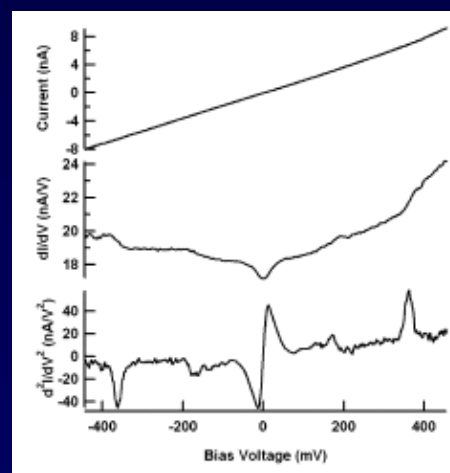
R. E. Holmlin, R. Haag, M. L. Chabinyc, R. F. Ismagilov, A. E. Cohen, A. Terfort, M. A. Rampi, G. M. Whitesides, *J. Am. Chem. Soc.* **123**, 5075 (2001).

# Crossed-Wire Junctions

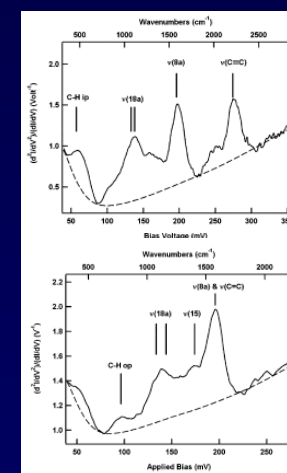
Lorentz Force deflection



I-V characteristics



Inelastic Tunneling Spectroscopy

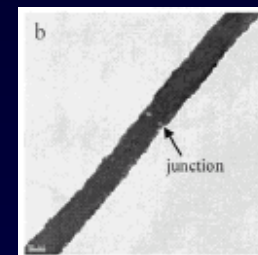
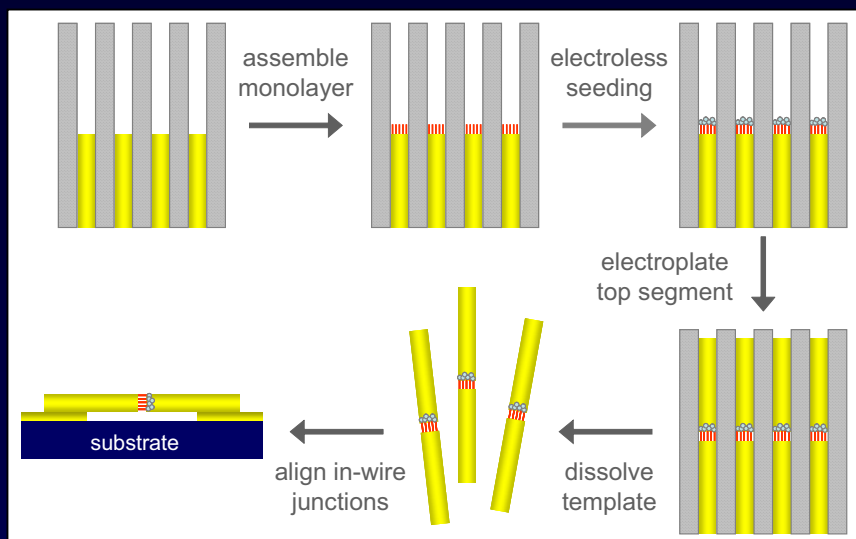


S. Gregory, *Phys. Rev. Lett.* **64**, 689 (1990).

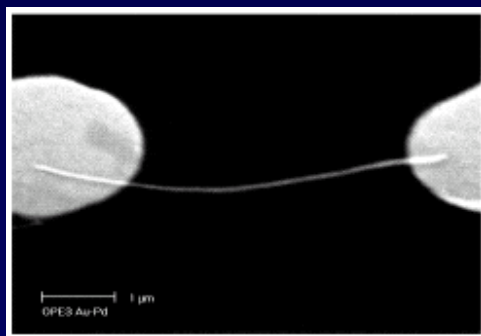
J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, J. C. Yang, T. L. Schull, J. Naciri, M. H. Moore, R. Shashidhar, *J. Am. Chem. Soc.* **124**, 10654 (2002).

J. G. Kushmerick, J. Lazorcik, C. H. Patterson, R. Shashidhar, D. S. seferos, G. C. Bazan, *Nano Lett.* **4**, 639 (2004).

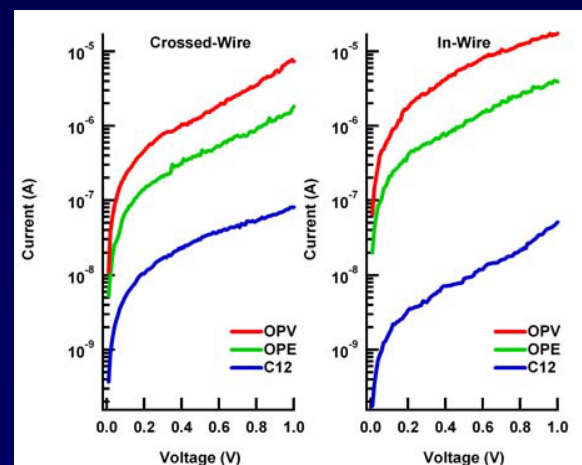
# In-wire Junctions



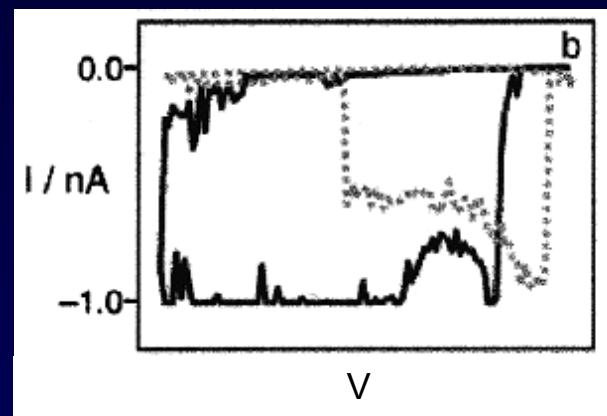
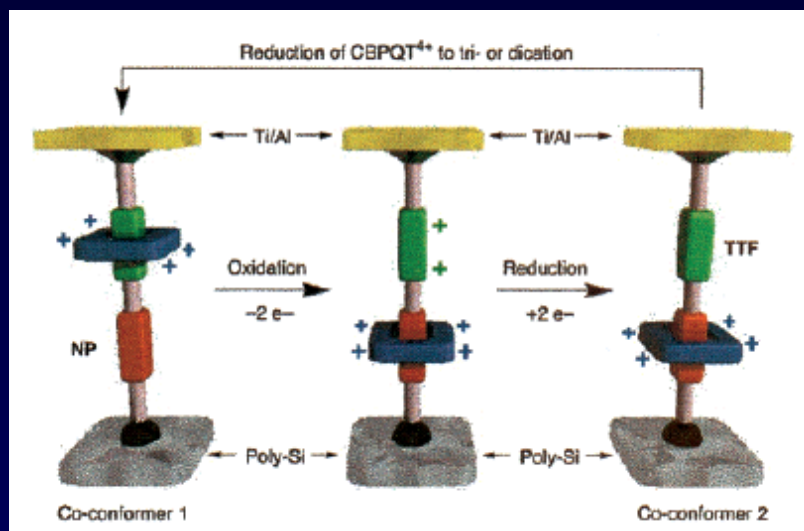
J. K. N. Mbindyo, T. E. Mallouk, J. B. Mattzela, I. Kratochvilova, B. Razavi, T. N. Jackson, T. S. Mayer, *J. Am. Chem. Soc.*, **124**, 4020 (2002).



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).

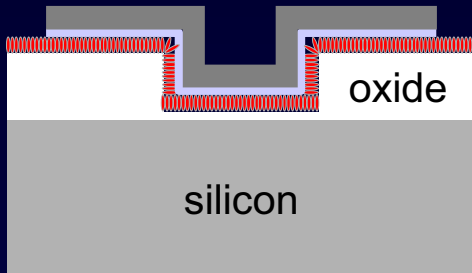


# Metal-Molecule-Semiconductor Junction



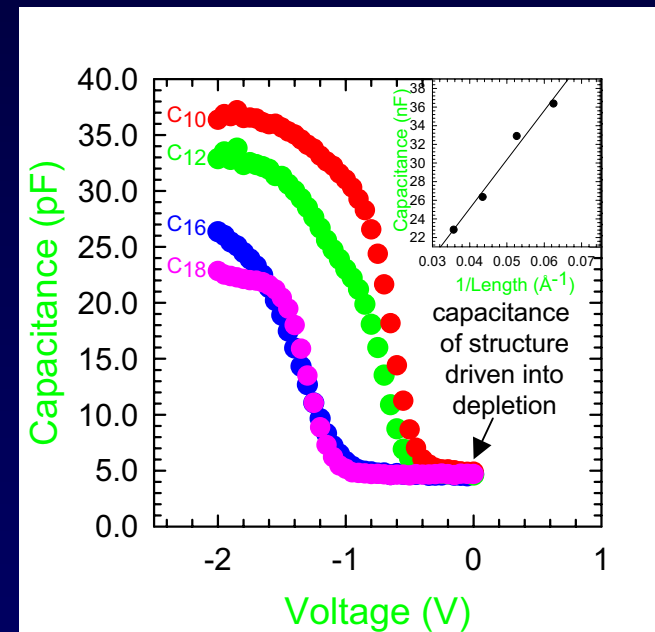
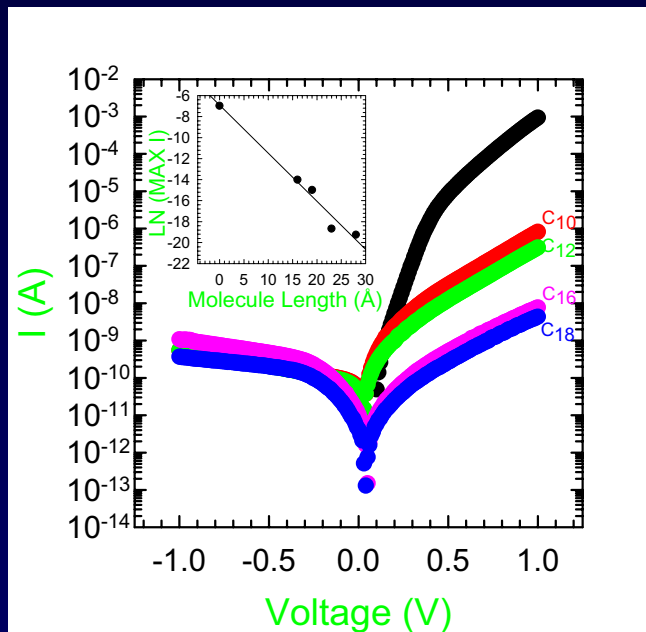
C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **123**, 12632 (2001).

# 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



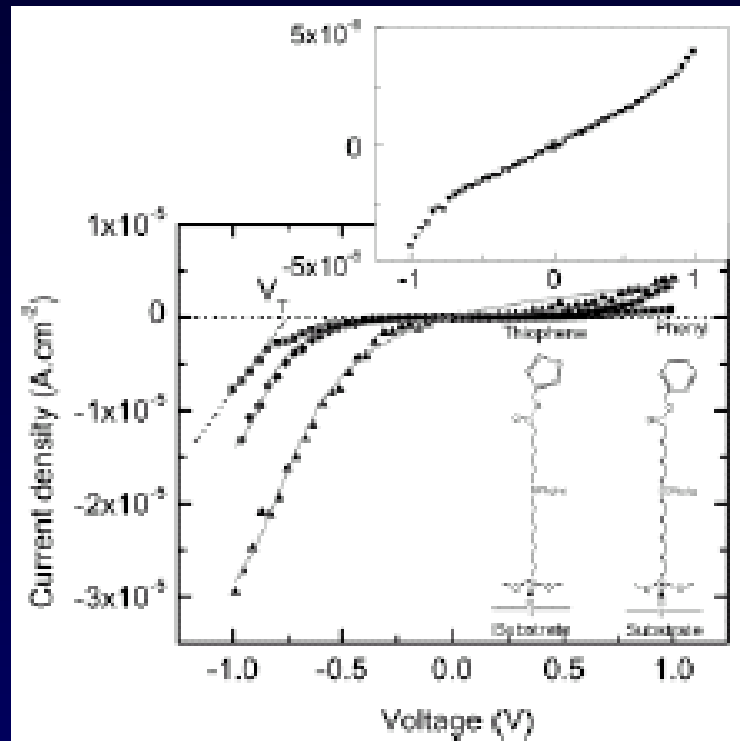
calculated capacitance agrees with MIS diode having organic molecules +  $\sim 10$  Å  $\text{SiO}_2$  native oxide

C. R. Kagan, C. T. Black

+ photoresponse measurements to understand barrier heights

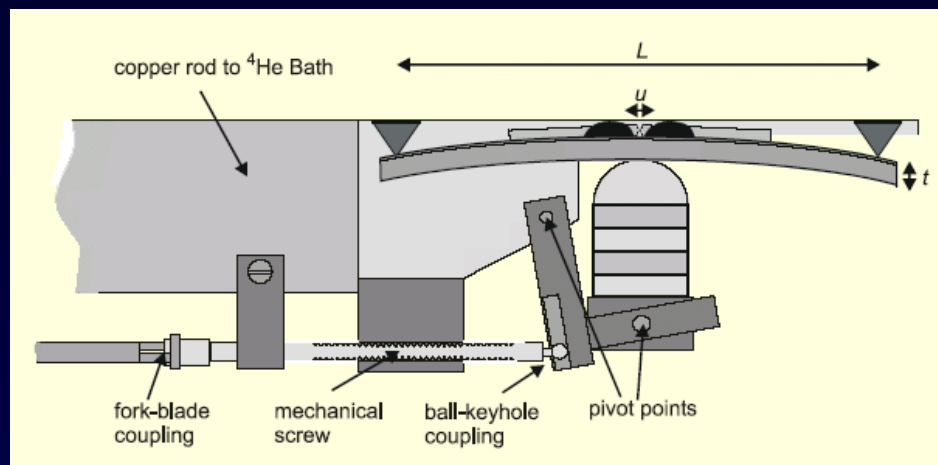
D. Vuillaume et. al. *Appl. Phys. Lett.* **69**, 1646 (1996).

# Molecular Junctions: Rectifiers on Si

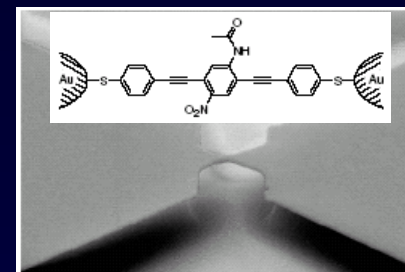


S. Lenfant, C. Krzeminski, C. Delerue, G. Allan, D. Vuillaume,  
*Nano Lett* **3**, 741 (2003).

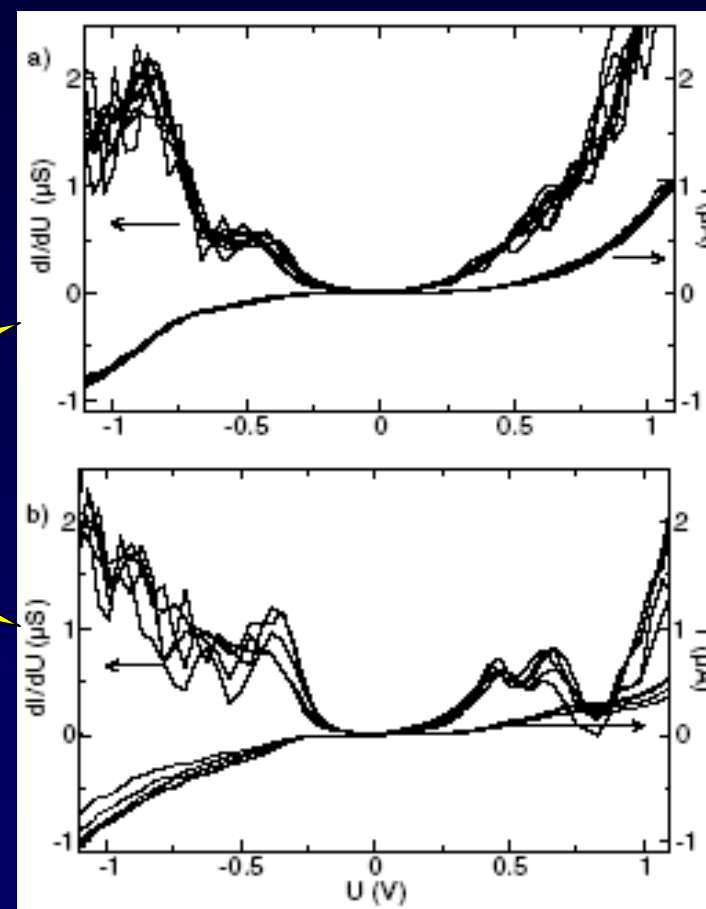
# Mechanically Controllable Break Junctions



J. van Ruitenbeek

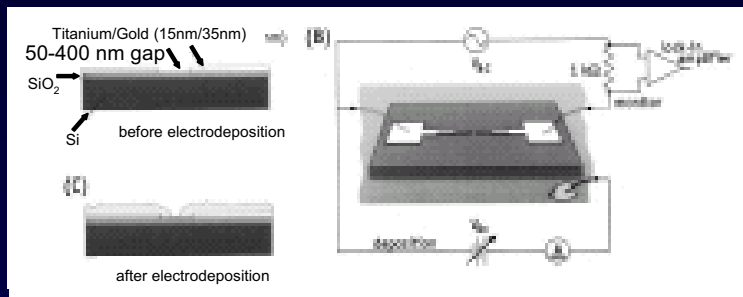


before and after  
reconfiguration of the  
molecule in the junction



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 [ $\text{KAu}(\text{CN})_2$ ]

buffer  $\sim \text{pH } 10$  composed of:

1 M potassium bicarbonate ( $\text{KHCO}_3$ ) and

0.2 M potassium hydroxide  $\text{KOH}$

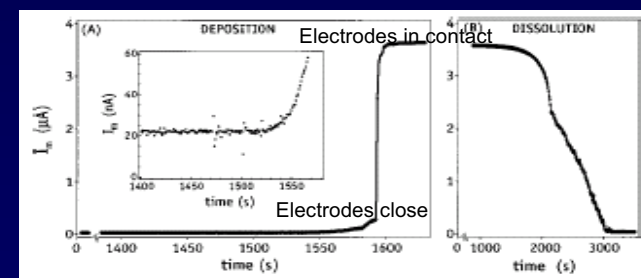
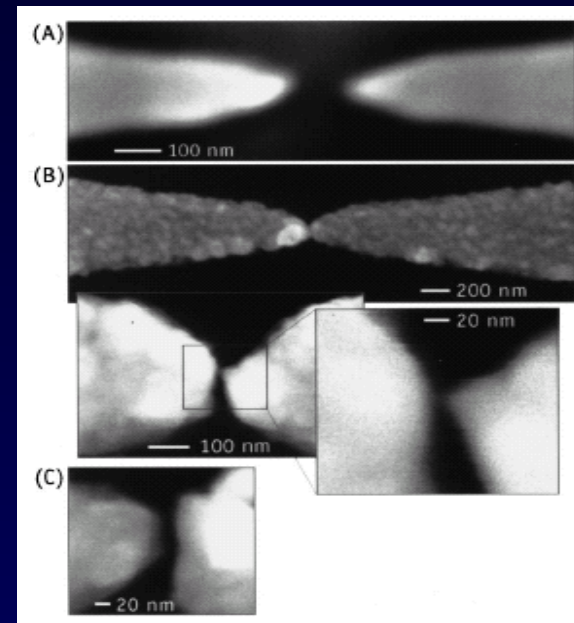
Cyanaurate accepts electron, liberating cyanide, depositing Au

Au counterelectrode

$V_{\text{app}} = -0.5 \text{—} -0.6 \text{ V}$  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

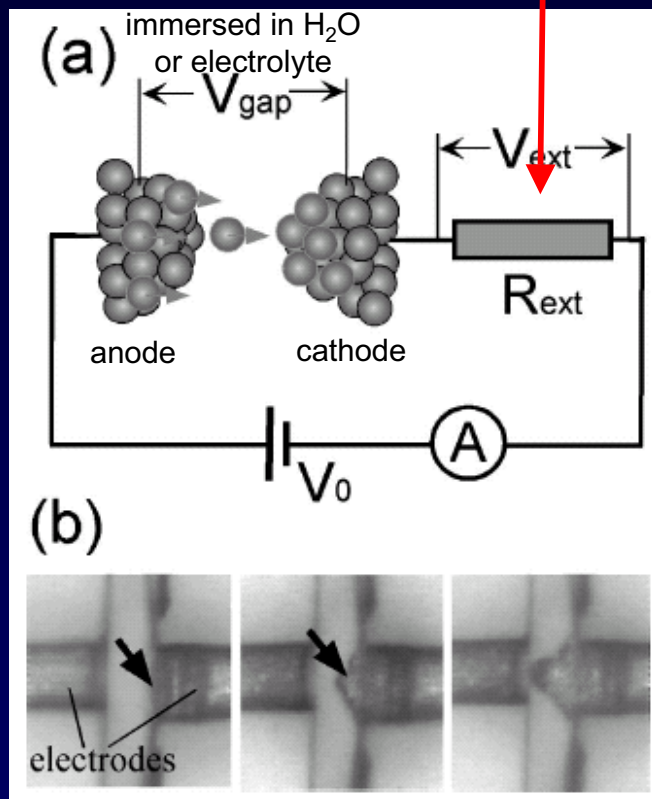
Gaps  $\sim 1\text{--}20 \text{ nm}$

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

Provides built-in self-termination

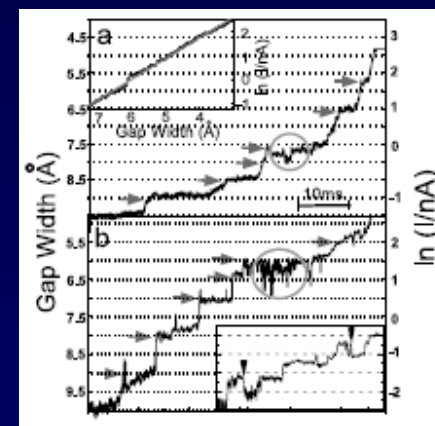
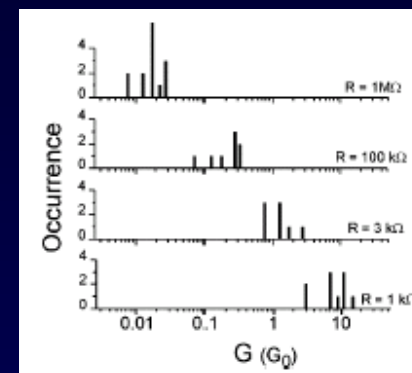
$1/R_{\text{ext}} < G_0$ , small gap with conductance determined by tunneling

$1/R_{\text{ext}} > G_0$ , conductance with multiple of  $G_0$



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

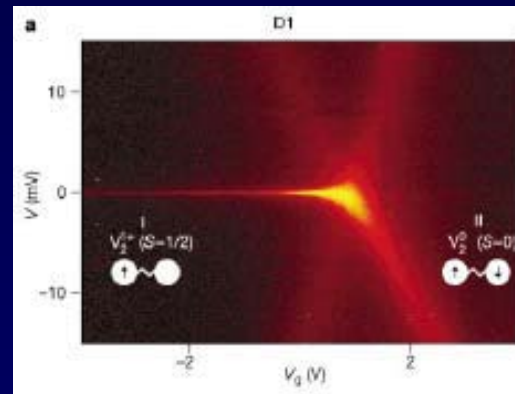
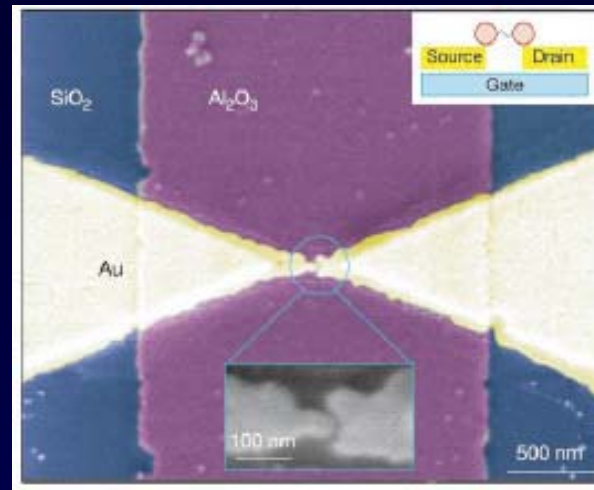
$R_{\text{gap}}$  depends on tunneling current and leakage current  
Leakage current depends on electrode geometry and electrolyte concentration



S. Boussaad and N. J. Tao, *App. Phys. Lett.* **80**, 2398 (2002).

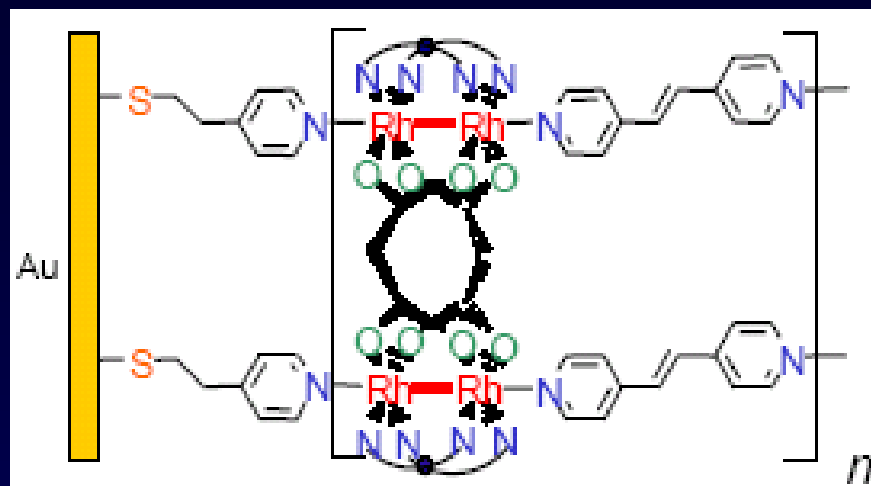
H.X. He, S. Boussaad, B.Q. Xu, C.Z. Li, N.J. Tao, *J. ElectroAnal. Chem.* **522**, 167 (2002)

# Electromigration Junctions

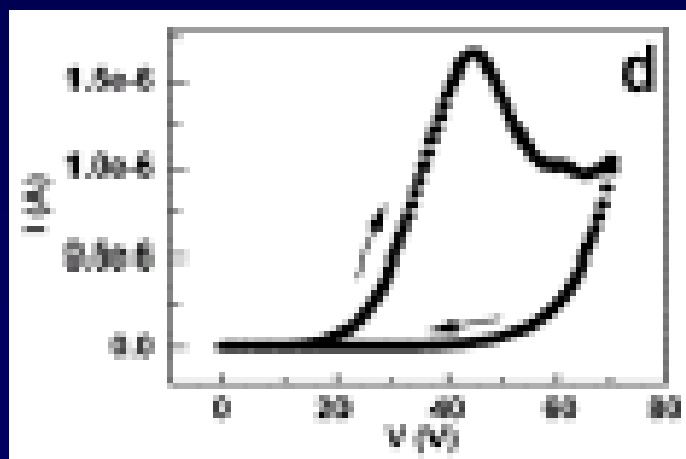


J. Park, A. N. Pasupathy, J. I. Goldsmith, C. Chang, Y. Yaish, J. R. Petta, M. Rinkoski, J. P. Sethna, H. D. Abruna, P. L. McEuen, D. C. Ralph, *Nature* **417**, 722 (2002); W. Liang, M. P. Shores, M. Bockrath, J. R. Long, H. Park, *Nature* **417**, 725 (2002).

## Bridging the Gap



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

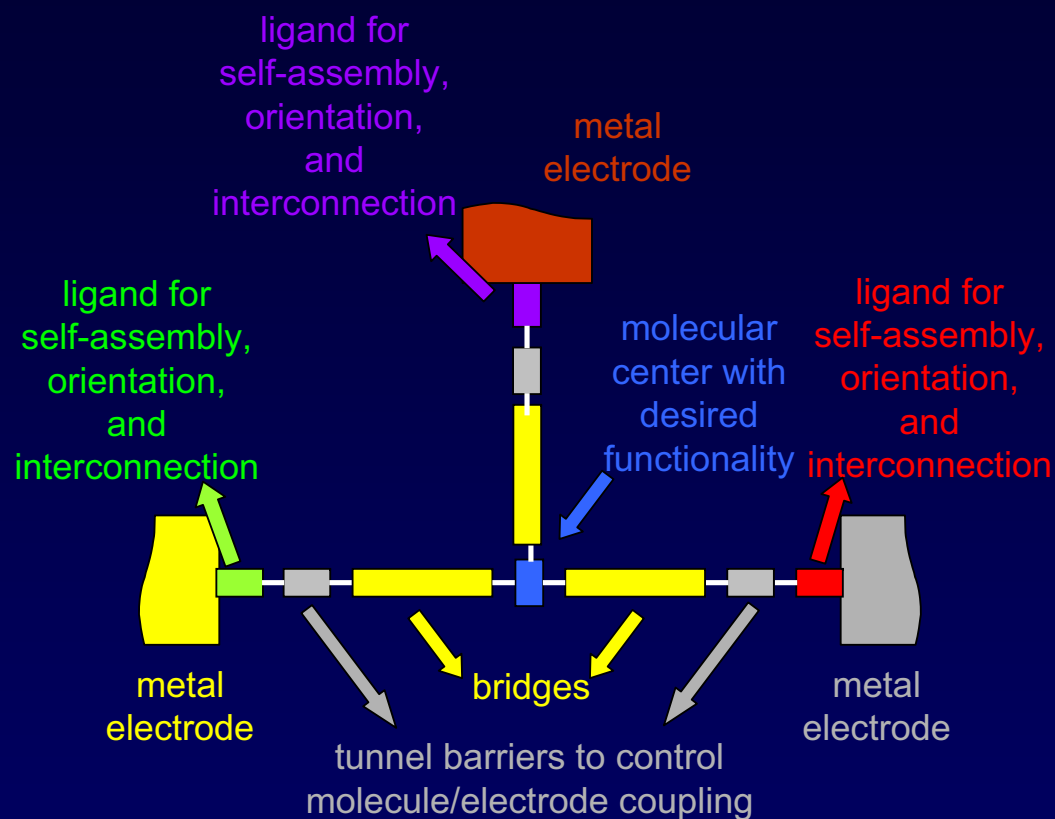


# **The Chemistry of Molecular Assembly**

**Cherie R. Kagan**

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

# Molecular Materials and Devices

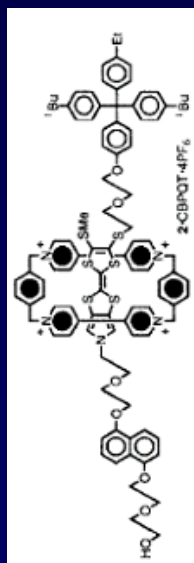
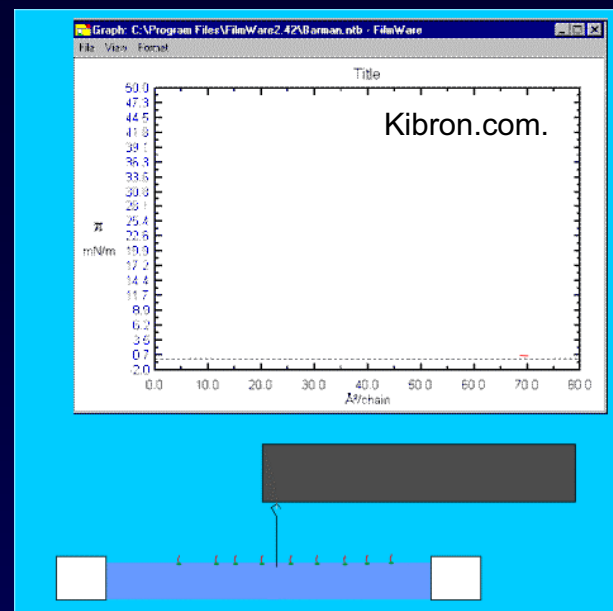


**Build desired functionality  
into single molecules**

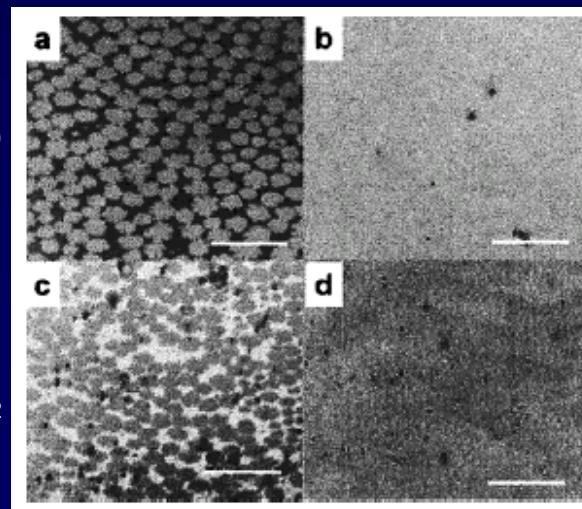
**Understand  
the physics and design  
of molecules  
and molecular devices  
to control:**

**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



6.4 mM CdCl<sub>2</sub>

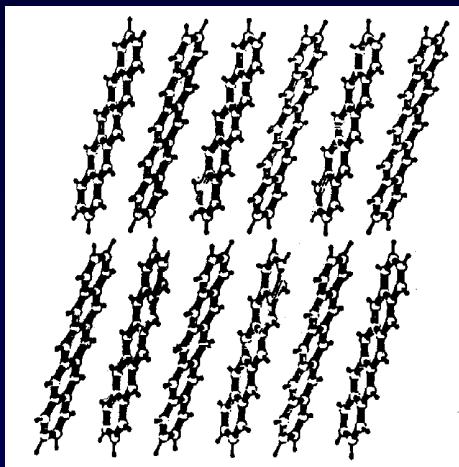


100 μm

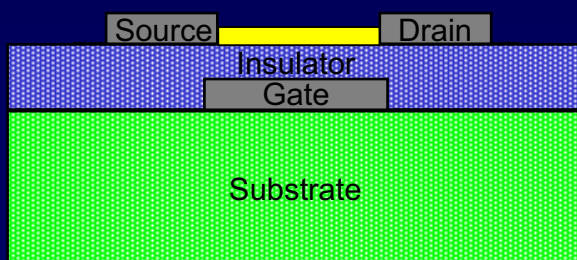
C. P. Collier, J. O. Jeppesen, Y. Luo, J. Perkins, E. W. Wong, J. R. Heath, J. F. Stoddart, *J. Am. Chem. Soc.* **123**, 12632 (2001).

# Physical Assembly As in Thin Film Organic Devices

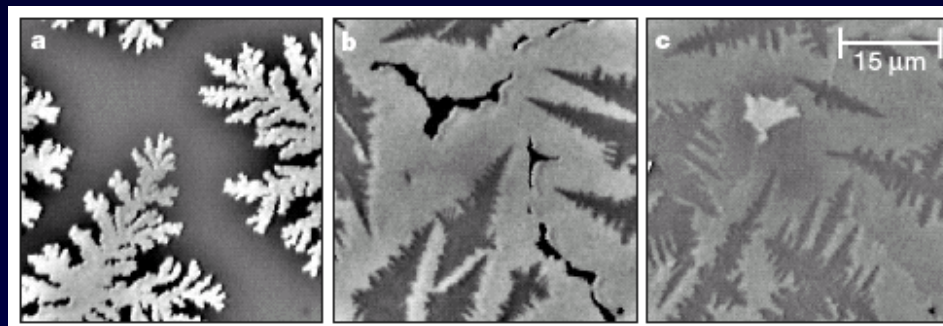
## Intermolecular Charge Transport



Collective property of molecules

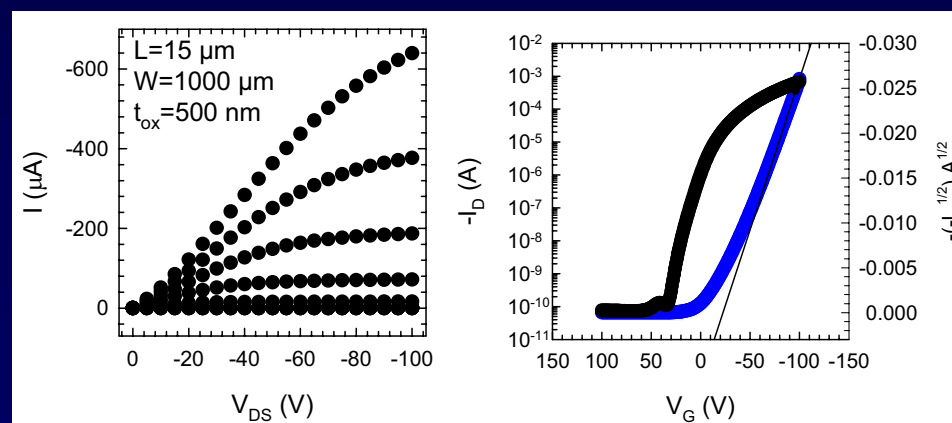


Channel Lengths  $\sim \mu\text{m}$



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).

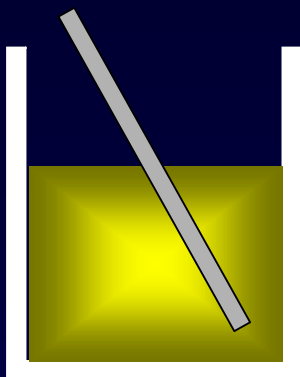


Mobility =  $0.5 \text{ cm}^2/\text{V}\cdot\text{sec}$

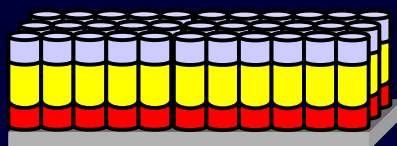
$I_{\text{ON}}/I_{\text{OFF}} = 10^7$

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,  $\pi$ - $\pi$ , ...)

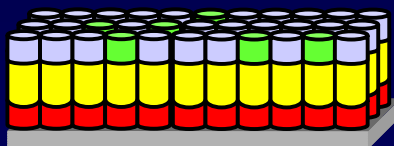
Surface-active head group  
providing chemisorption to the surface

## Interactions:

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

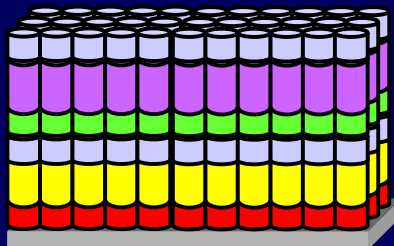
## Affects:

ordering, growth, wetting, ....



Different tail groups may interact through hydrogen bonding, dipolar interactions

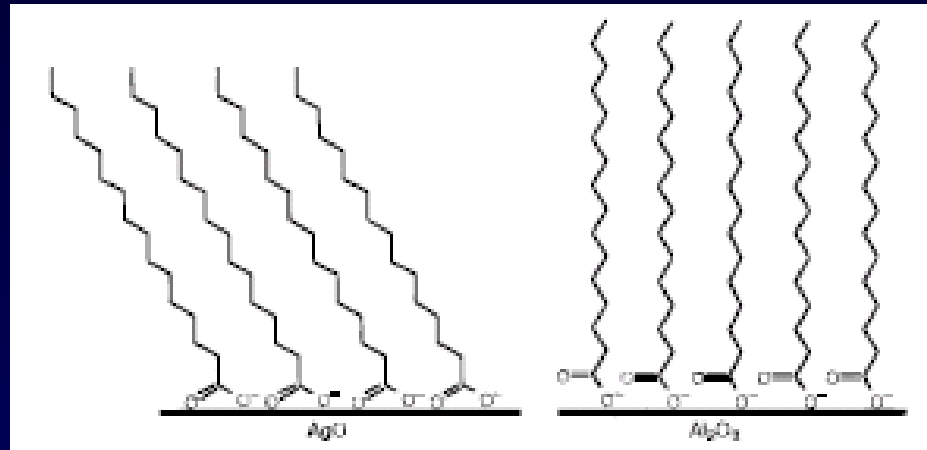
⋮



Reactive tail groups for multilayer assembly

## Classic Example of Fatty Acids

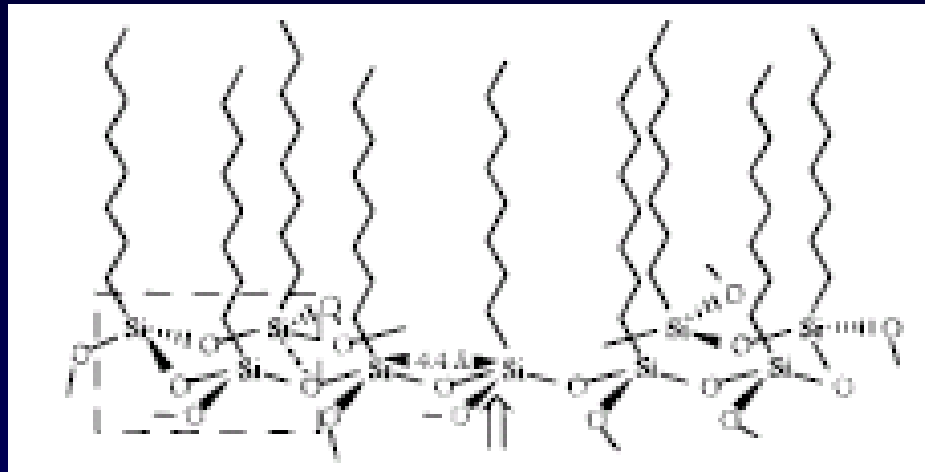
Example:



acid-base reaction between carboxylic acid and surface metal cation

# Classic Example of Silanes

silane + hydroxylated surface surface →

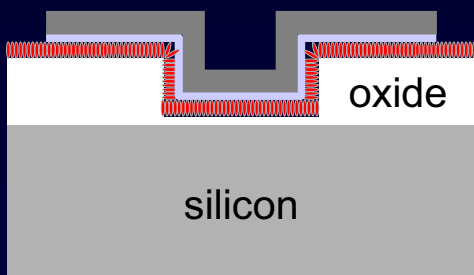


Driving force:

Polysiloxane connected to surface silanol  
or other hydroxylated surface

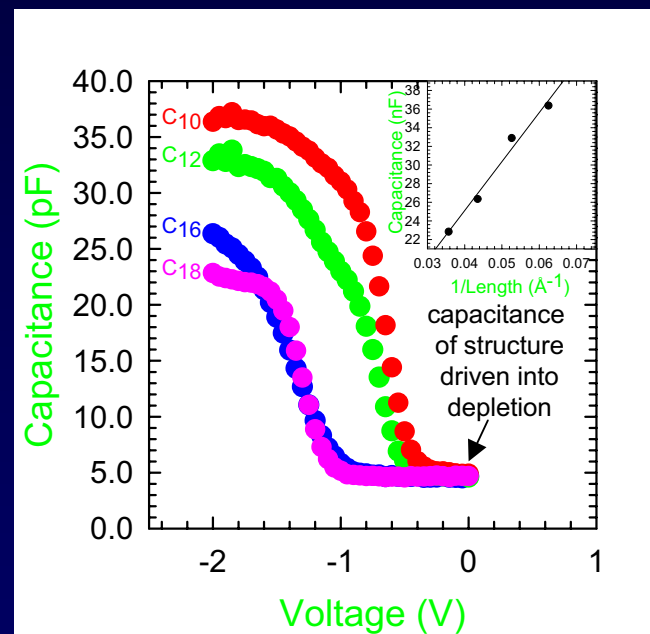
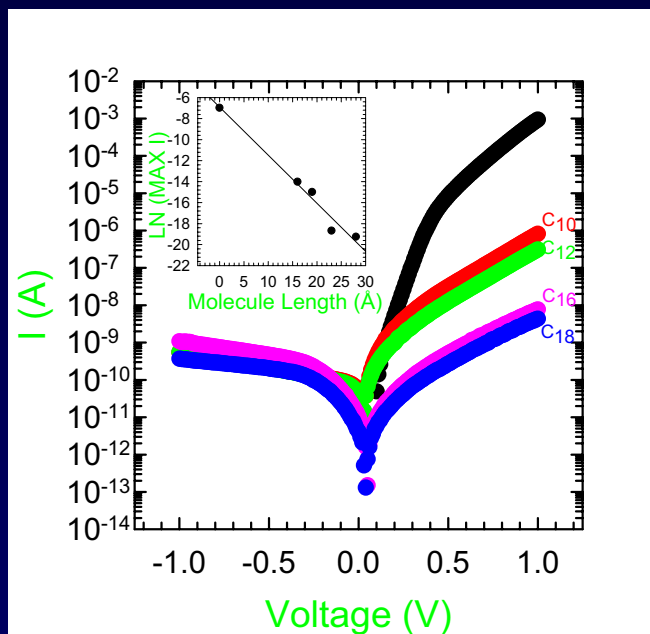
Note: monolayer formation is highly sensitive to surface water

# 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



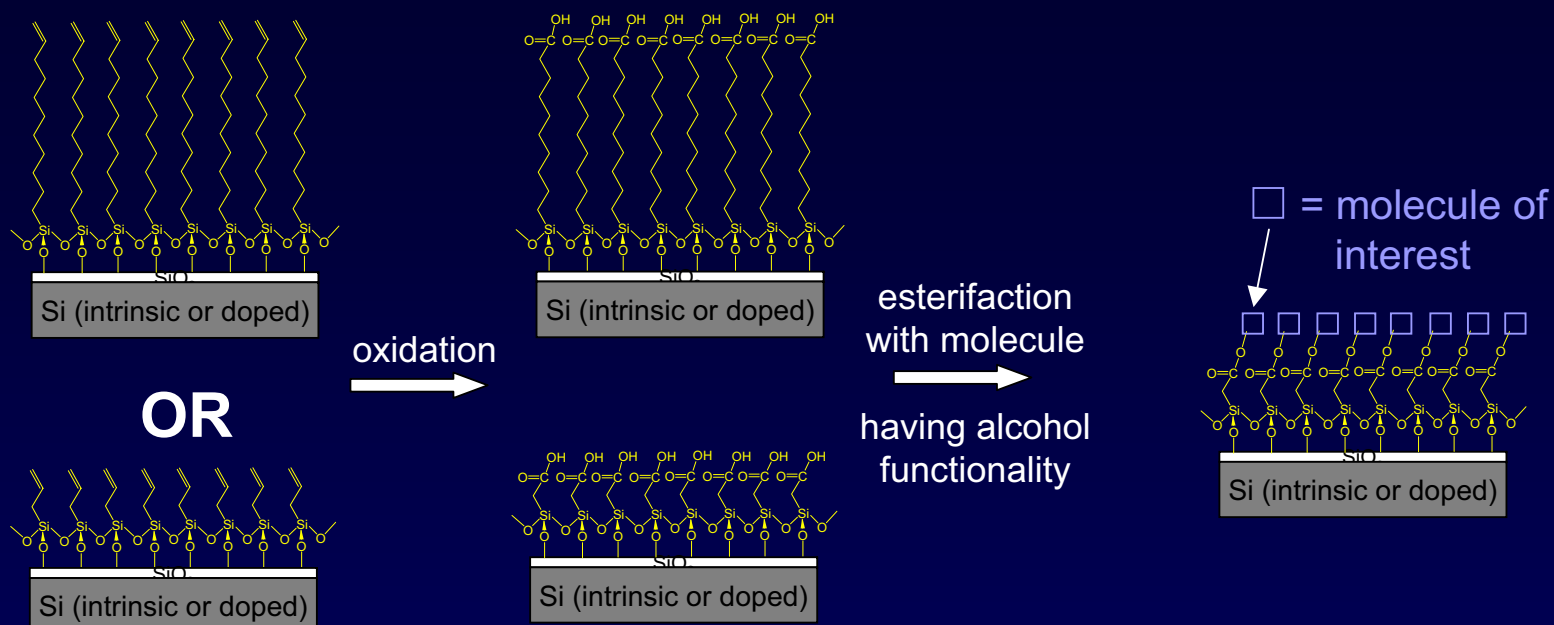
calculated capacitance agrees with MIS diode having organic molecules +  $\sim 10$  Å  $\text{SiO}_2$  native oxide

C. R. Kagan, C. T. Black

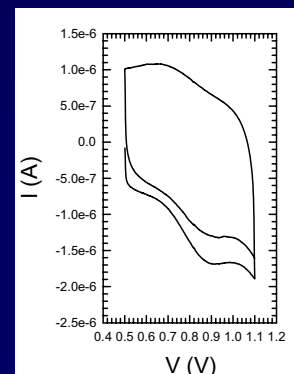
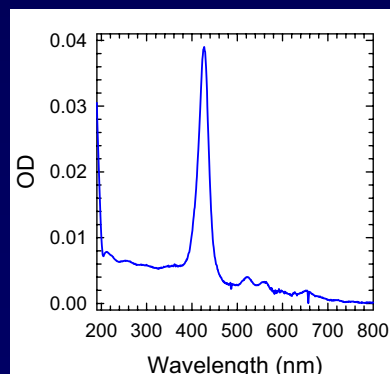
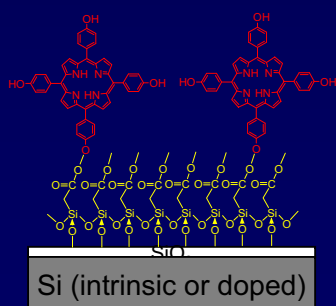
+ photoresponse measurements to understand barrier heights

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

# Chemistry to Covalently Bind Molecules to Oxides



## Example: tetrahydroxyphenylporphine

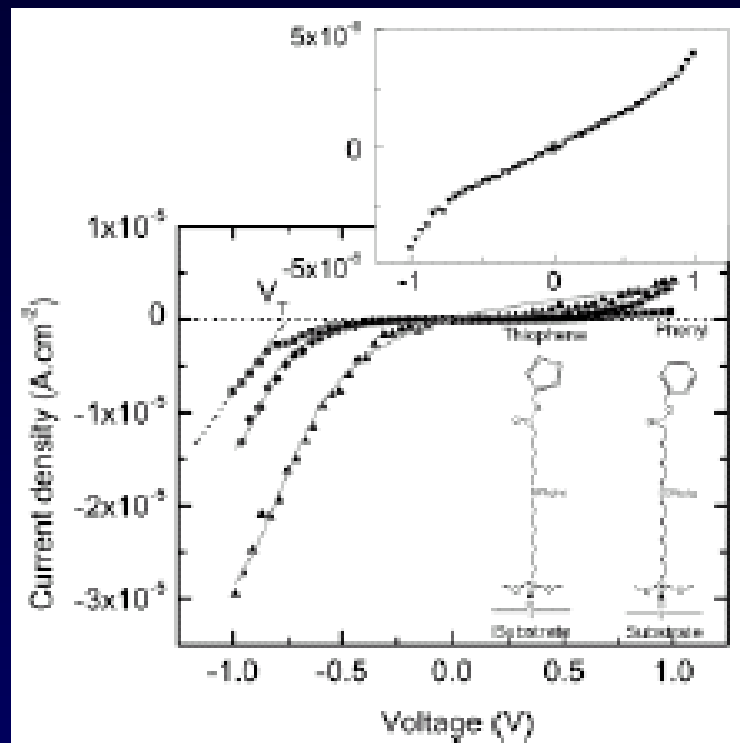


Molecules tried :

- porphyrins
- ferrocene
- pyrene
- anthracene
- all-trans retinol

Works for alcohols, phenols,  
.....?

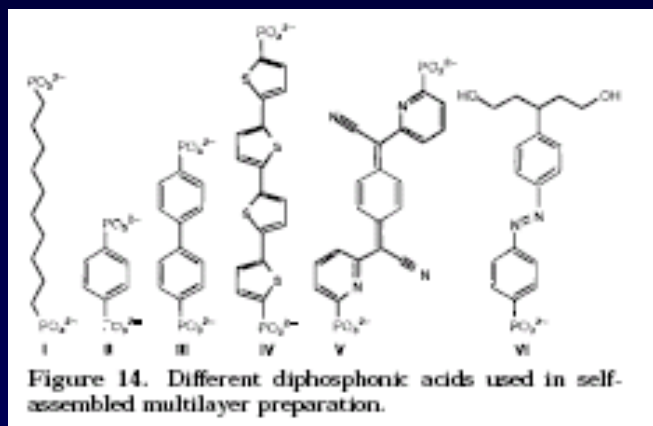
# Molecular Junctions: Rectifiers on Si



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 –



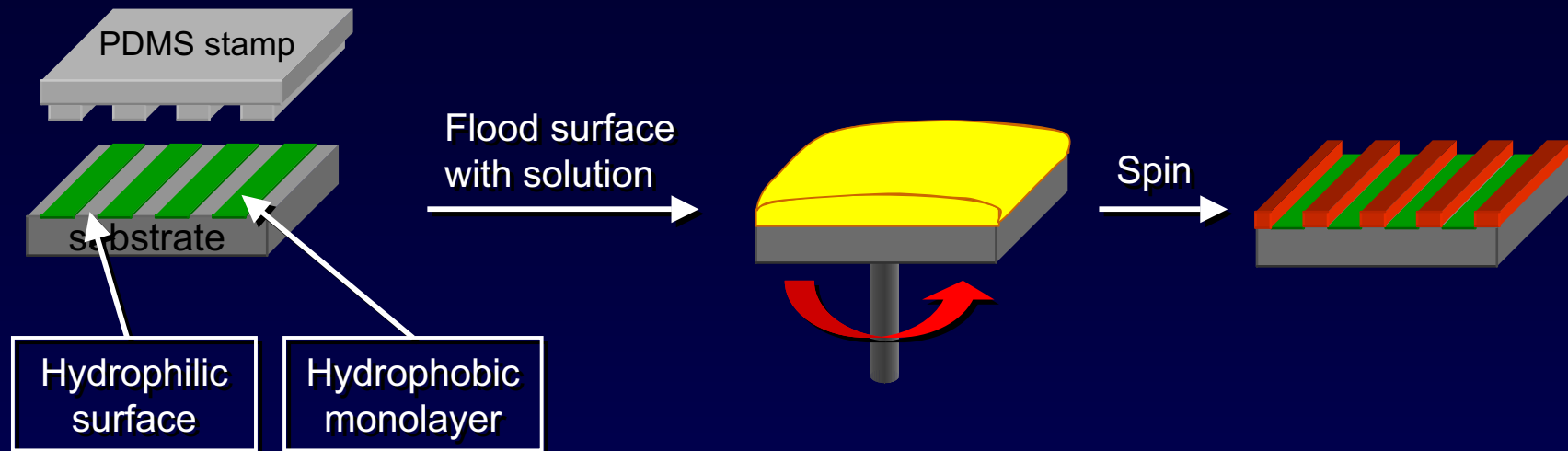
+  $\text{Zr}^{4+}$   $\longrightarrow$  Zirconium Phosphate Multilayers

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



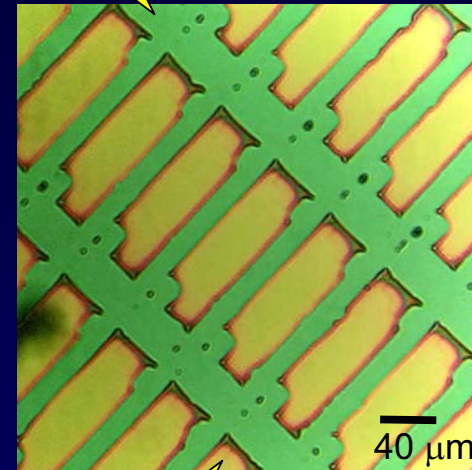
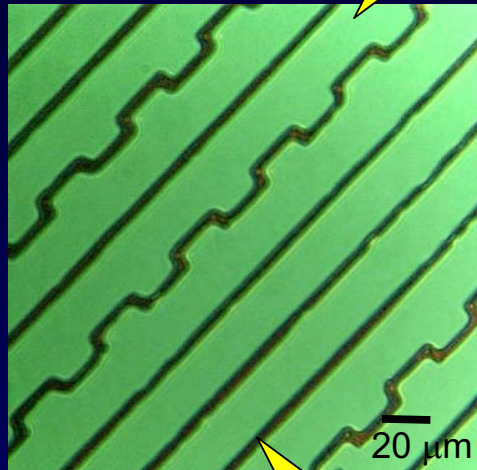
To pattern subsequently  
Solution deposited thin films

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

# Patterned Organic-Inorganic Hybrid Thin Films

## Example: Hydroxamic acids on Oxide Surfaces

Hydrophobic  
monolayer –  
repels hybrid  
material

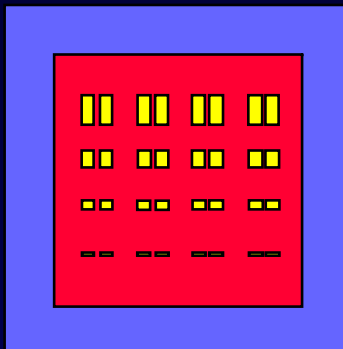


Hybrid material  
selectively deposits  
on hydrophilic oxide  
surface

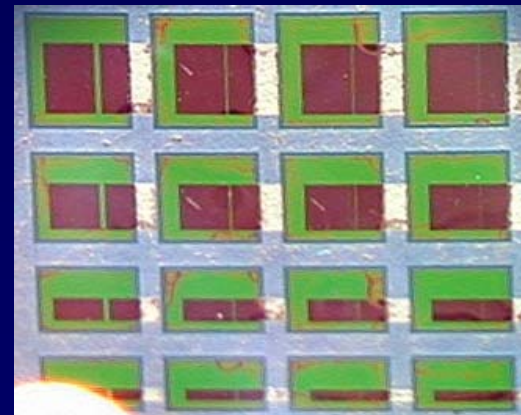
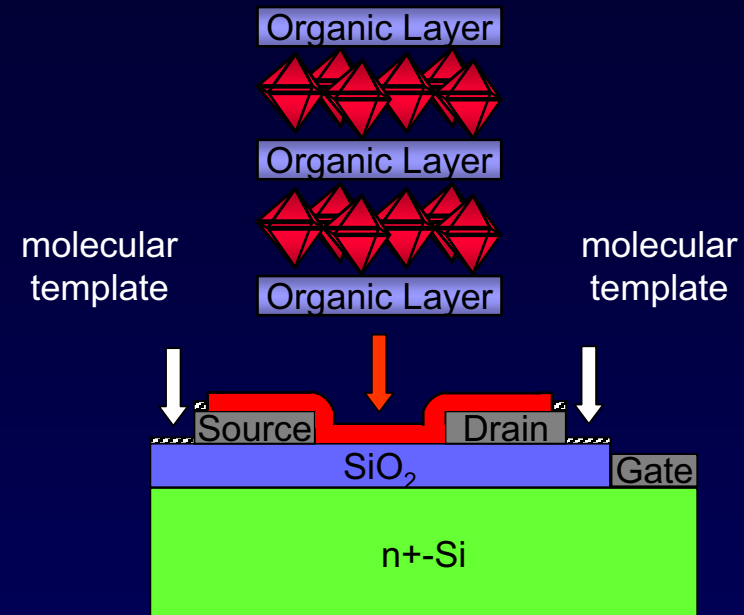
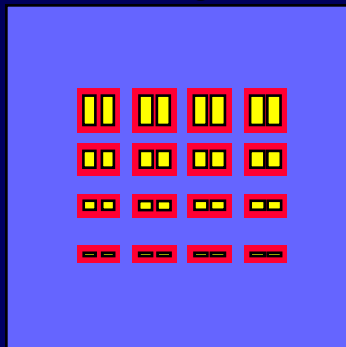
Hydrophobic monolayer – hexadecylhydroxamic acid  
Substrate –  $\text{ZrO}_2/\text{SiO}_2/\text{Si}$

# Patterned Organic-Inorganic Hybrid Thin Film Transistors

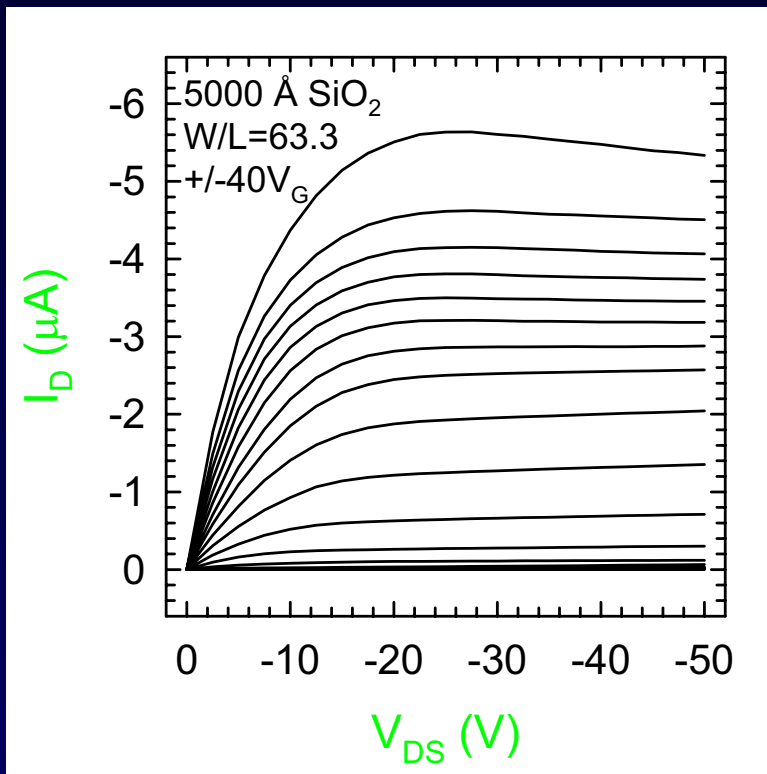
Unpatterned



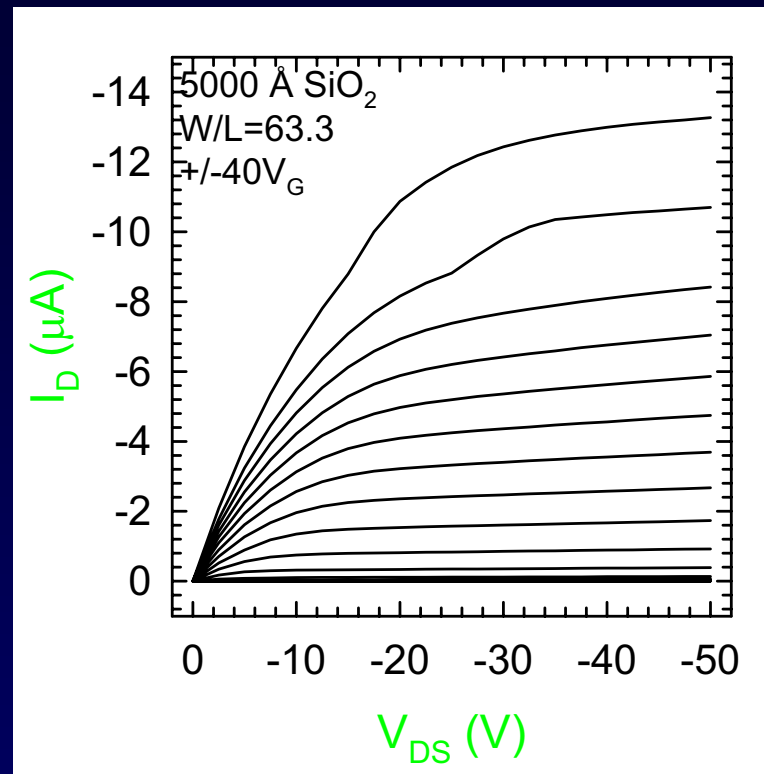
Isolate devices from each other and from back gate



# Organic-Inorganic Hybrid Material (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>SnI<sub>4</sub> Patterned Devices

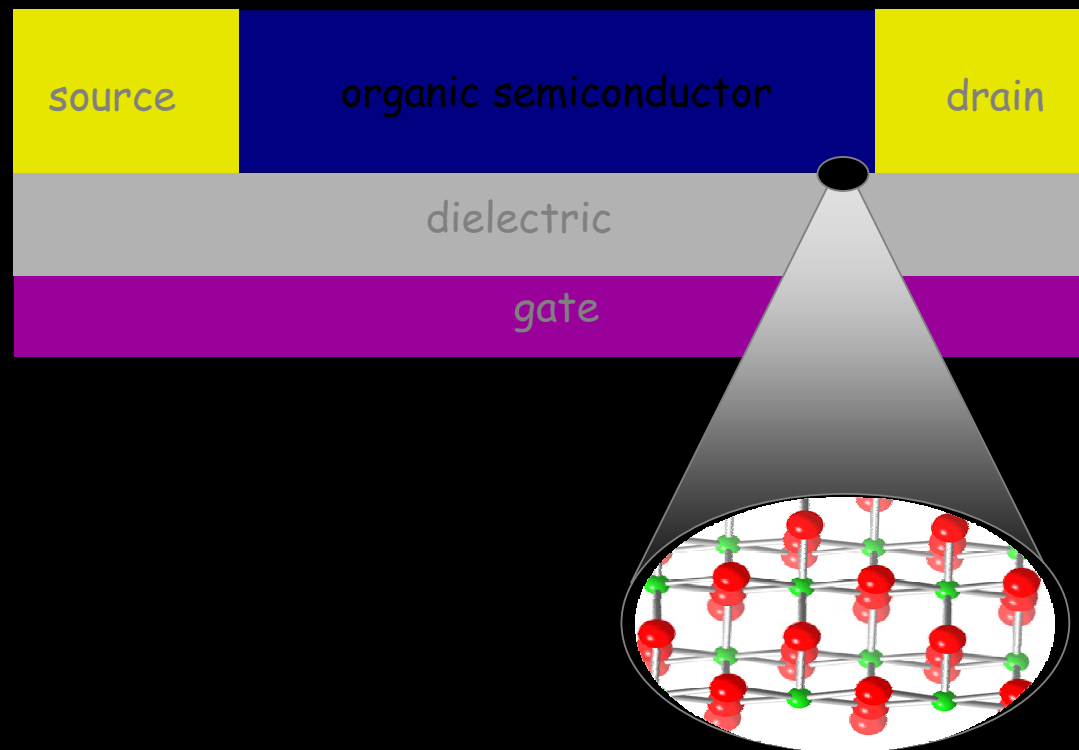


Template:  
Octadecylphosphonic  
acid  
 $\mu = 0.1 \text{ cm}^2/\text{V-sec}$   
 $I_{ON}/I_{OFF} \sim 10^4$

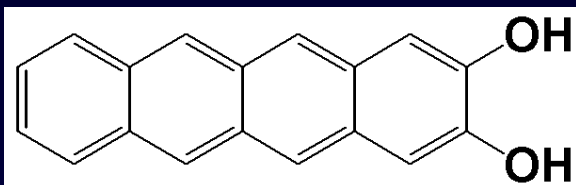


Template:  
fluorinated alkylsilane  
 $\mu = 0.52 \text{ cm}^2/\text{V-sec}$   
 $I_{ON}/I_{OFF} \sim 10^5$

# Self-Assembly of linear acenes on gate oxides



# Self-Assembly on High K-Dielectrics



THF solution with  
 $\text{Al}_2\text{O}_3$  Surface

**Water Contact Angle:**

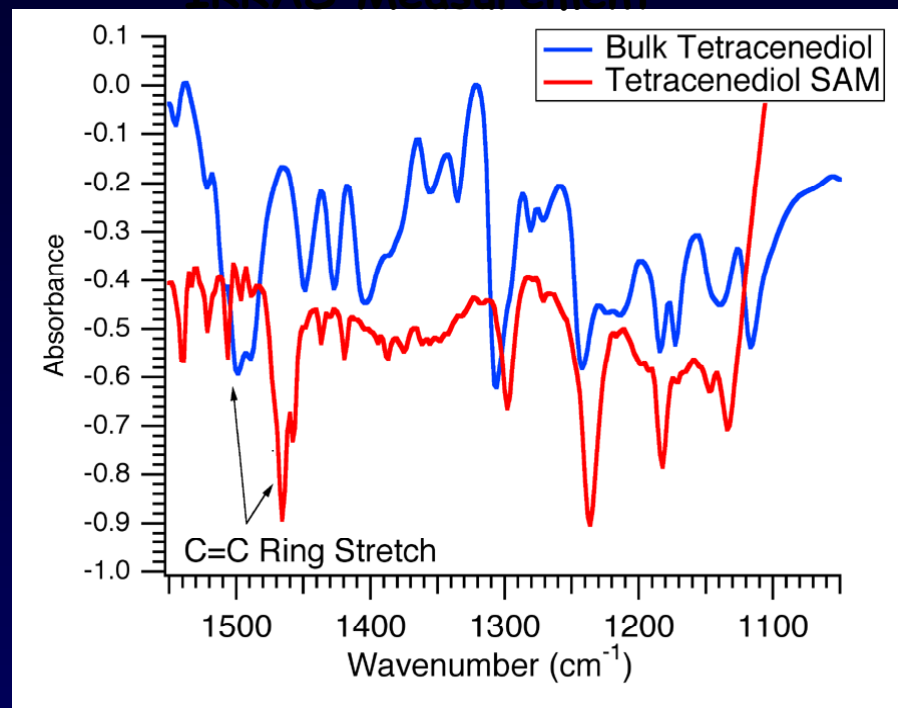
Advancing =  $76^\circ$

Receding =  $63^\circ$

## XPS

|      | $15^\circ$ | $35^\circ$ | $70^\circ$ |
|------|------------|------------|------------|
| 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



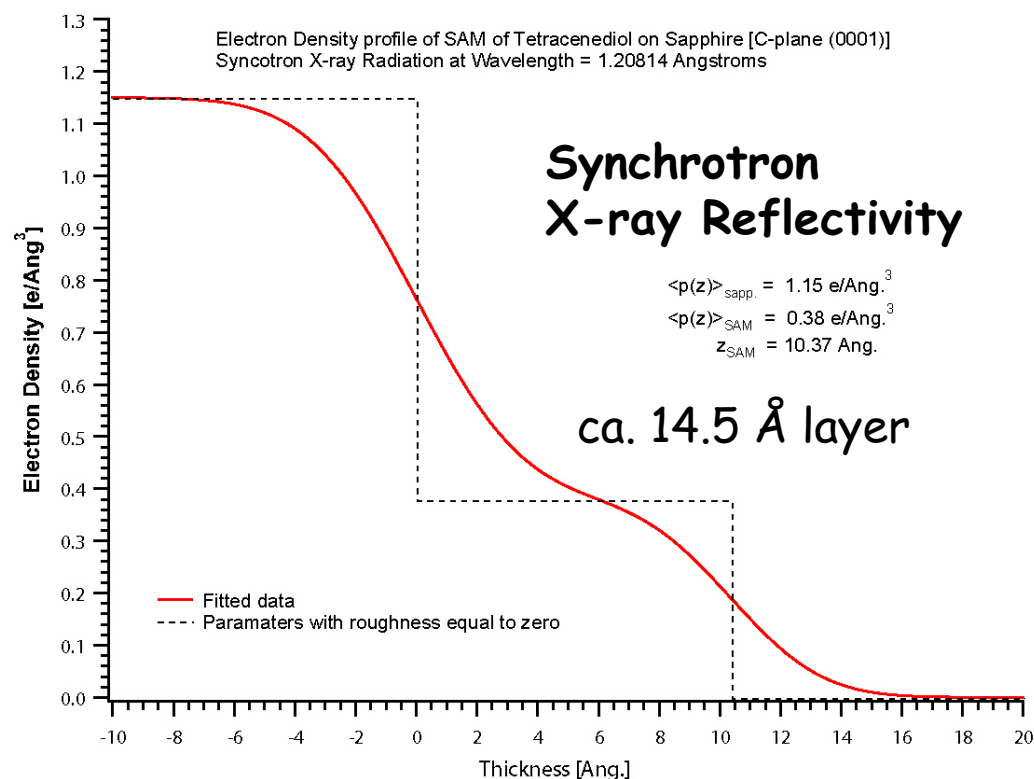
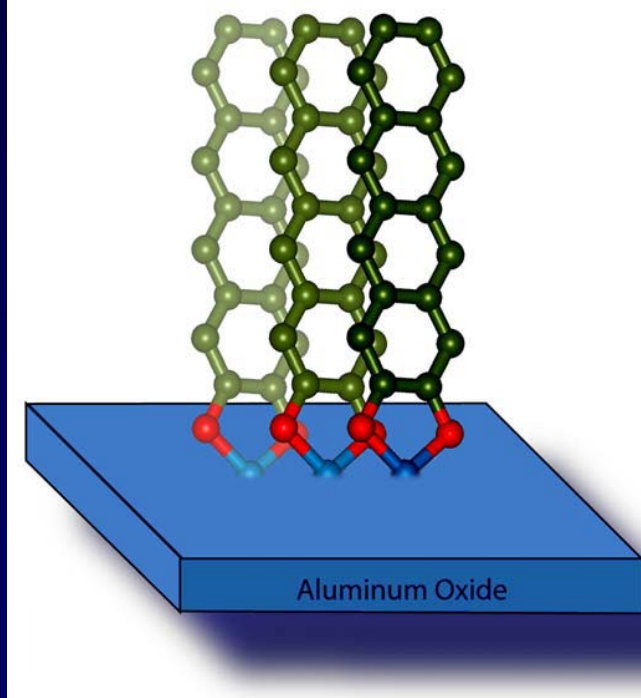
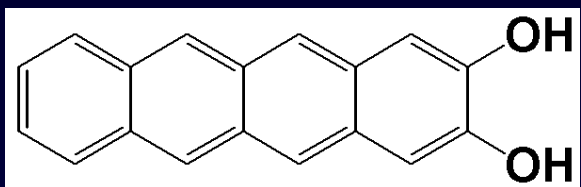
## Ellipsometry:

Measured Thickness =  $14.8 \text{ \AA}$

Calculated:  $14 \text{ \AA}$

Also:  $\text{HfO}_2$ ,  $\text{ZrO}_2$ , and  $\text{Y}_2\text{O}_3$

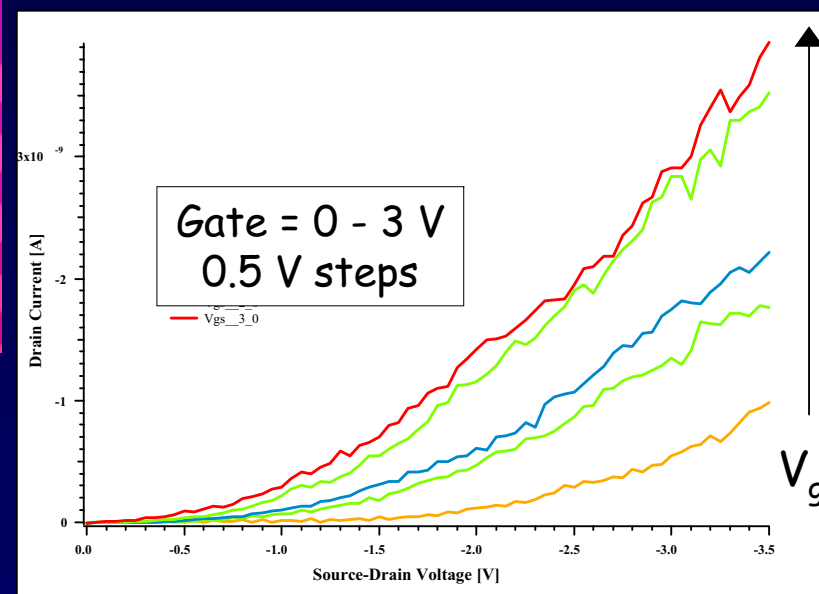
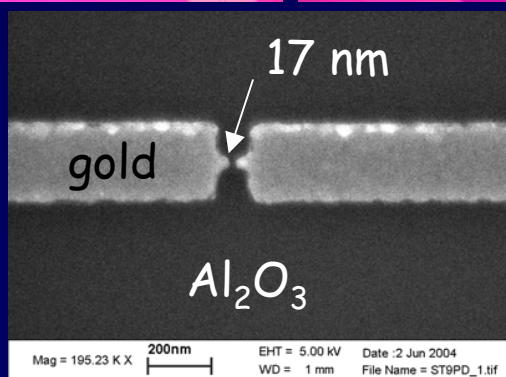
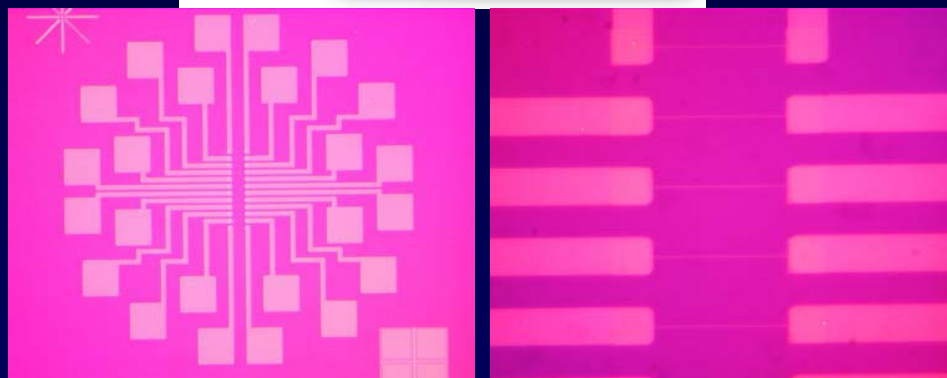
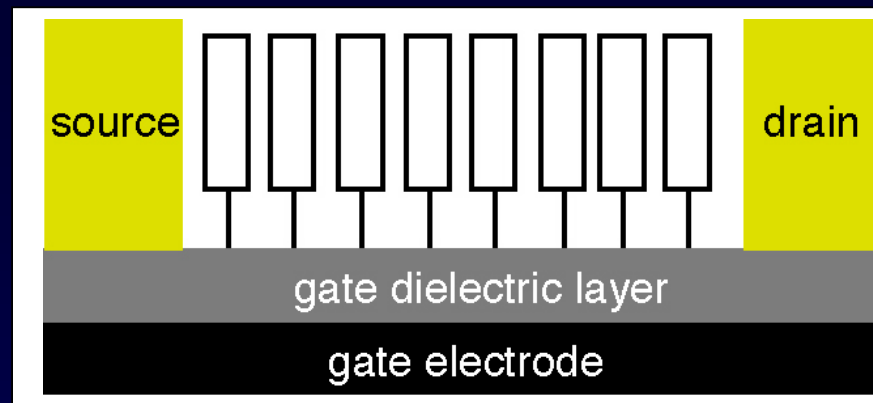
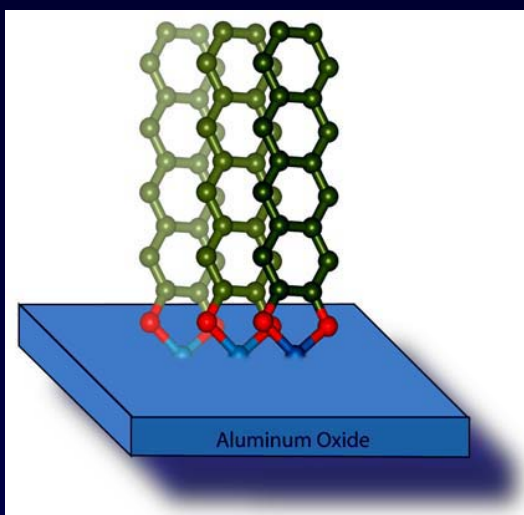
# Monolayers on sapphire crystals



electron density  
 0.38  $\text{e}/\text{\AA}^3$  for monolayer  
 0.39  $\text{e}/\text{\AA}^3$  for tetracene crystal

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

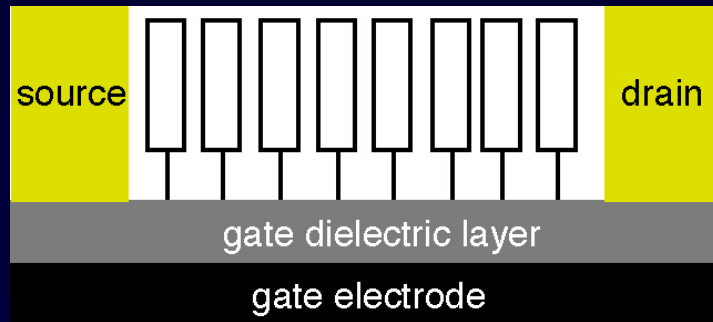
# Monolayer devices



Yield of similar devices: approx. 90%

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

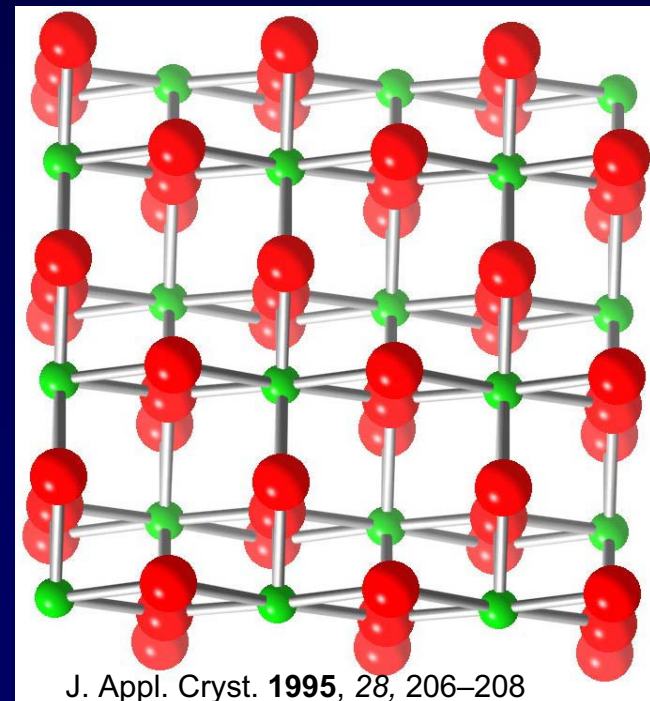
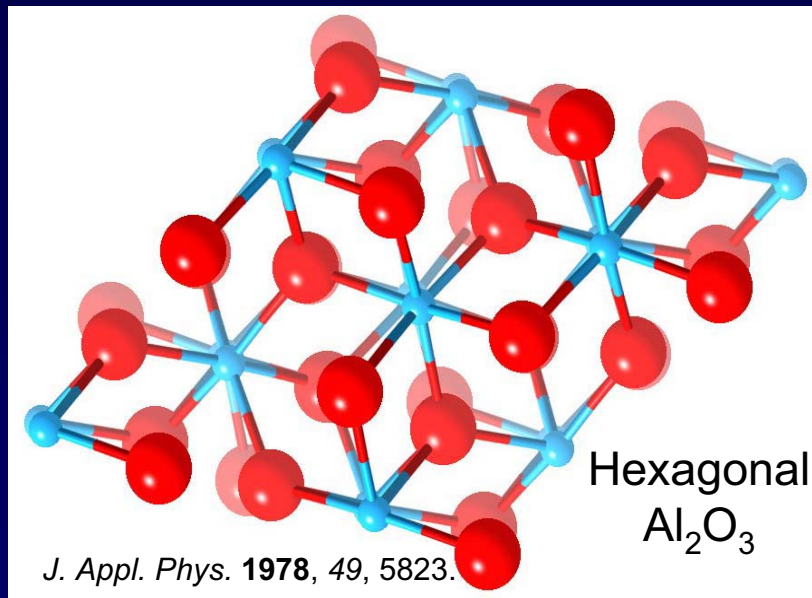
## The next step: tune the three interfaces



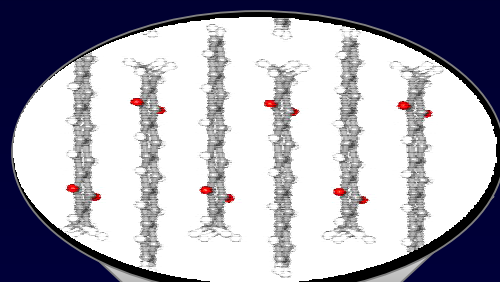
Source/Drain:  
Gold (adhesion layer?)  
Platinum  
Derivatized

Gate dielectric:  
Aluminum oxide  
Hafnium oxide  
Zirconium oxide  
Crystalline

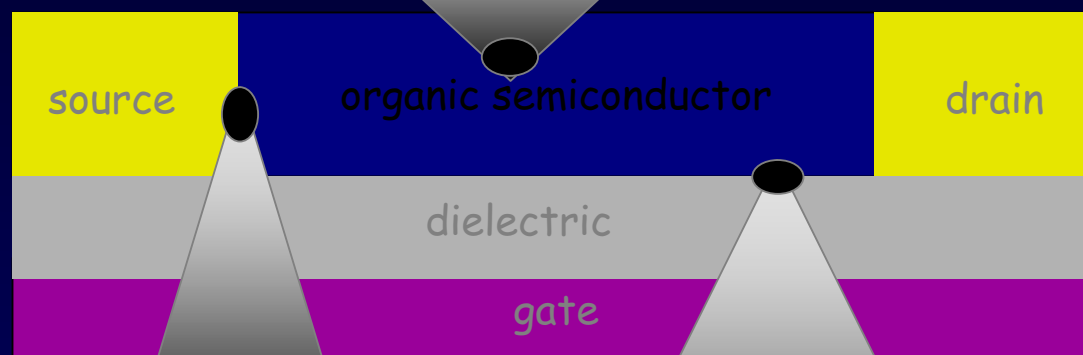
Viewing down the z-axis of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$



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

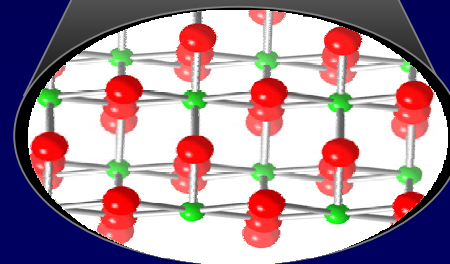
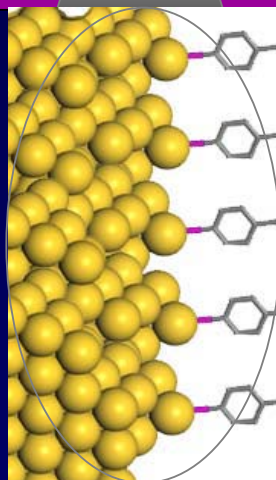


Molecular Assembly  
 •directing the assembly  
 •close contacts



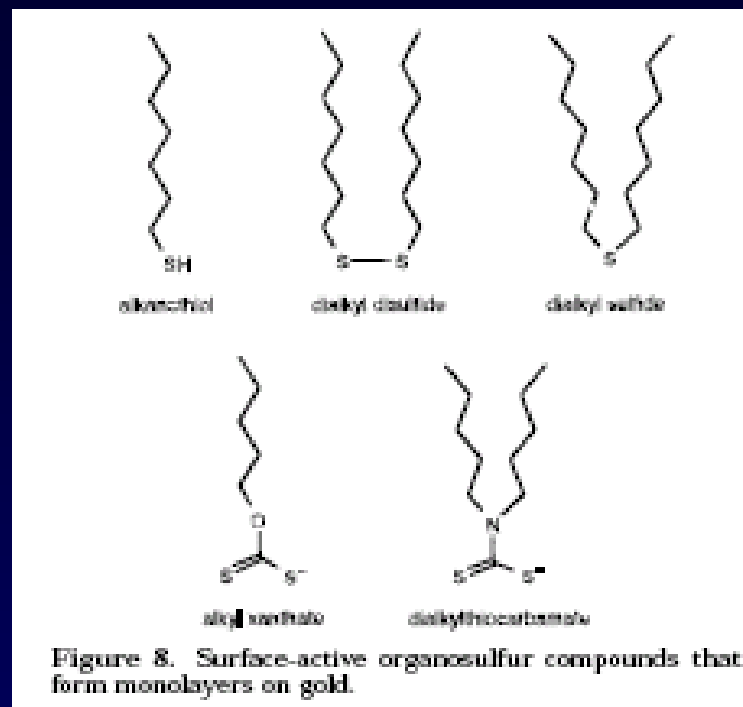
Metal-Molecule Linkage

- Structure
- Electronics

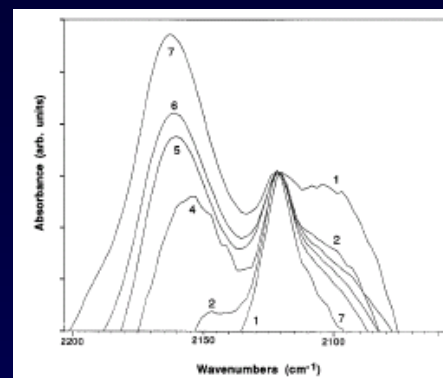
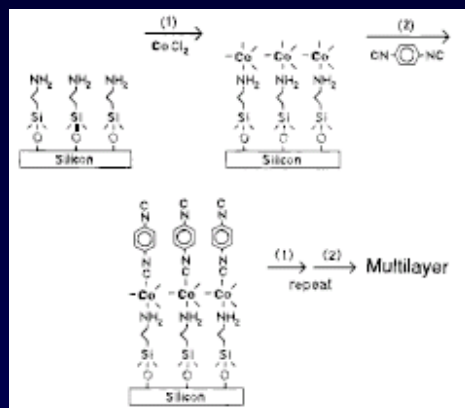


Interfacial Assembly  
 •crystalline vs. glassy  
 •direct the assembly

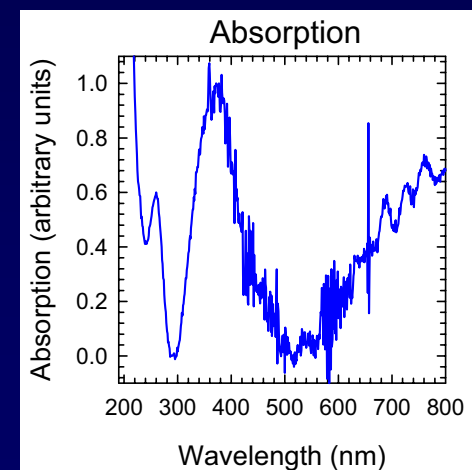
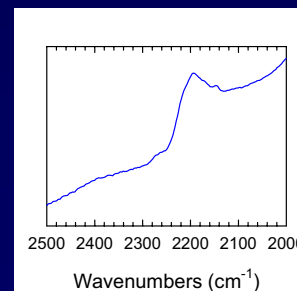
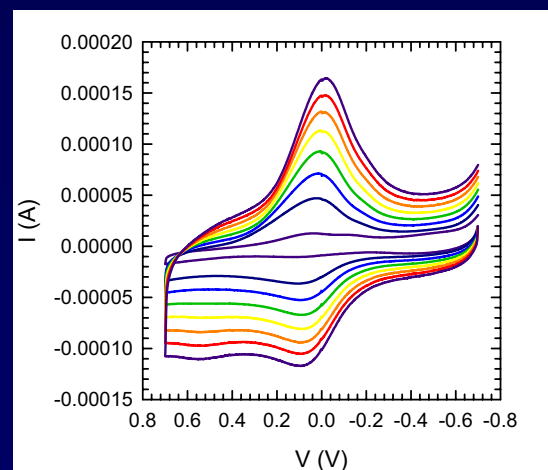
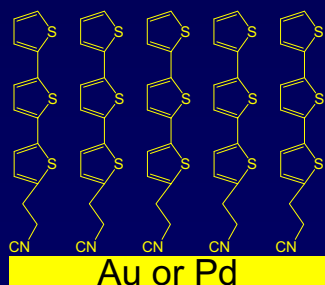
## Classic Example: Organosulfur, organoselenium



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

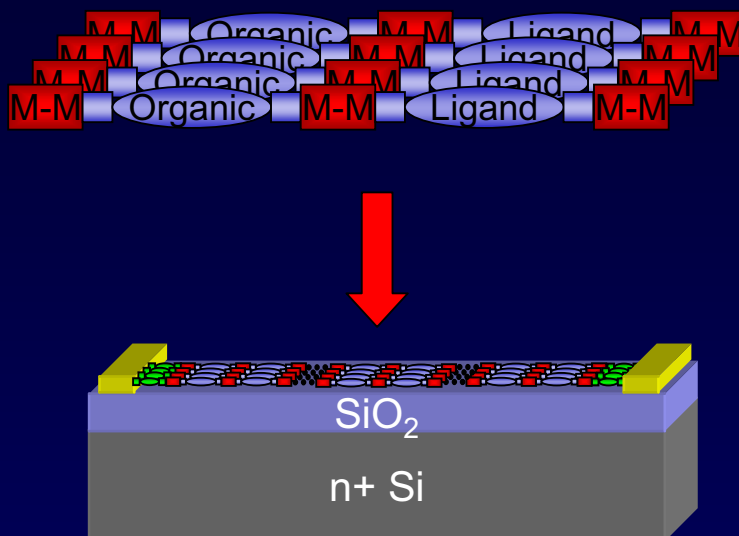


M. A. Ansell, E. B. Cogan, C. J. Page, *Langmuir* **16**, 1172 (2000).

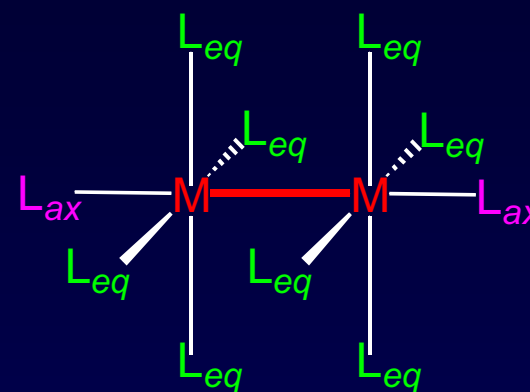


C. R. Kagan, A. Afzali, V. Sundar

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



- Bridge channels > 3 nm
- Chemistry meet lithographic capabilities



**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 ....

# Tailoring the Metal-Metal Bonded Supramolecule

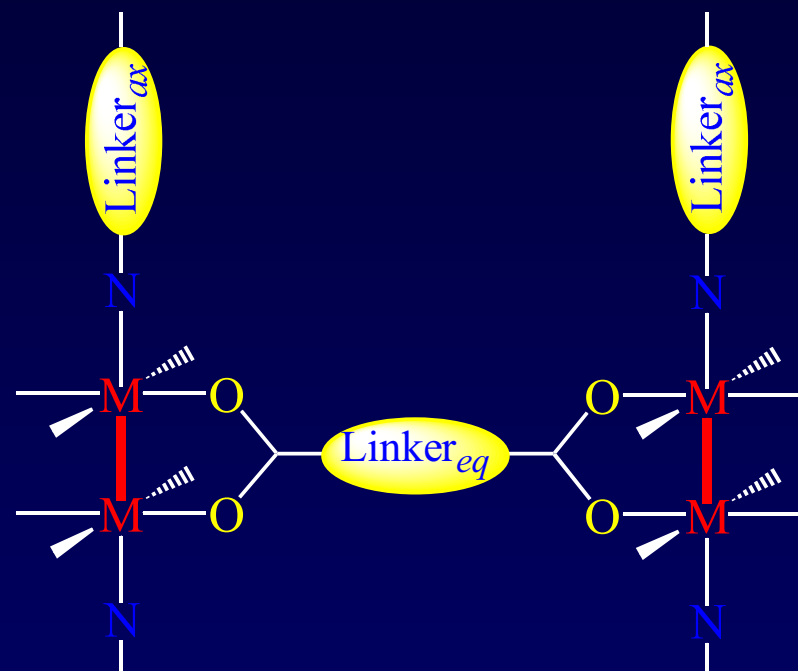
## ◆ With equatorial linker



## ◆ With axial linker



## ◆ With equatorial and axial linkers

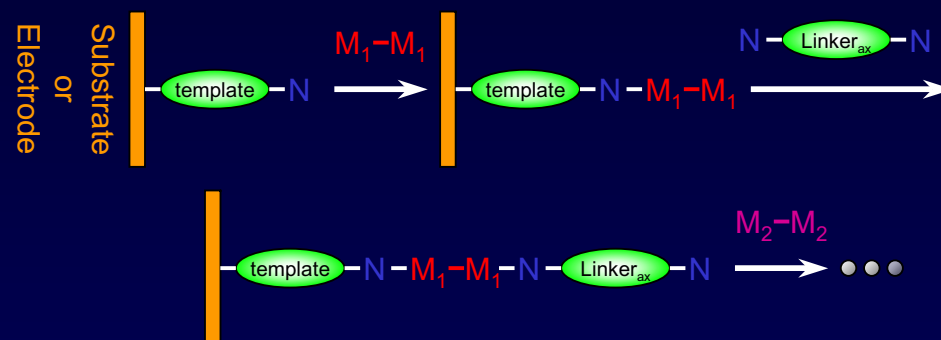


Supramolecules with a variety of crystal structures  
Compounds previously studied in solution or single crystal form

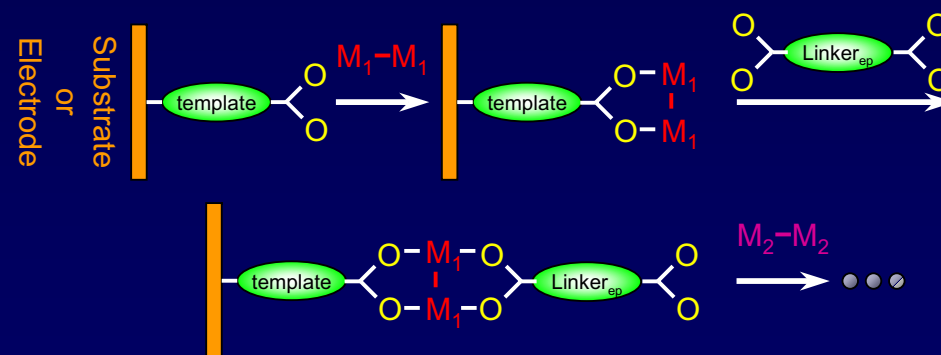
# Metal-Metal Bonded Supramolecules

## Assembling Devices:

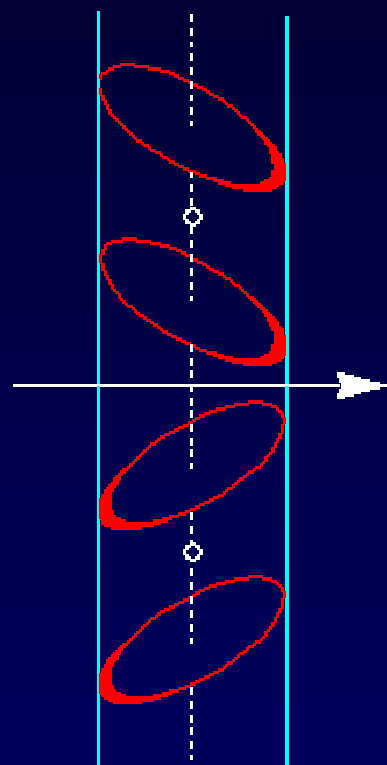
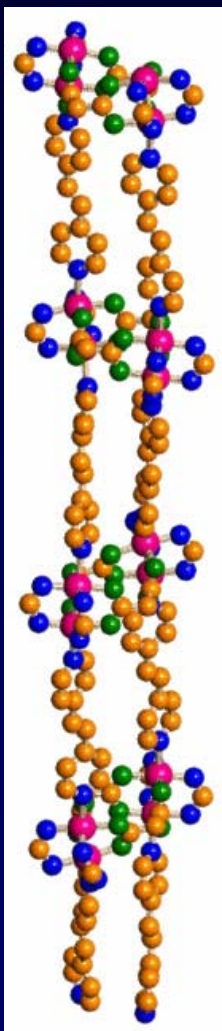
### 1 Link axially, functionalize equatorial positions



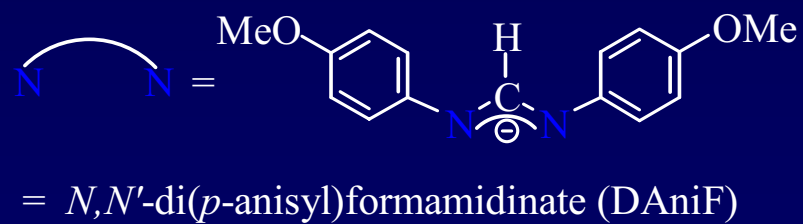
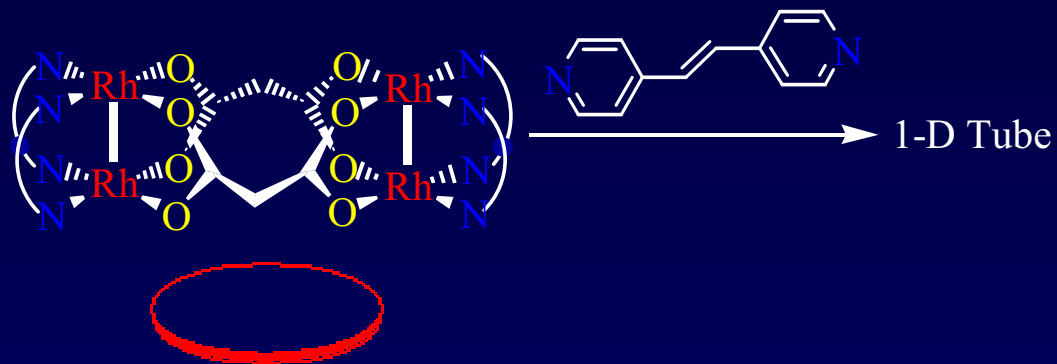
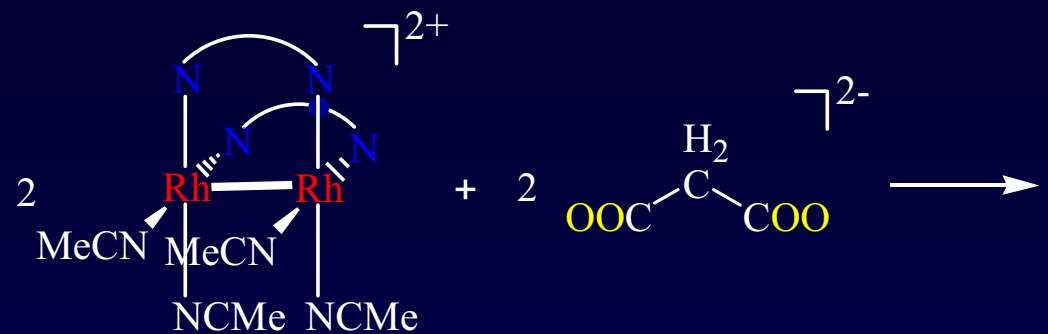
### 2 Link equatorially, functionalize axial positions



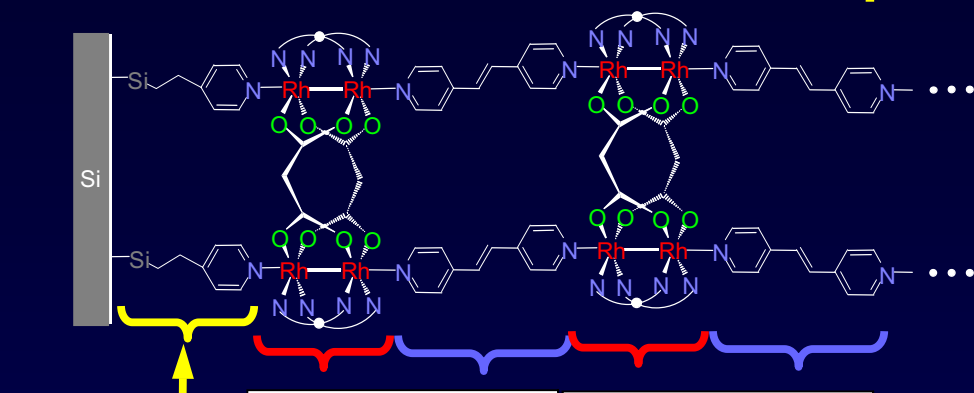
# Molecular Tube



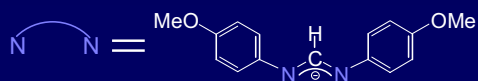
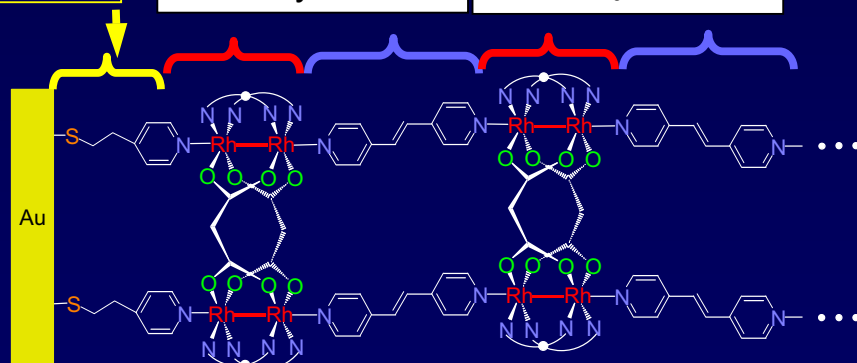
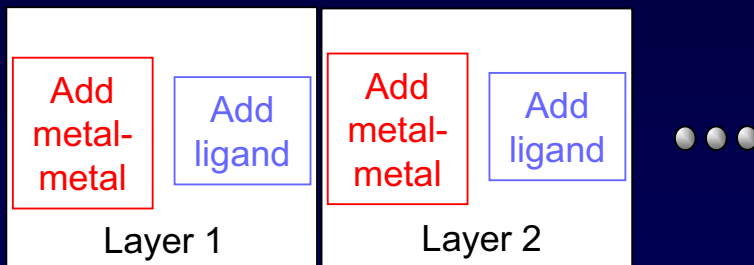
○ = inversion center  
 → = twofold axis



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



Ligand to bind to desired substrate surface



*N,N'*-di(*p*-anisyl)formamidinate

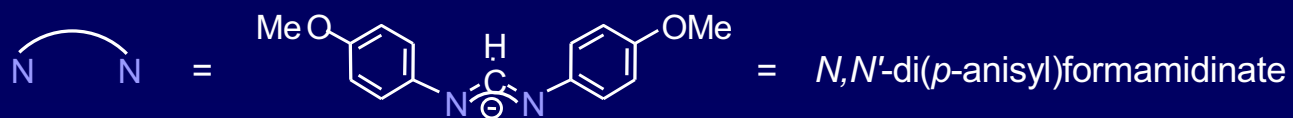
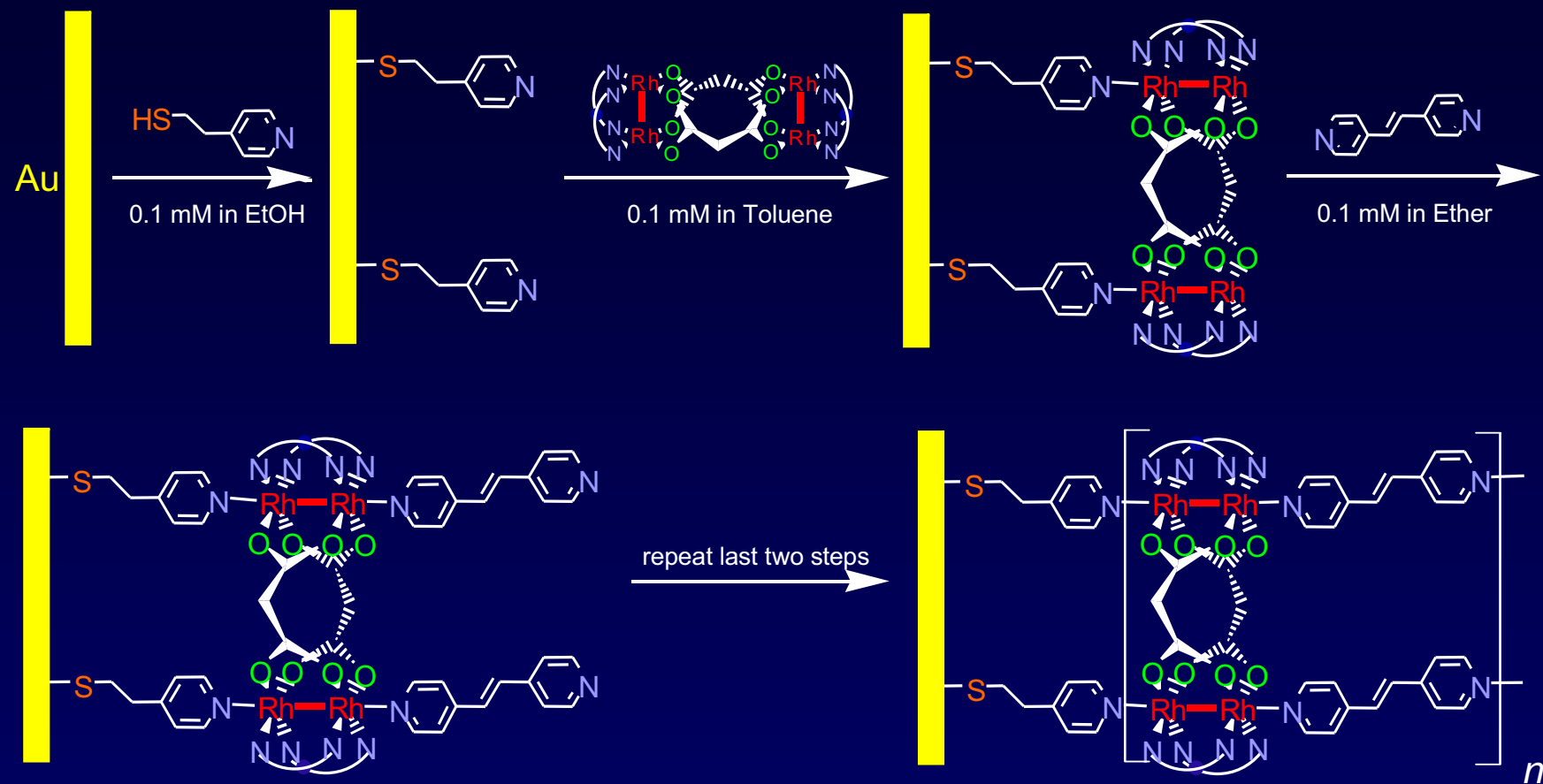
Tailor head group of ligand to bind to particular substrate surface

Tailor end group to template metal-metal bonded unit

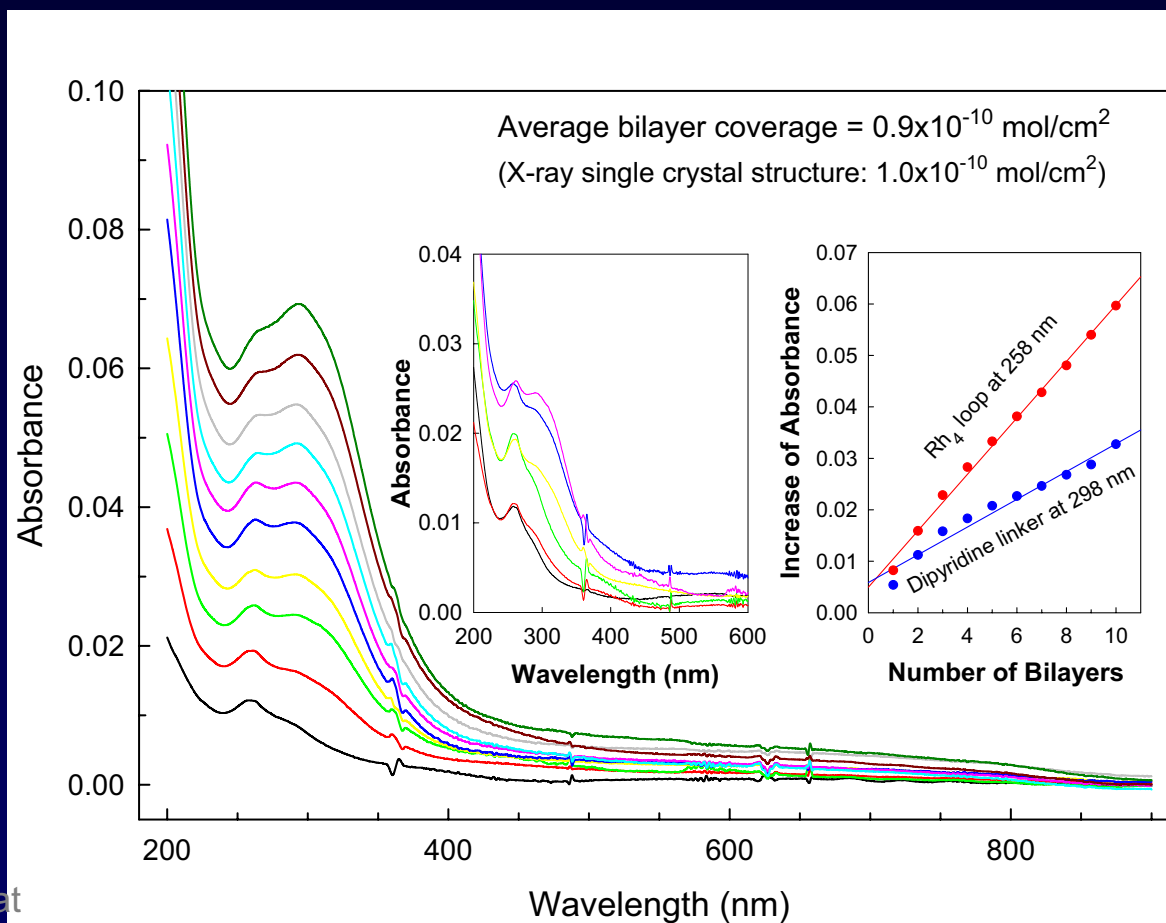
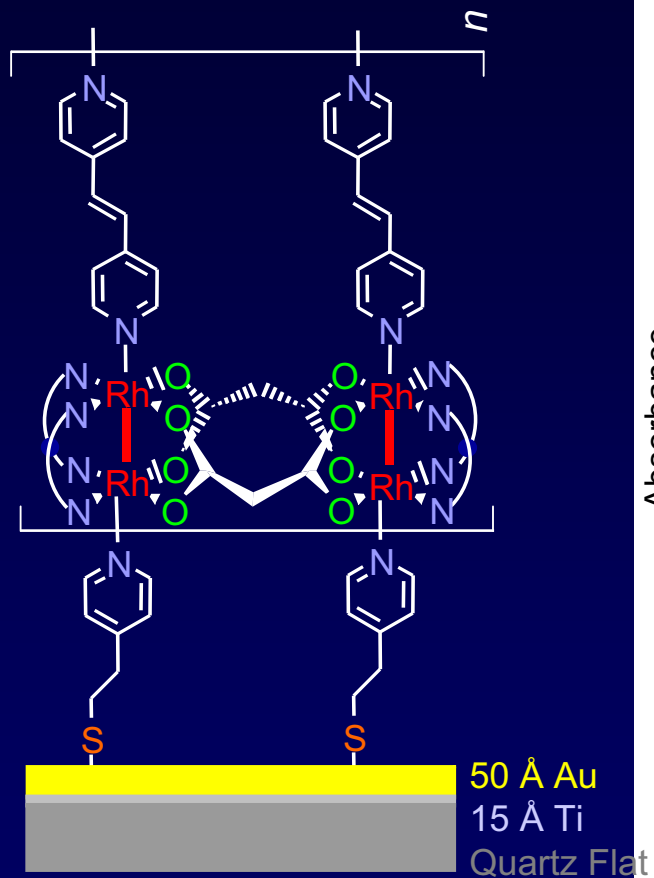
Choose M-M bond

Choose ligand to bridge M-M bonded units

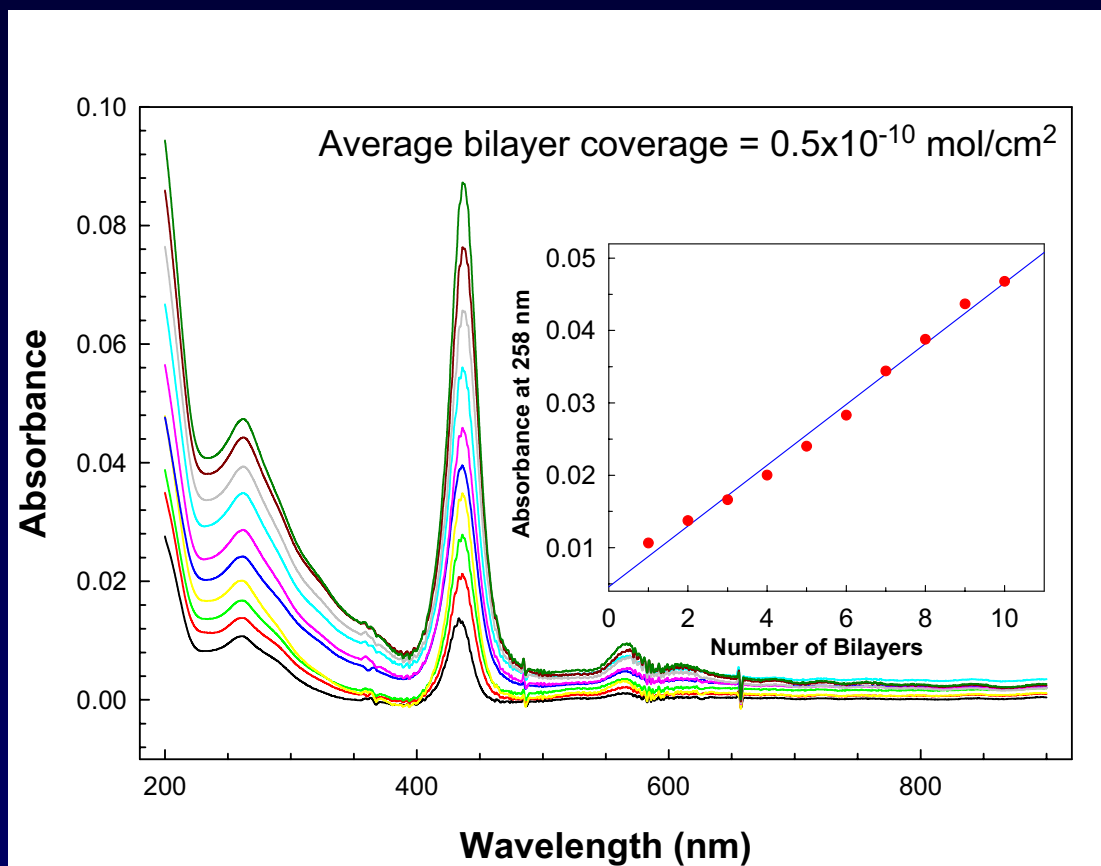
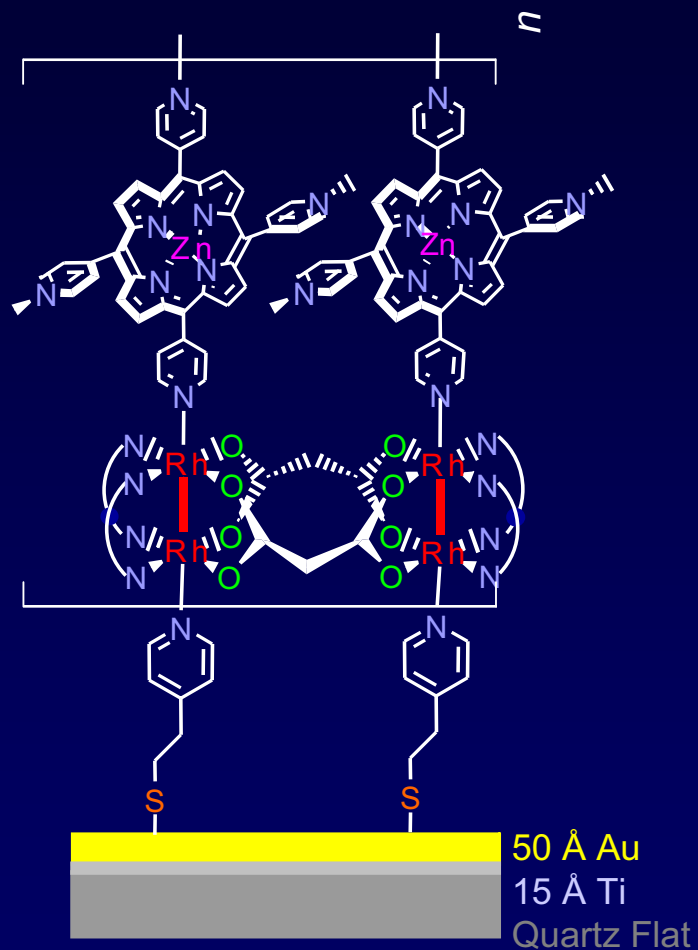
# Synthetic Steps for Layer-By-Layer Growth



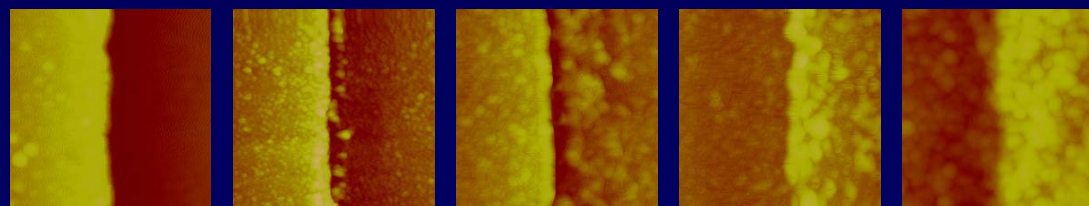
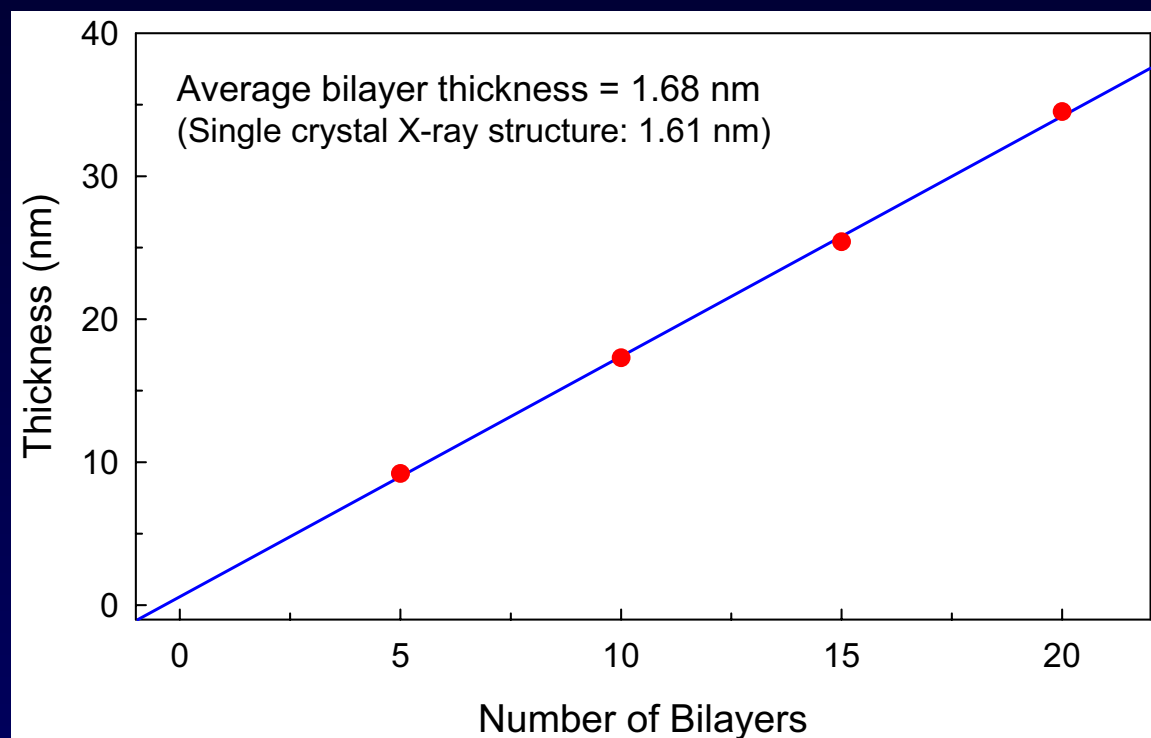
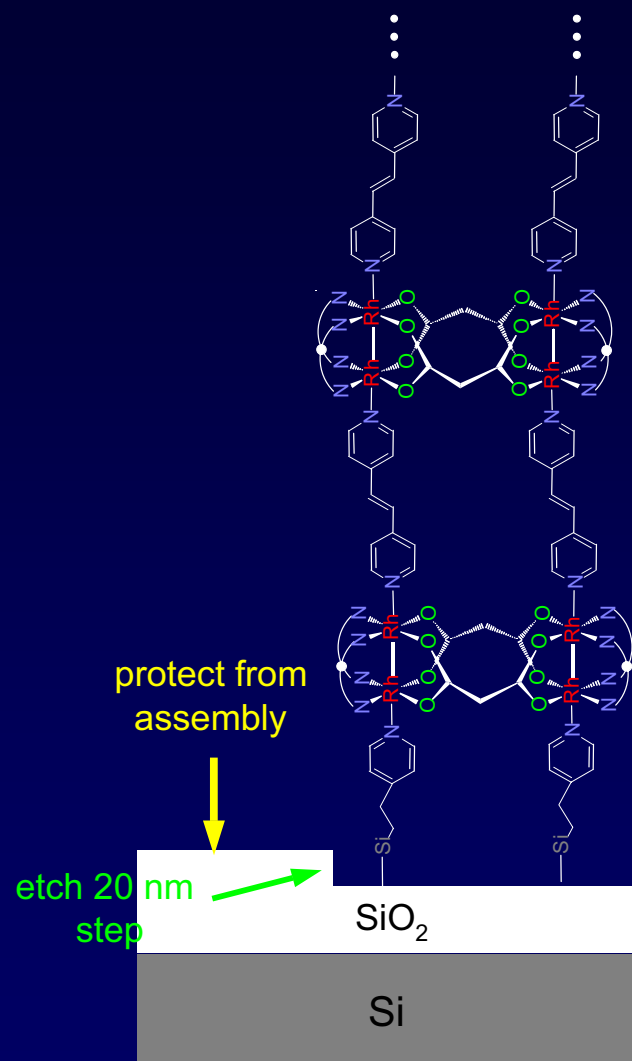
# Monitor Layer-By-Layer Growth by UV-vis Absorption



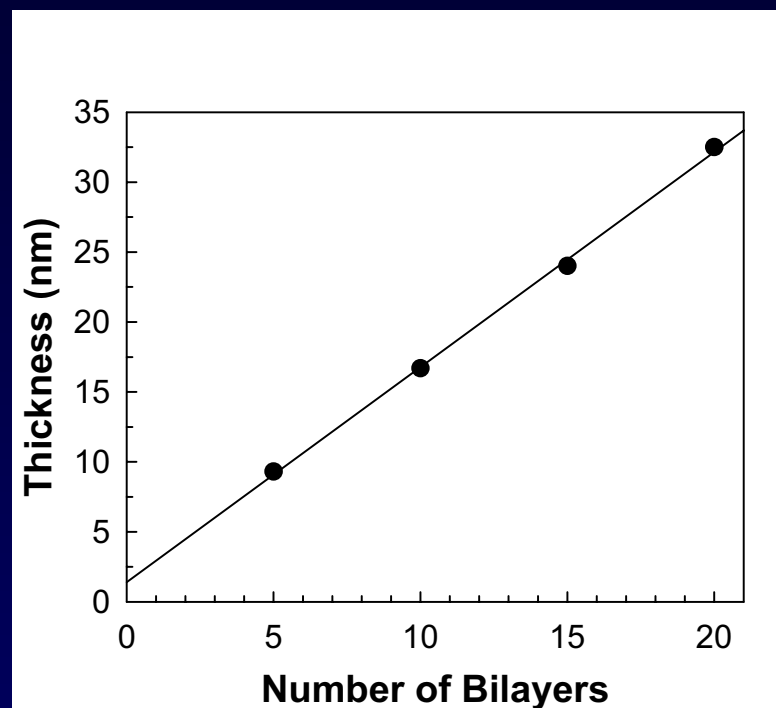
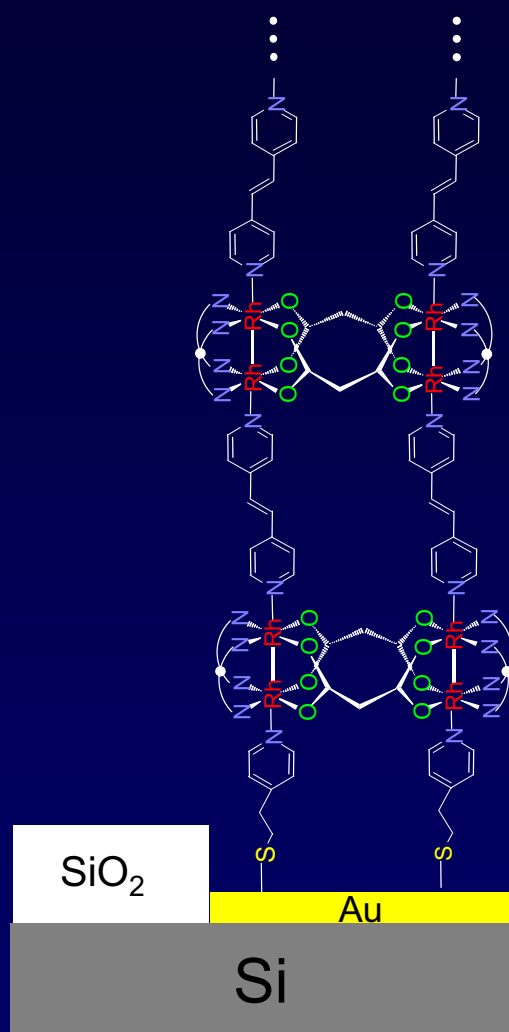
# Monitor Layer-By-Layer Growth by UV-vis Absorption



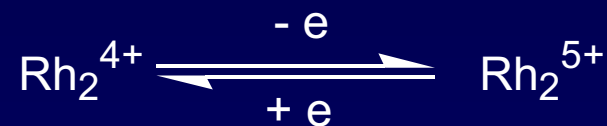
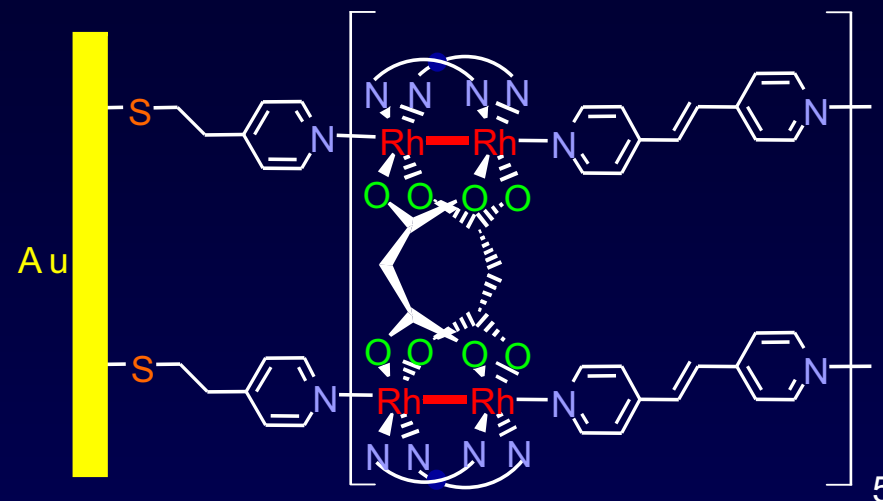
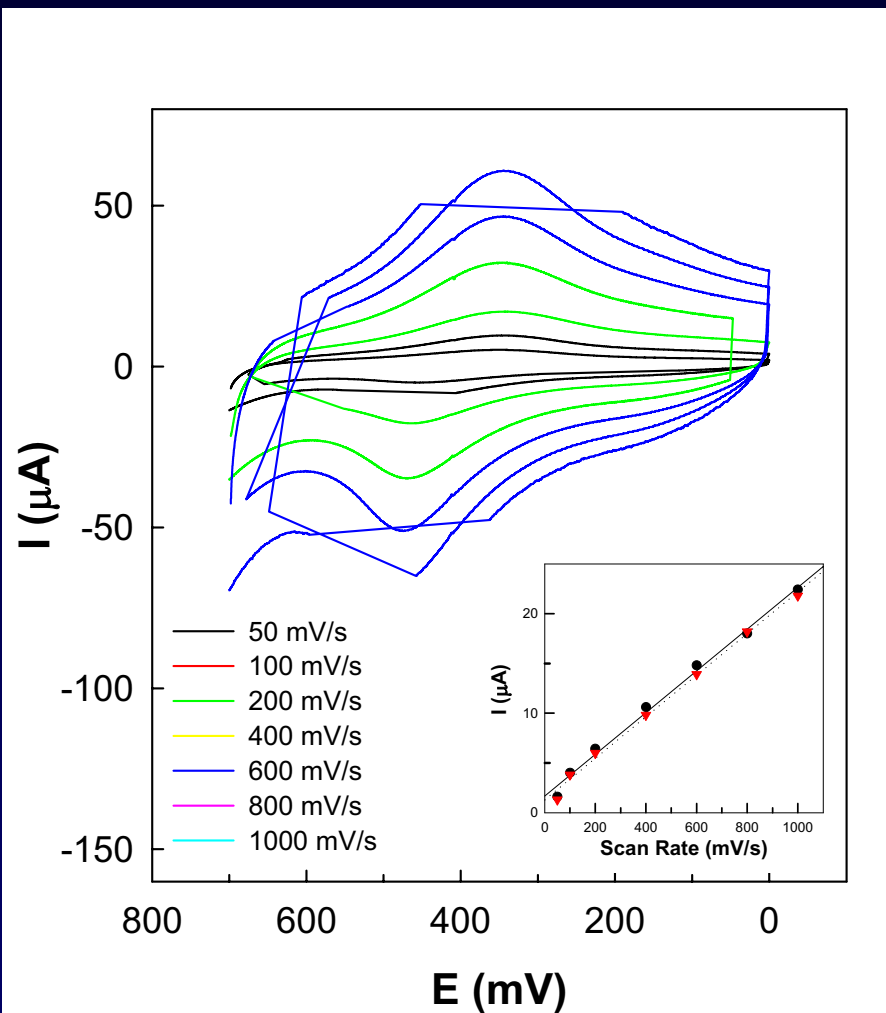
# Monitor Layer-By-Layer Growth via AFM on $\text{SiO}_2$



# Monitor Layer-By-Layer Growth via AFM on Au

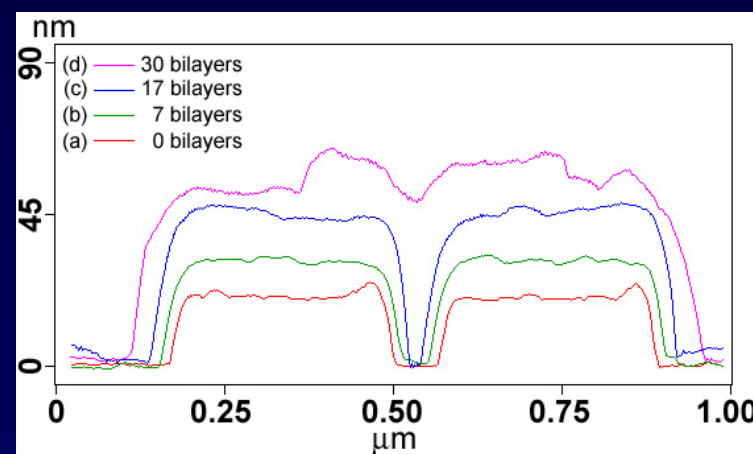
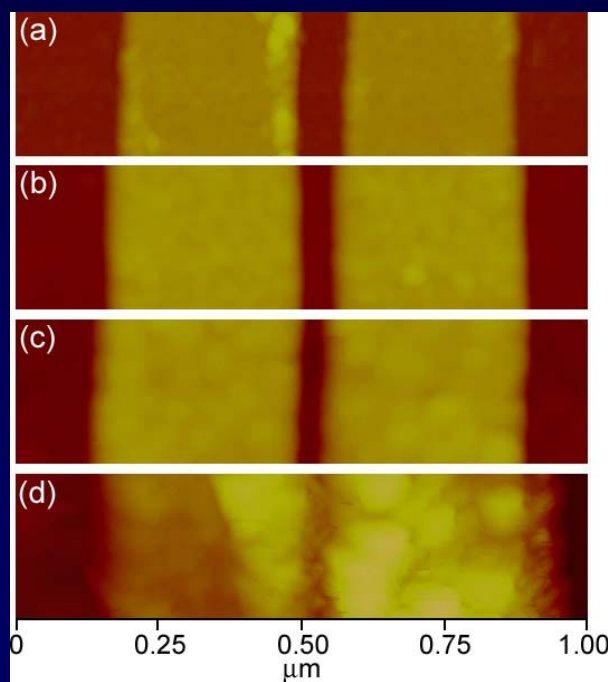
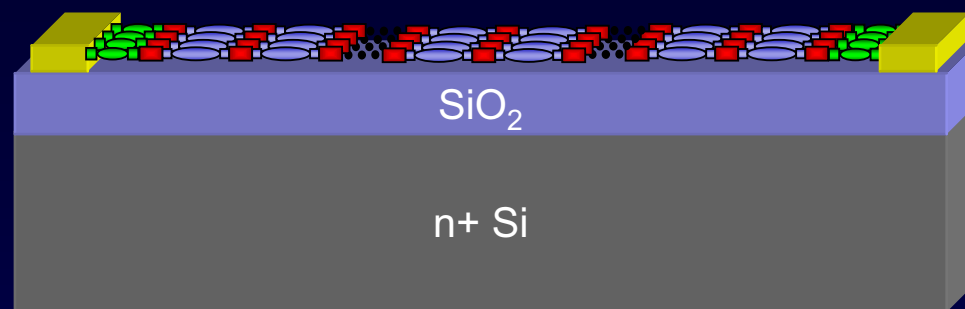


# Electrochemistry of Metal-Metal Bonded Layers

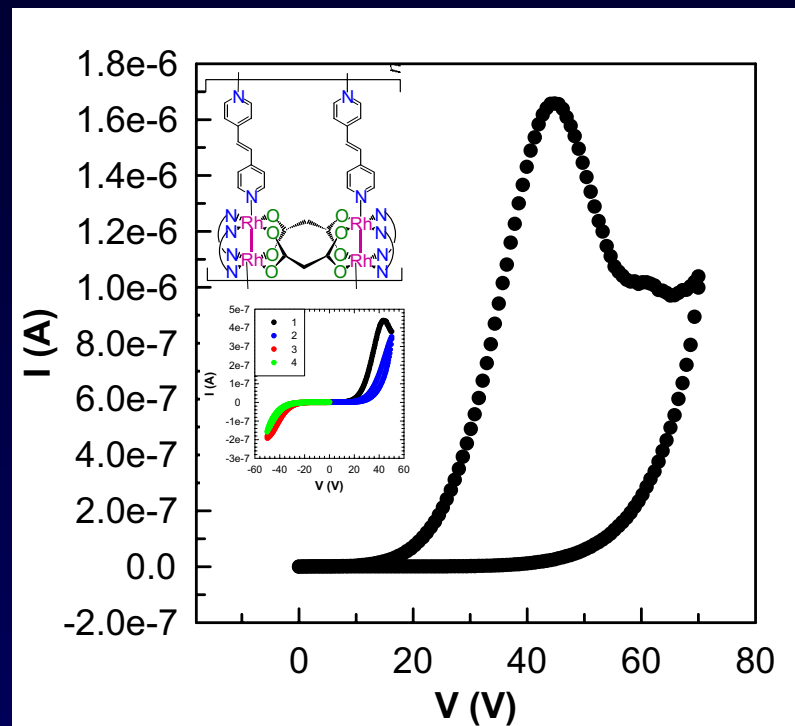
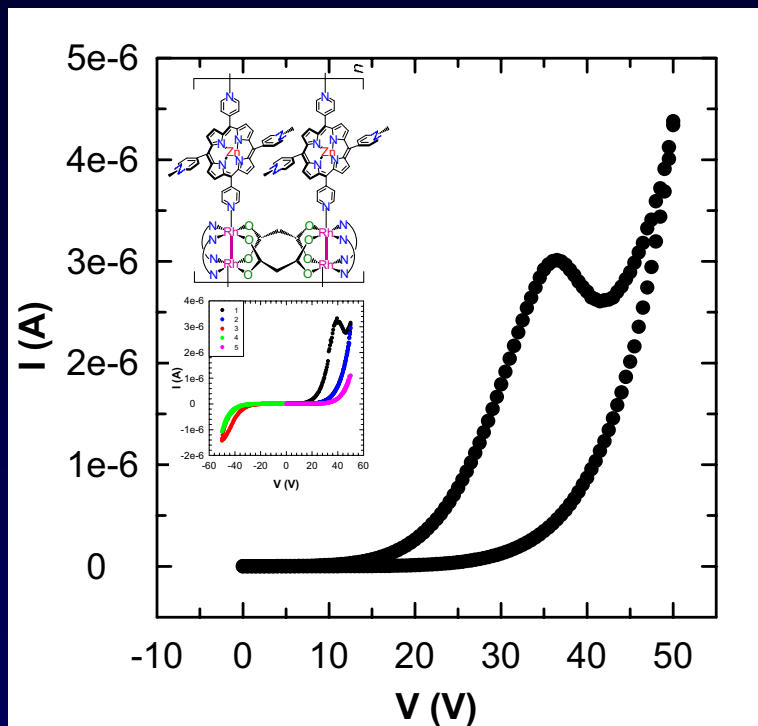


- $i_p \propto \nu$
- $E_p \neq f(\nu)$
- $E^0 = 406 \text{ mV vs Ag/AgCl in 1M NaCl}$

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

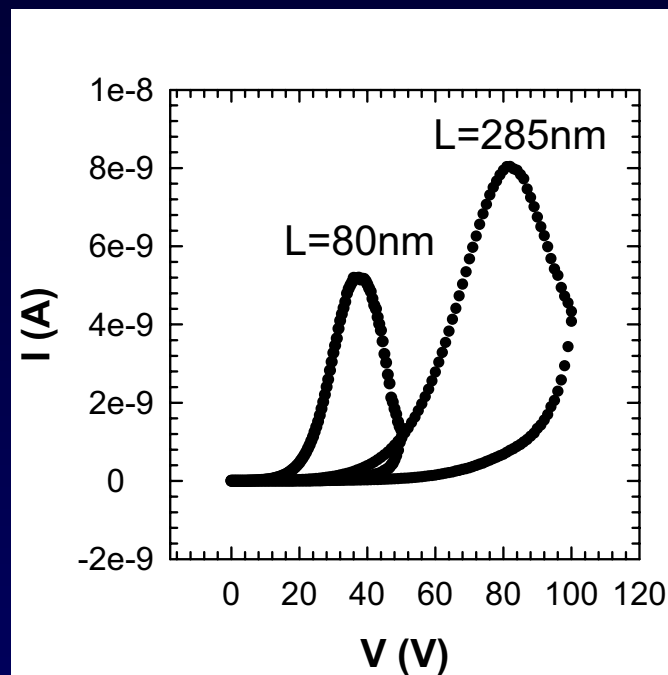
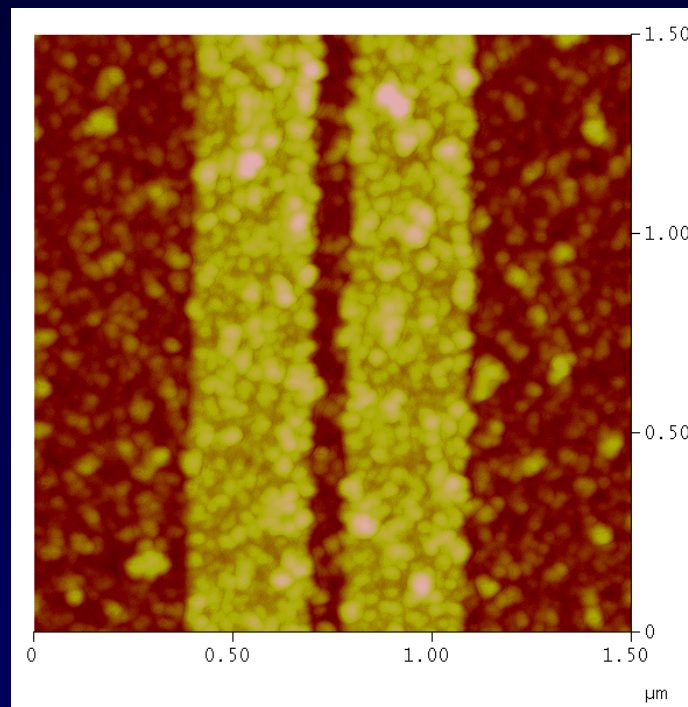
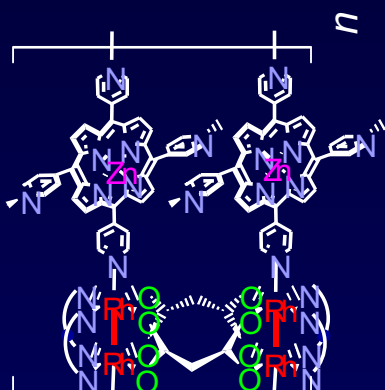


# I-V Characteristics of Rh-Rh Supramolecules Grown Layer-by-Layer Across Device Channel



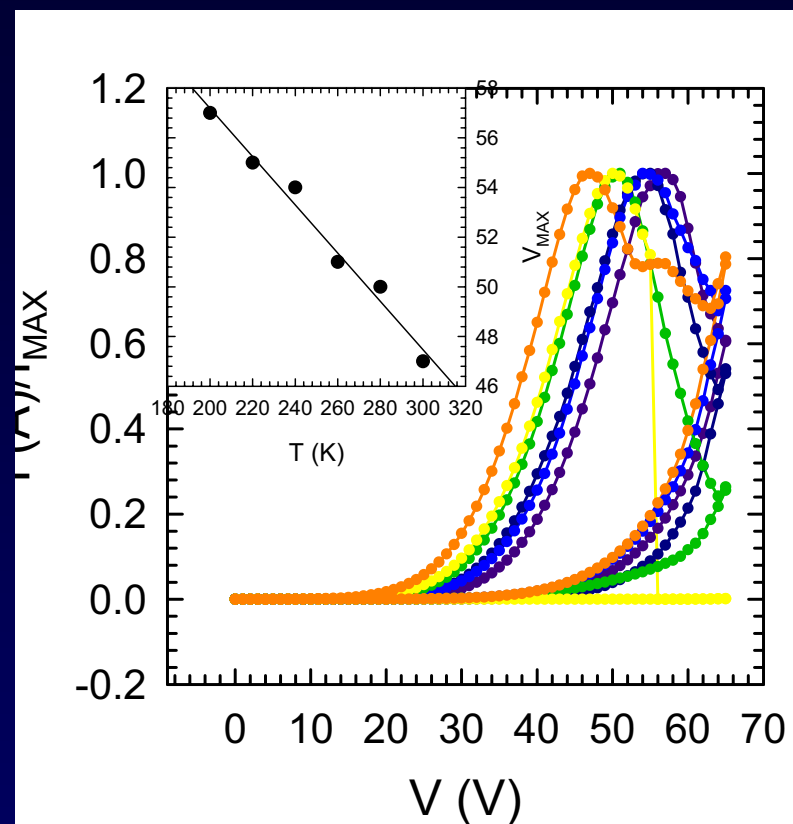
- Room Temperature
- Reproducible “Negative Differential Resistance”
  - Device-to-Device on Same Chip
  - Different Chip
  - Near Perfect Yield
- Not Reversible

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

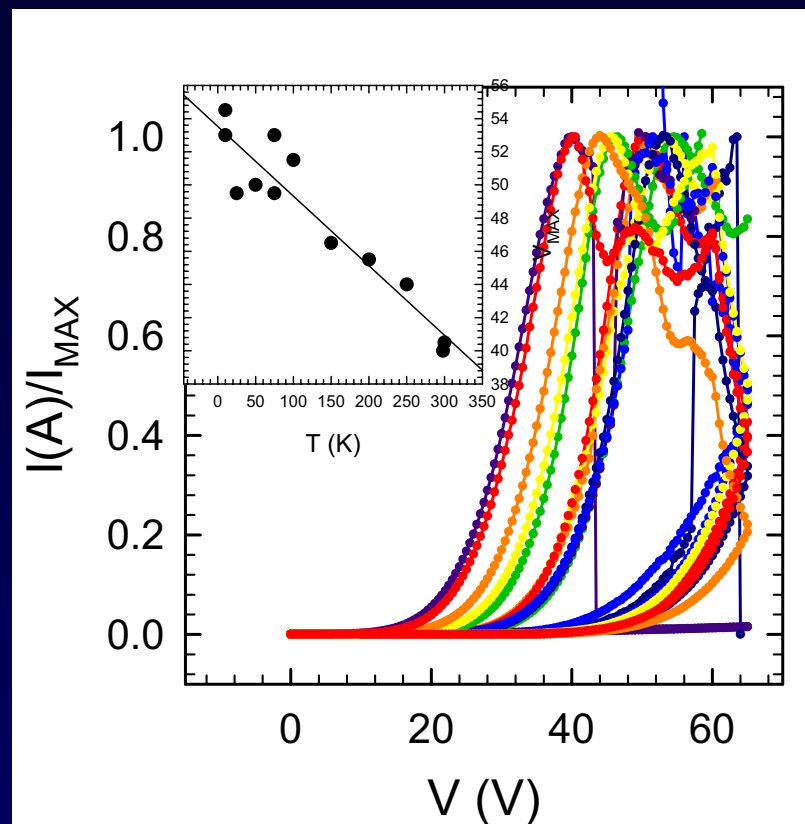


- compound assembles to form a polycrystalline thin film
- grain structure characteristic of underlying structural motif
- I-V characteristic show similar behavior
- peak potential increases with increasing channel length

# Temperature Dependent I-V Characteristics Rh-Rh Supramolecule with DipyriddyEthylene Ligand



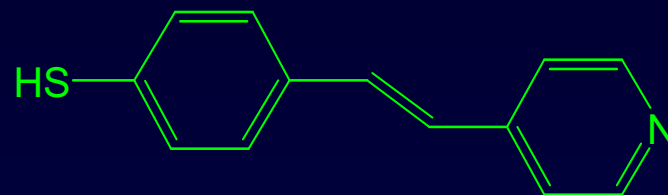
200-300K



5-300K

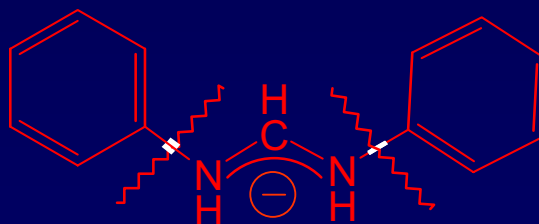
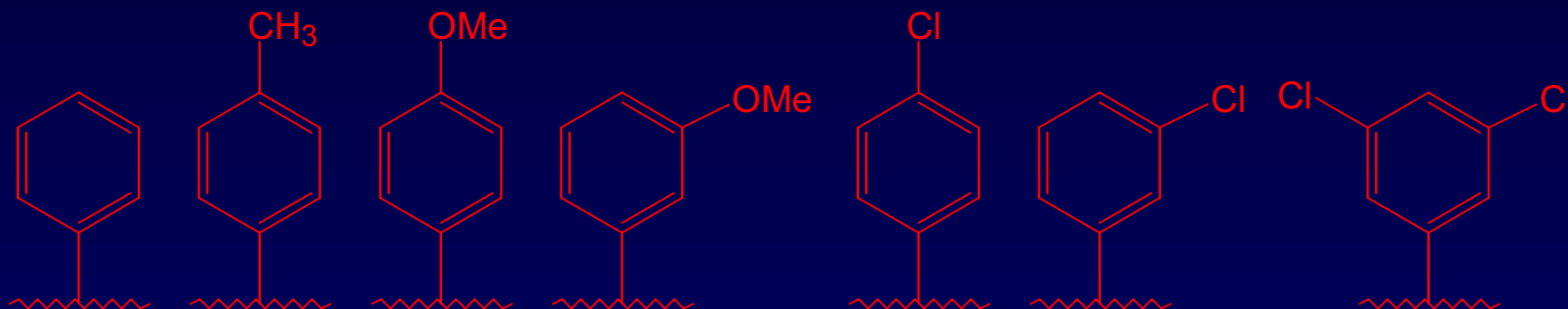
# Chemical Manipulation : Examples

## Surface Template – Molecule-Metal Contact



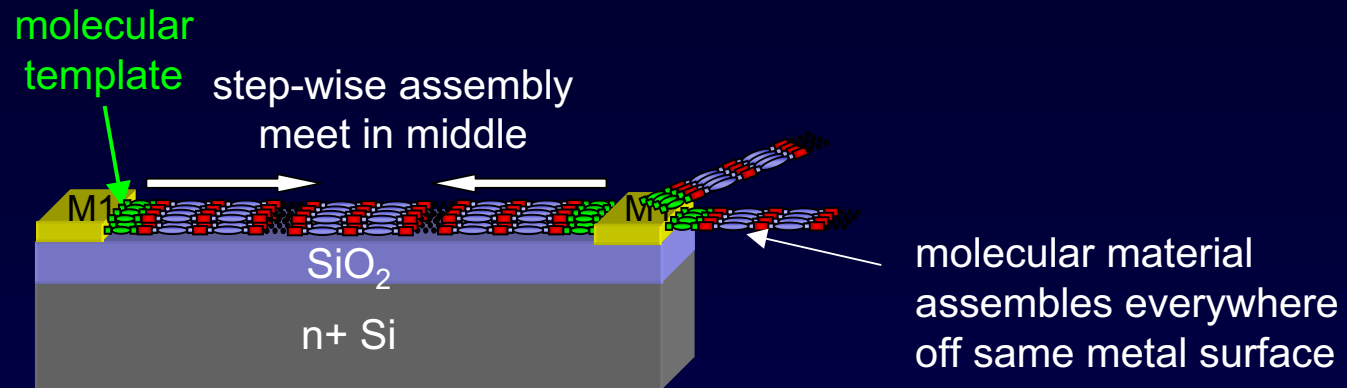
A. Afzali

## Equatorial Ligands – “Switching” Potential, Receptors

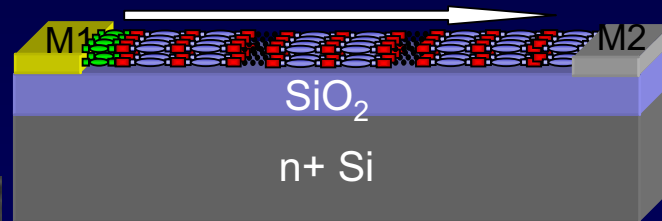


L. Vyklicky

# Controlling Molecular Assembly through Device Geometry

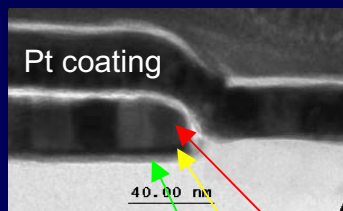


step-wise assembly from one-side to the other

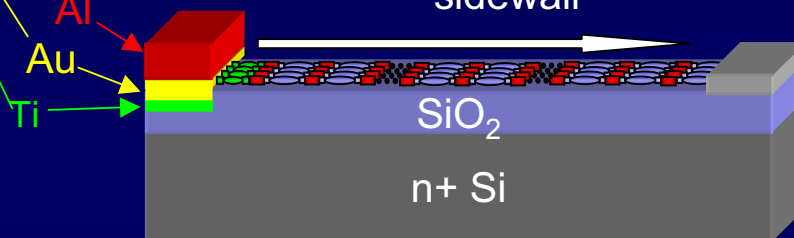


different metal electrodes

a start



limit assembly to electrode sidewall



embedded electrodes  
hide adhesion layer  
limit molecular assembly  
↓  
control charge flow in device

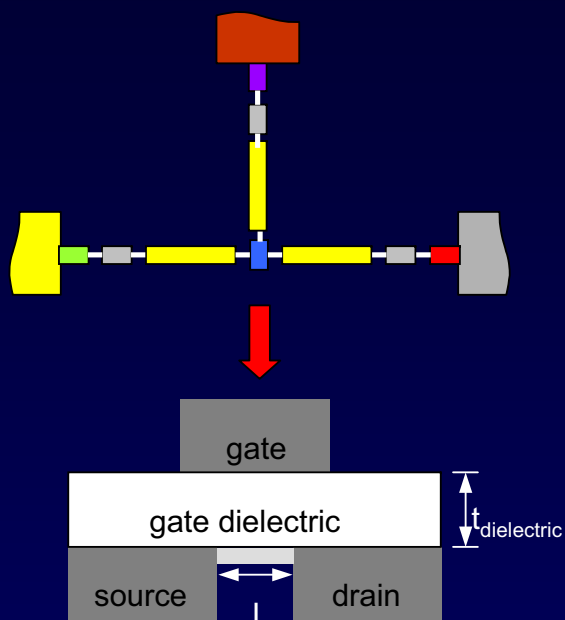
# **The Physics of Molecular Devices**

**Cherie R. Kagan**

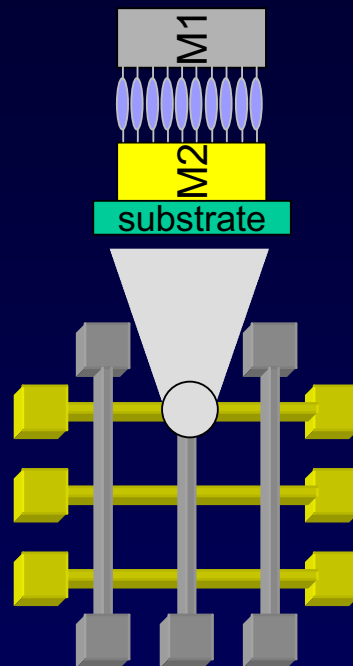
**IBM T. J. Watson Research Center  
Yorktown Heights, NY**

# Molecular Electronics, Memory, Sensors

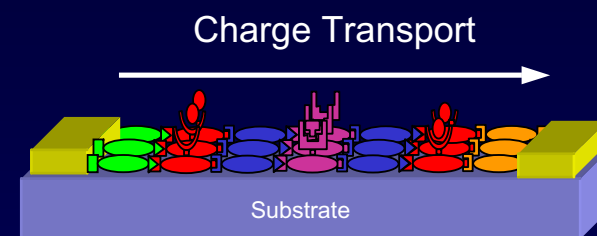
## Transistors



## Memory



## Sensor

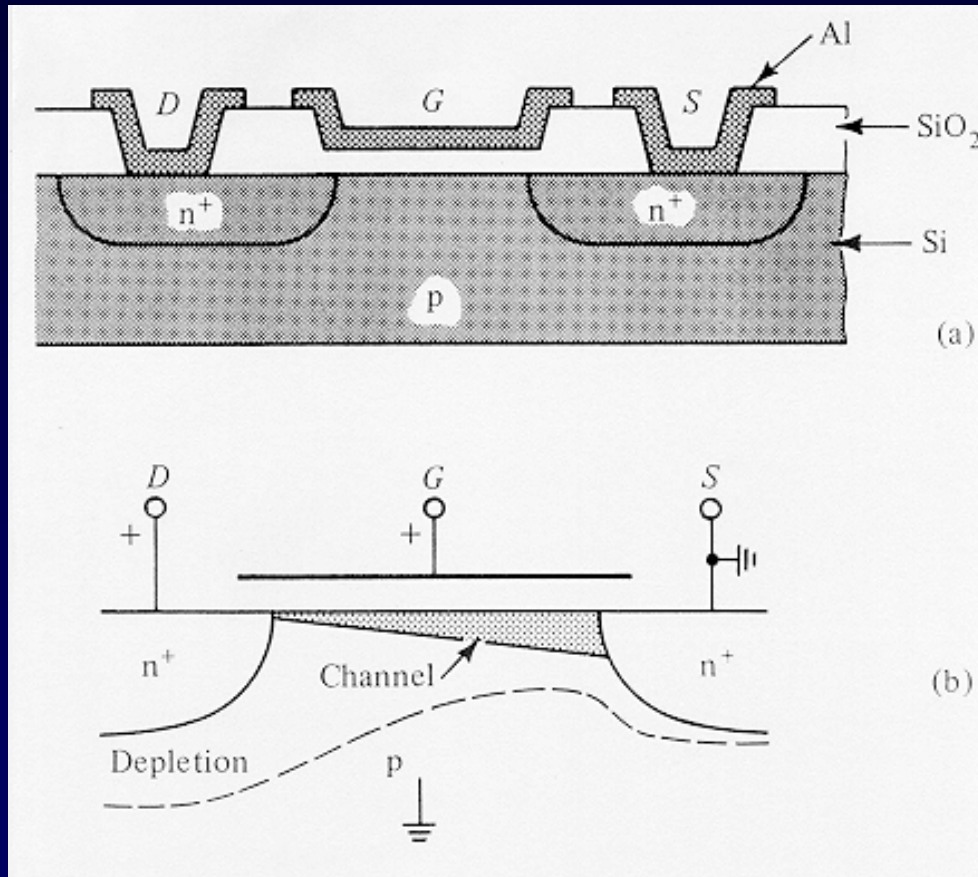


## Molecular Electronics, Memory, and Sensors Opportunity for Solid State Chemistry and Physics

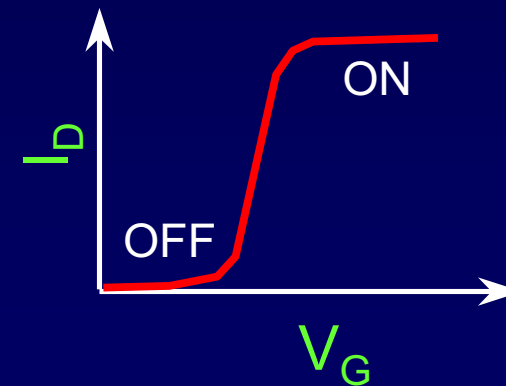
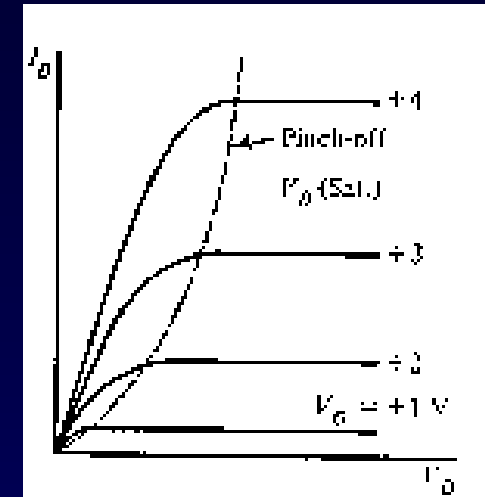
Understand:

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

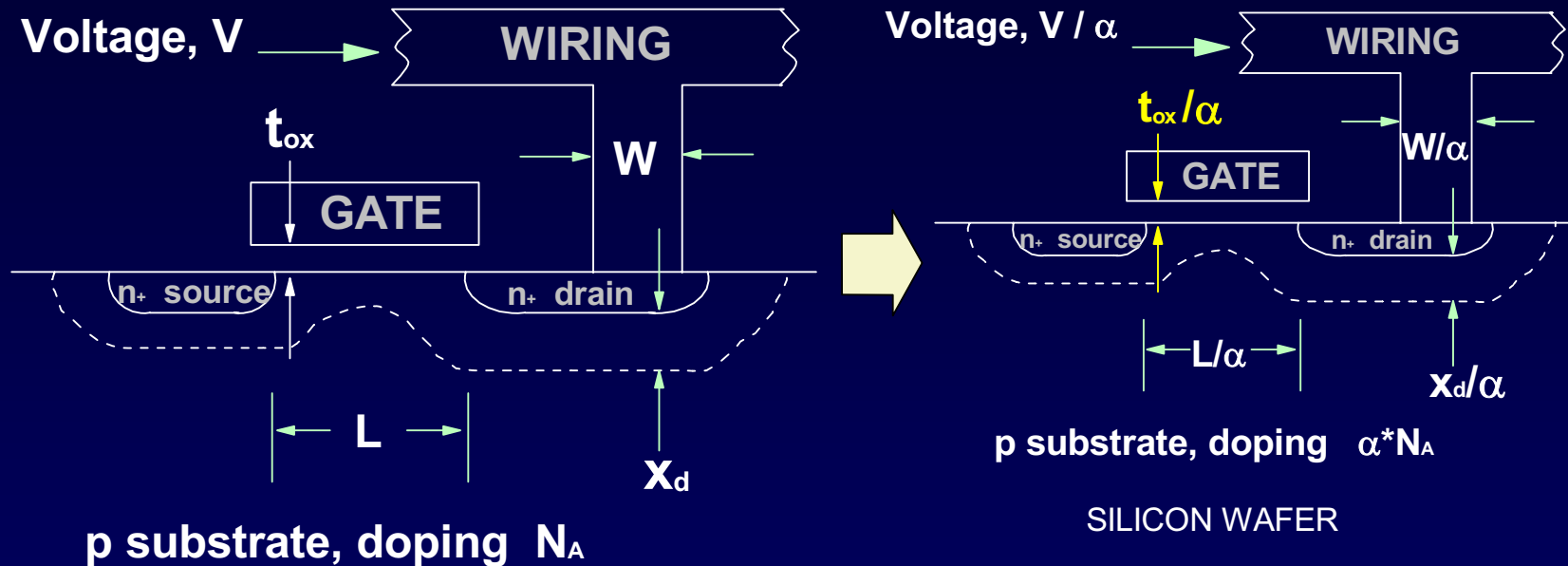
# Metal-Insulator-Semiconductor Field Effect Transistor (MISFET)



Cross section and schematic illustration of a MOS transistor.



# Transistor Scaling (Dennard Scaling)



SILICON WAFER

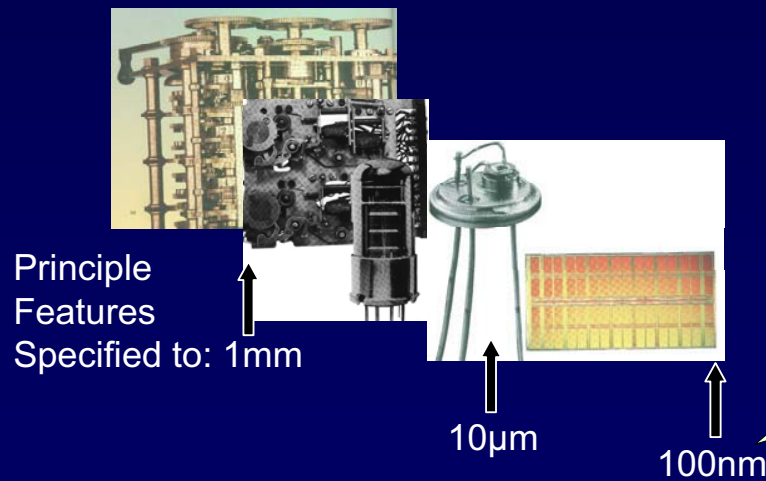
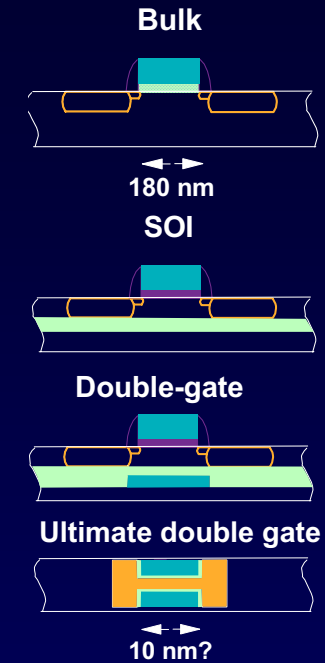
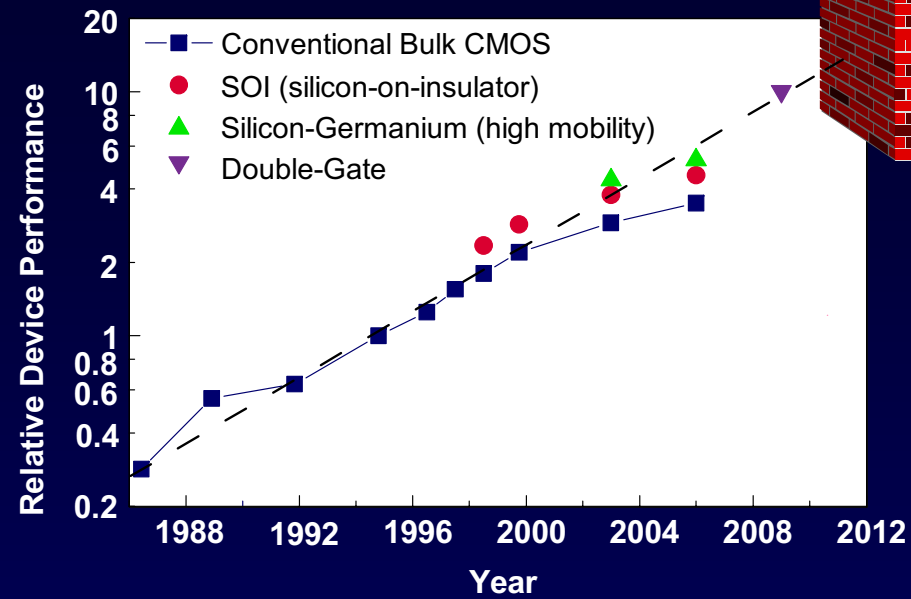
SILICON WAFER

## RESULTS:

|                 |              |
|-----------------|--------------|
| Higher Density: | $\alpha^2$   |
| Higher Speed:   | $\alpha$     |
| Lower Power:    | $1/\alpha^2$ |
| per circuit     |              |
| Power Density:  | Constant     |

# Whats Next?

Molecular  
Electronics

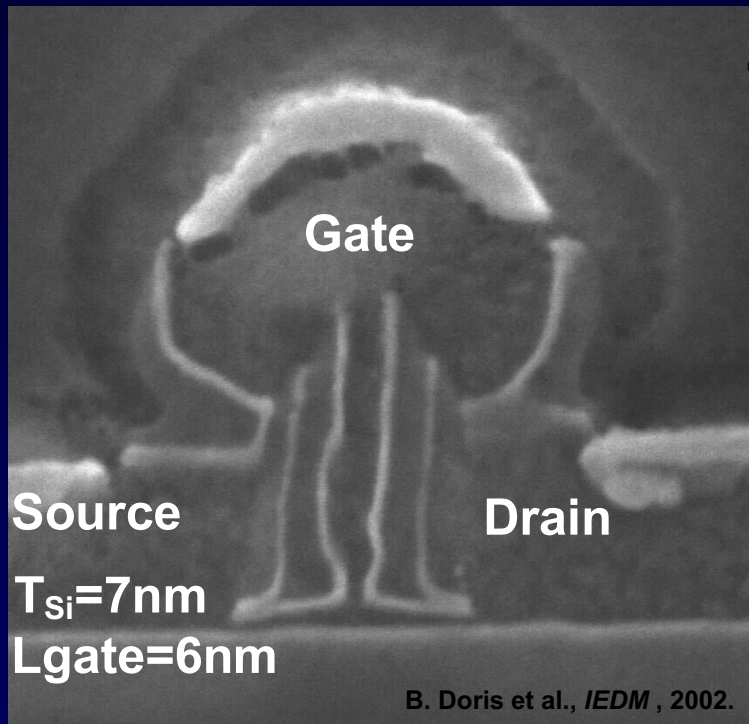


Nanoscale  
Science  
and  
Technology

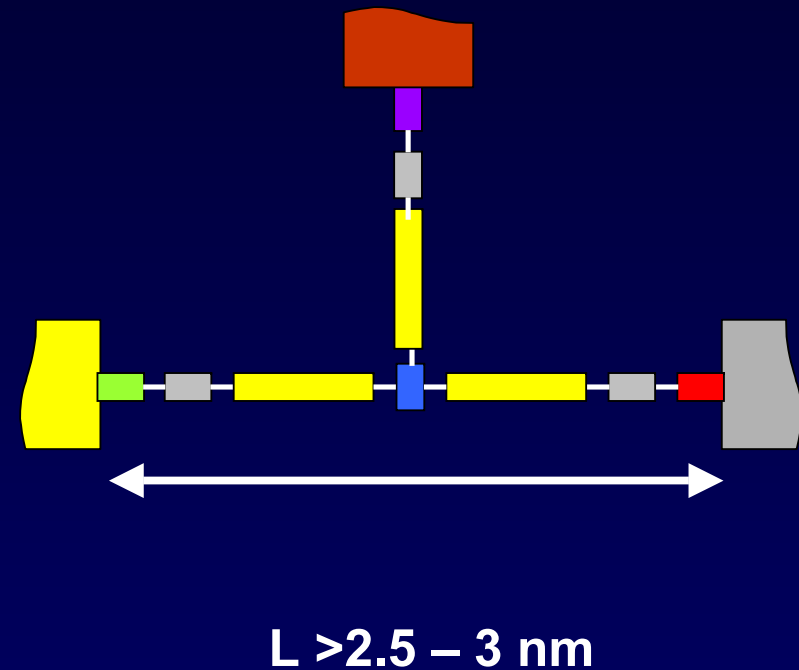
The Future is in  
Nanoscale  
Science, Materials,  
and Devices

# Its Not Only in Size, But Cost and Functionality

## Si FET



## Molecular Device

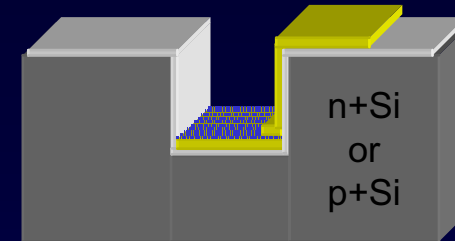


- Silicon and Molecular Devices are governed by electrostatics and eventually limited by tunneling
  - difficult to be much smaller than 2 - 3 nm

# 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, Phaeton Avouris,  
Philip Wong

# Self-Assembled Monolayer FETs?

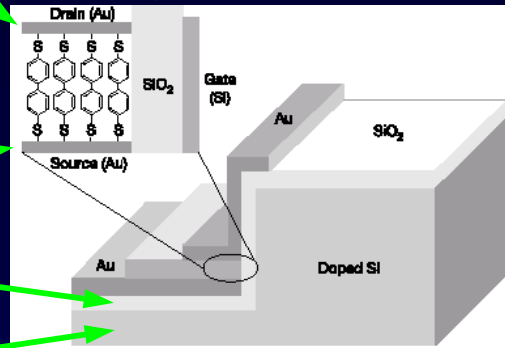
Drain by  
shadow evaporation  
using trench wall

Source by  
collimated evaporation

30 nm SiO<sub>2</sub>

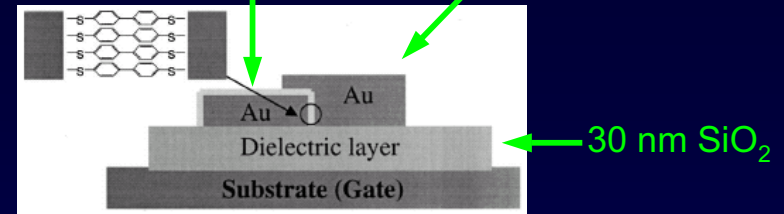
Trench anisotropically  
etched into (110) n+ Si

verbally amended SiO<sub>2</sub> thickness on  
sidewall from 30 to 3-6 nm



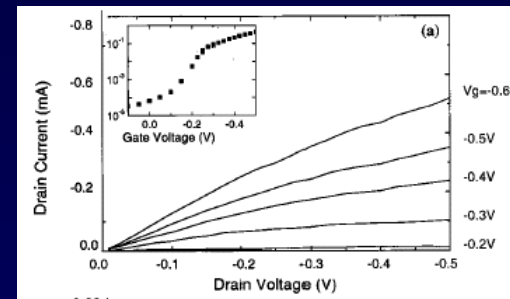
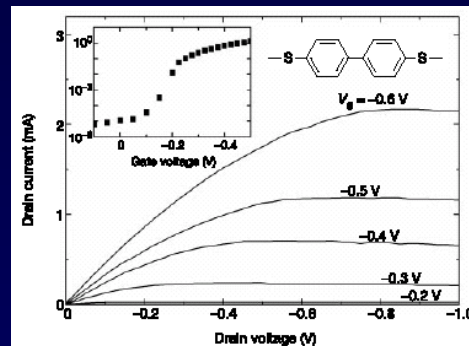
Source 150 Å Au

Drain by low angle  
evaporation



30 nm SiO<sub>2</sub>

**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?

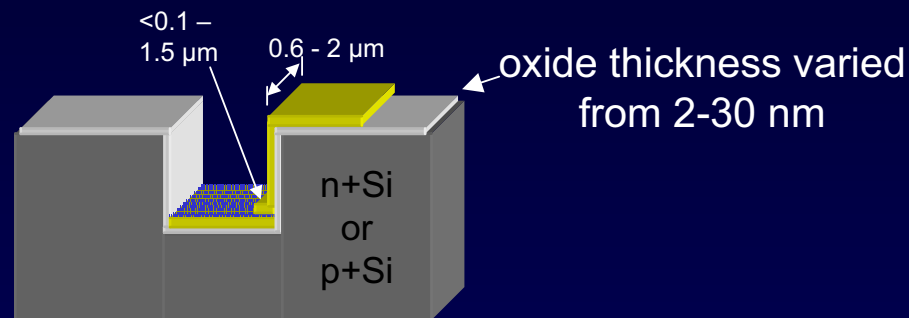
## Device Mysteries:

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

# Device Structures - Trenches

Cross-section:

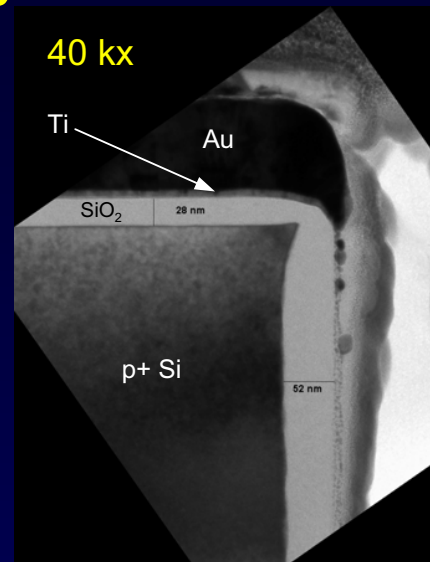
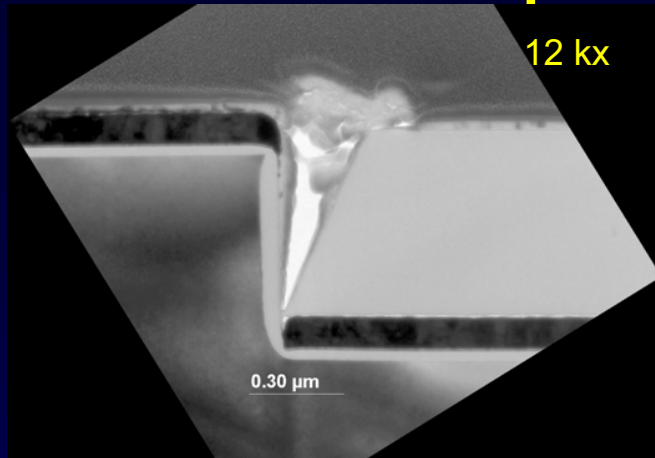
Channel dimensions depend  
on which set of structures are chosen  
as defined by mask sets



**Two approaches:**

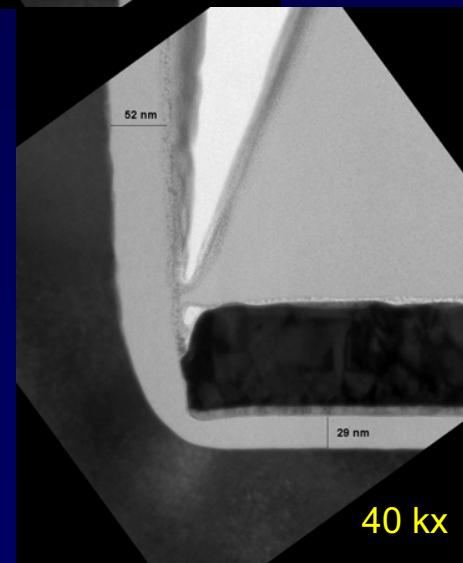
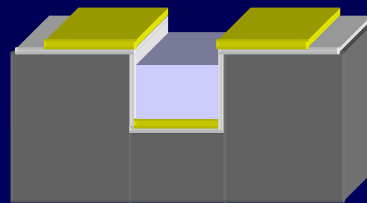
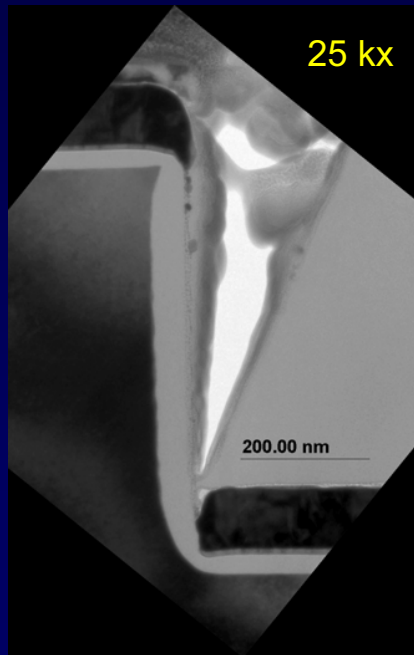
1. RIE using (100) p+ Si  
(note difficult to RIE vertical  
sidewalls in n+ Si, too much  
lateral etching)
2. Wet chemical etch into (110) n+ Si  
(note can't wet etch into p+ Si)

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

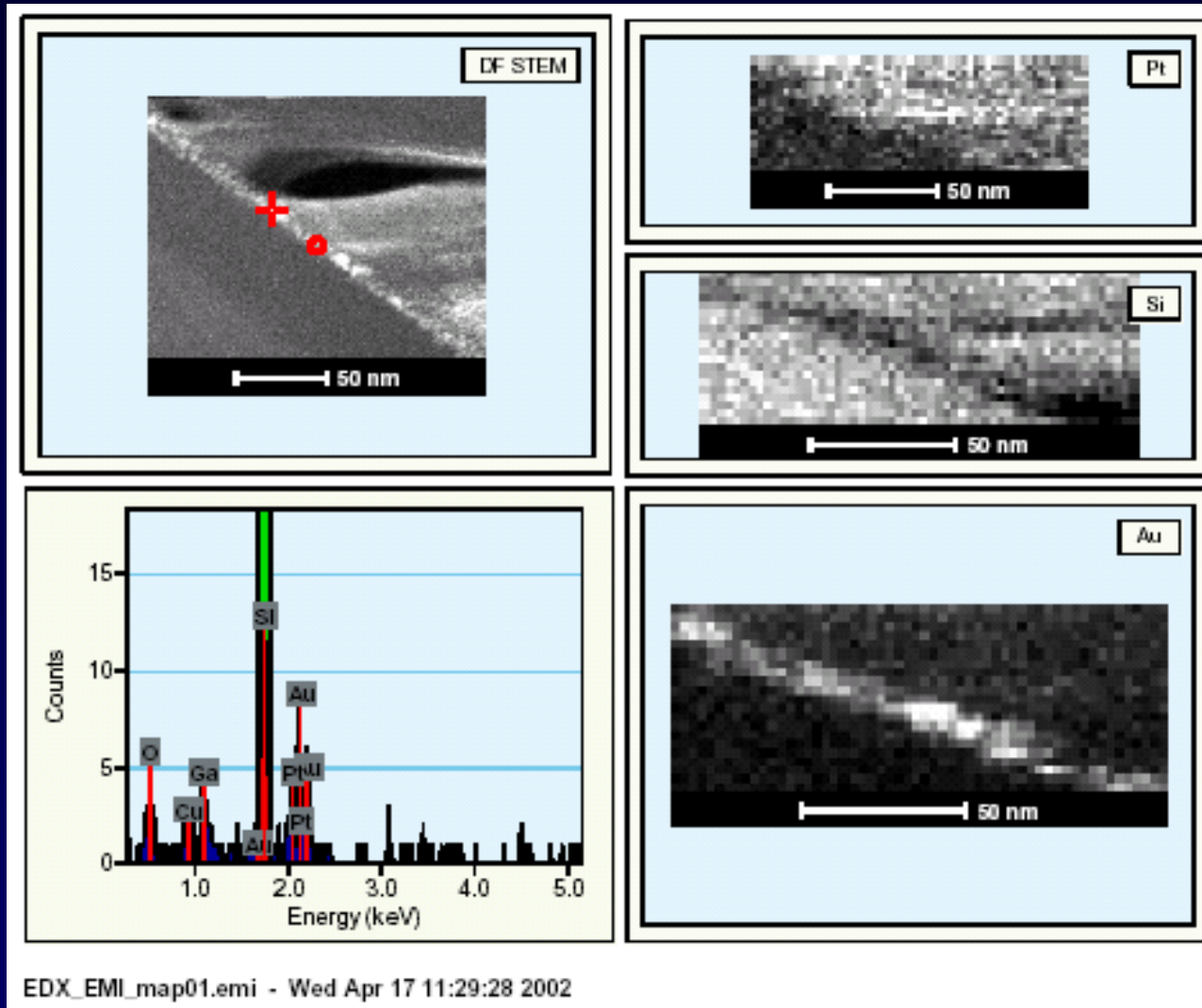


Collimation :  
In large part, it is good  
but, there are particulates  
on the sidewall

RIE (100)  
Sidewall  $\sim 1.8\times$  thicker  
Than bottom and  
top surface



## EDS Data of Gold Electrode in RIE Trenches

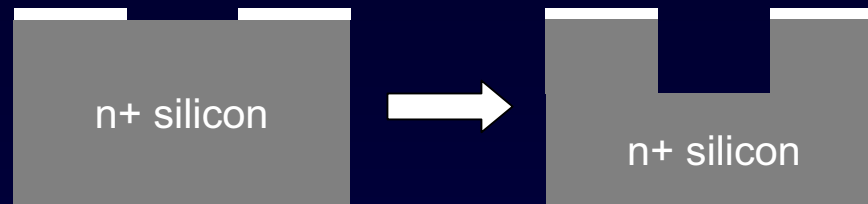


Pt is used to FIB  
the structure

Sidewall is rotated  
from  
12 to 4'oclock  
in images

Au is on sidewall  
although not  
continuous

# (110) Trenches: KOH Anisotropic Etch



Alignment within  $\pm 0.1^\circ$  necessary

- wafer flat cut accurate to  $\pm 0.5^\circ$
- Two stage process: alignment pattern first be etched to accurately locate  $\{-1,1,1\}$

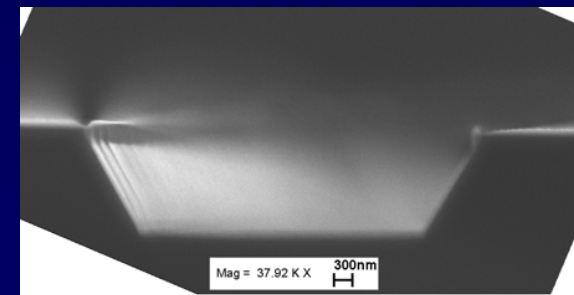
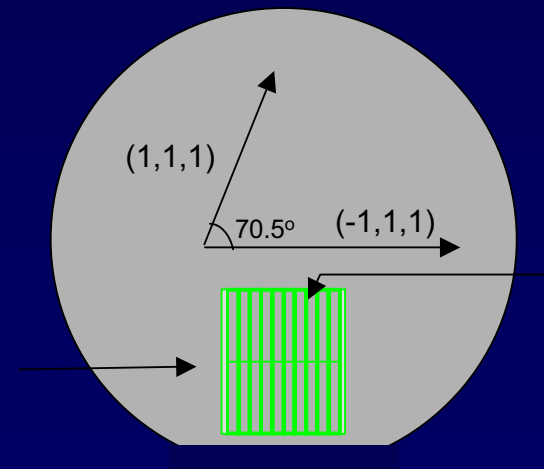
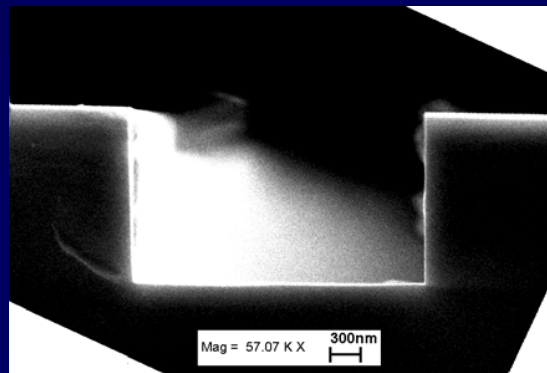
Small misalignment produces:

- Lower aspect ratio (h/L)
- Non-vertical sidewalls

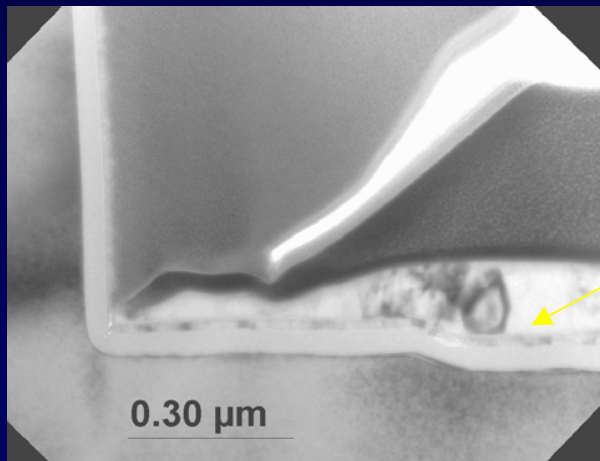
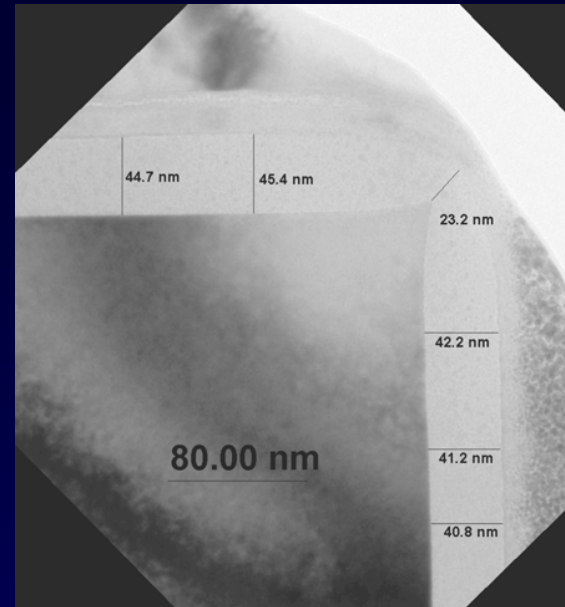
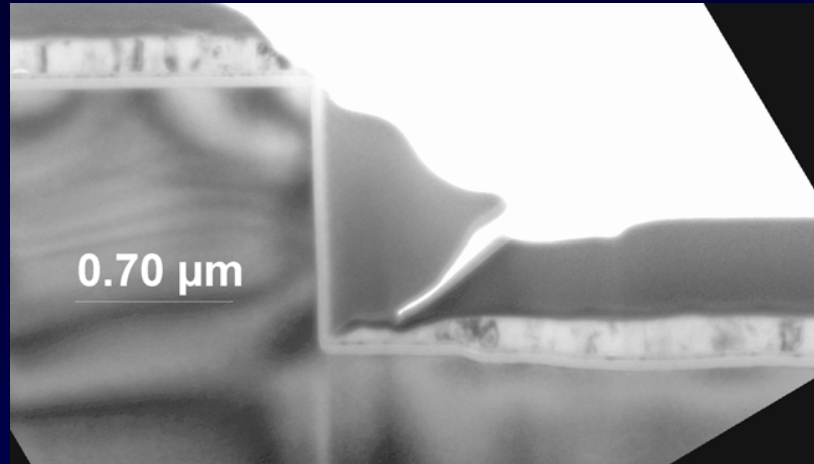
Additional requirements for high aspect ratio and finish:

- 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)

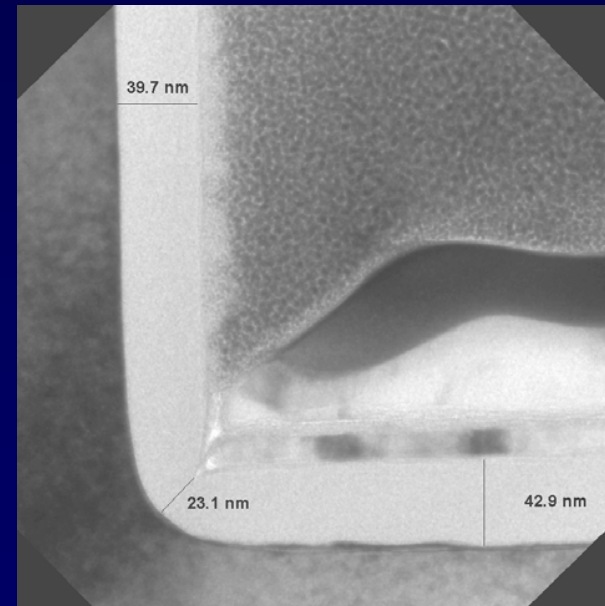
Alignment of mask with the  $\{-1,1,1\}$  plane is critical



## (110) Trench After Oxidation



Roughness in trench bottom

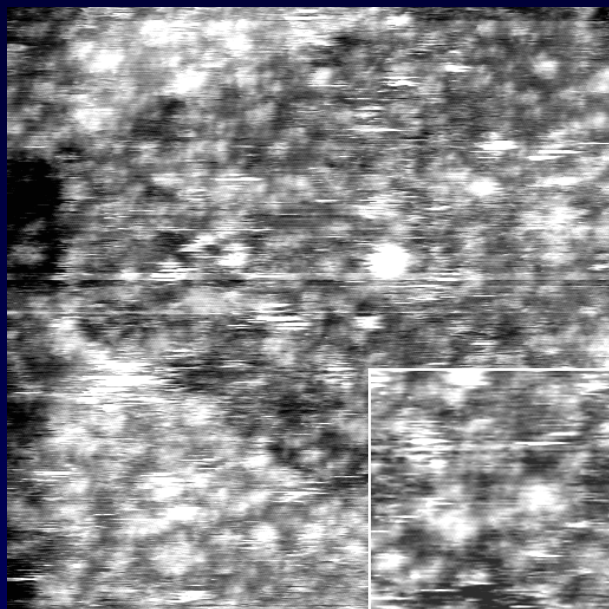


Aim: 30 nm oxidation, always greater in n+ Si than on n, p, or p+ Si

Conclusion:  $t_{\text{oxide}}(\text{sidewall}) \sim t_{\text{oxide}}(\text{top/bottom})$

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

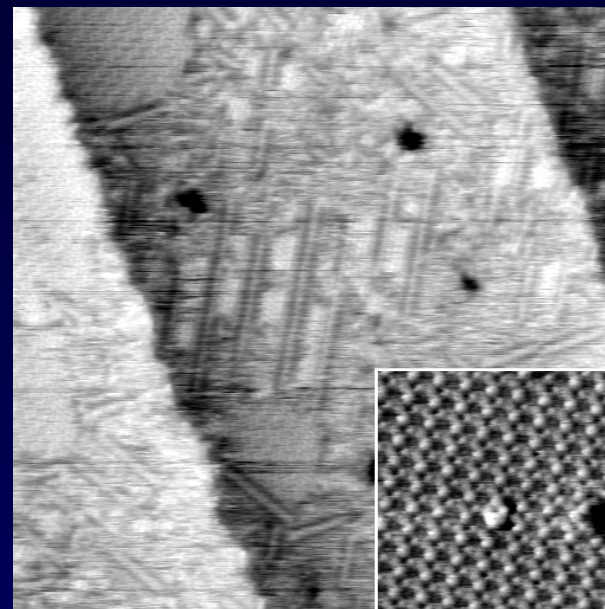
1,1'-biphenyl-4,4'-dithiol



60 nm

5 nm

hexanethiol

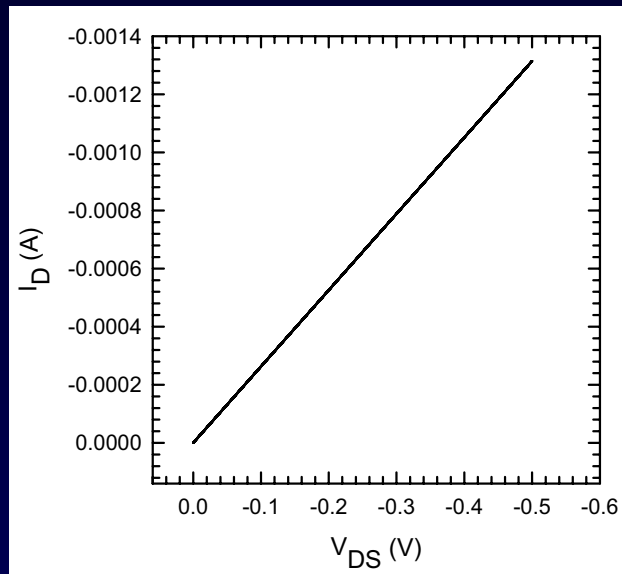


50 nm

10 nm

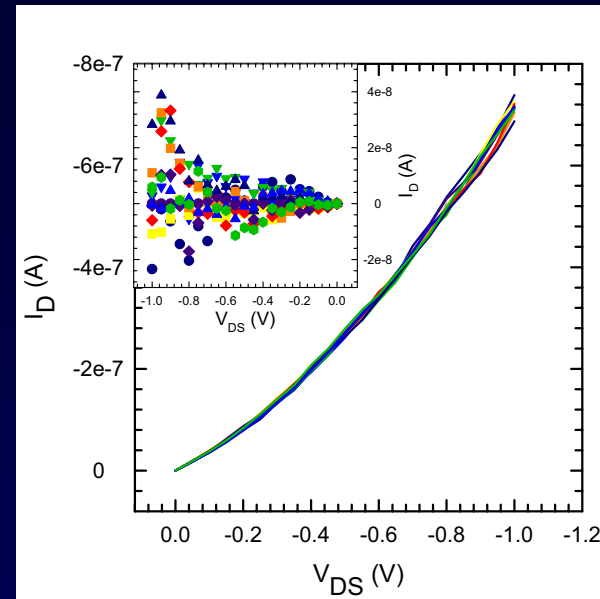
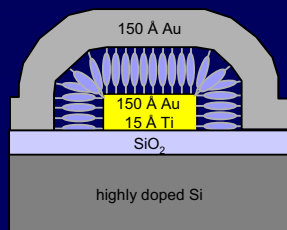
- biphenyldithiol bound to surface, but not well-ordered
- disorder in dithiols consistent with literature
- disorder in biphenylthiols consistent with literature

# 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



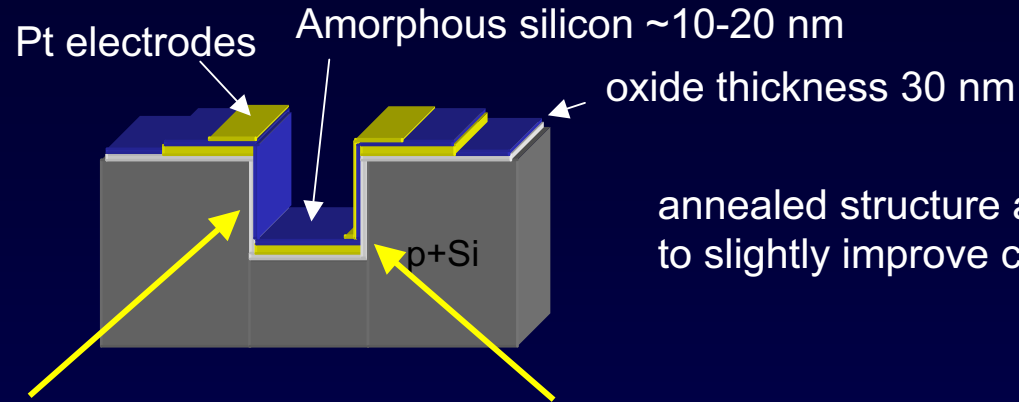
“Multilayer”

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

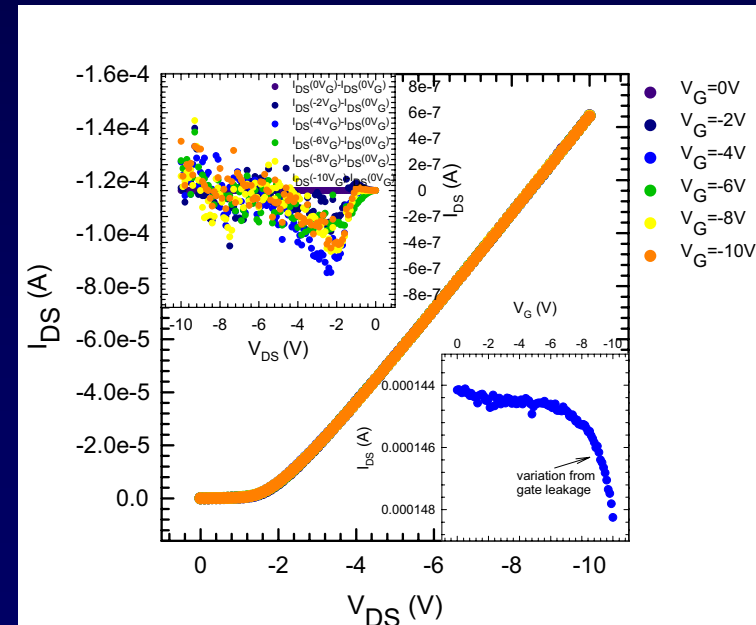
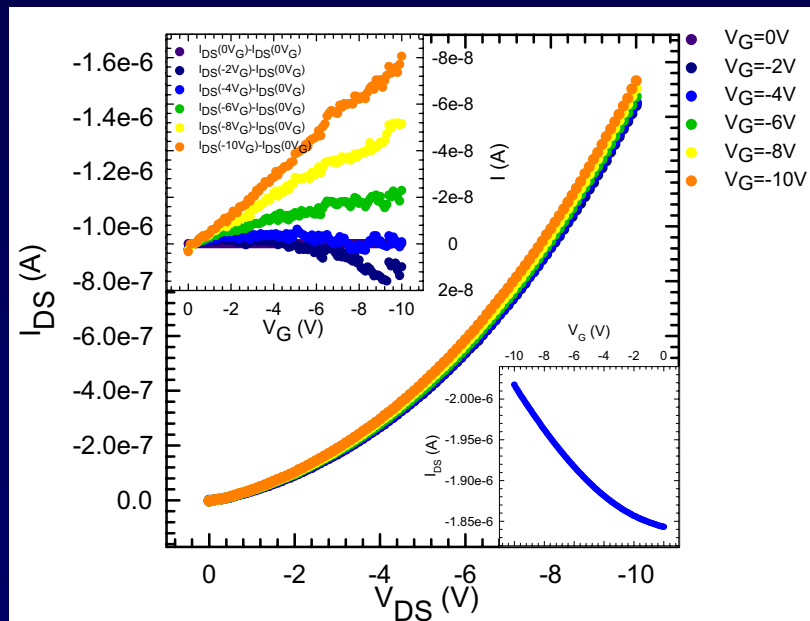
## The Sanity Check



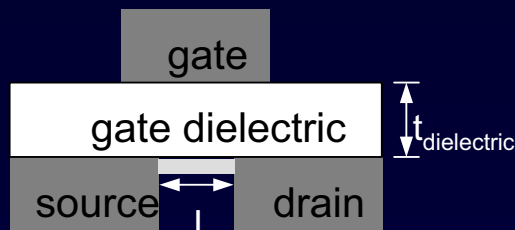
annealed structure at 200 °C in N<sub>2</sub>  
to slightly improve contacts

“Longer” Channel  
transistor

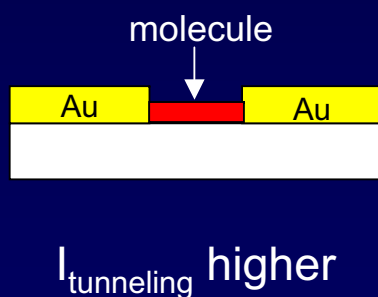
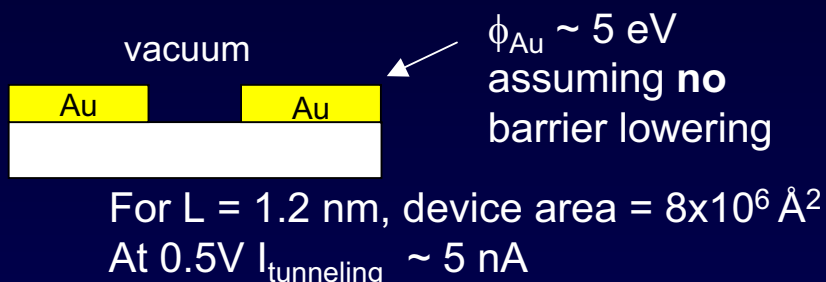
“Tiny” Channel  
transistor



# Key Requirements for Molecular Devices: The Off State

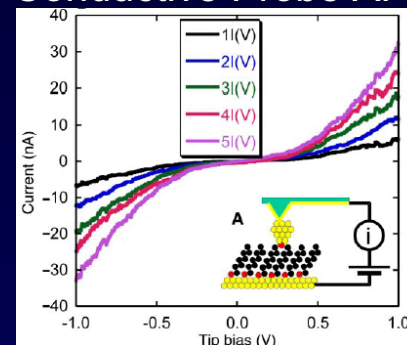


How small can L be?



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

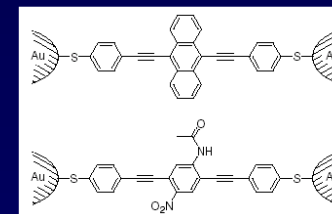
## Conductive Probe AFM



At  $0.5 \text{ V}$   
 $I \sim 1 \text{ nA}$

[Lindsay group]

## Break Junction Measurements



At  $0.5 \text{ V}$   
 $25 - 200 \text{ nA}$

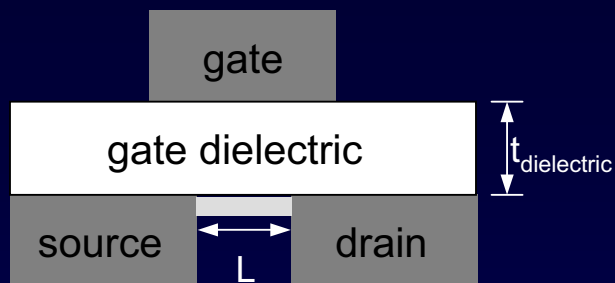
[Reichert et. al. PRL (2002)]  
[Reed, Science (1997)]



- **Design molecules  $\gtrsim 2\text{-}3 \text{ nm}$  long**
- **Tunnel barriers to tune coupling between molecule and electrode**

**Scaled to  
device dimensions  
 $I \sim \text{mA}$**

# Key Requirements for Molecular FETs: Gate Modulation of the Conductance



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

to attain a gate field  
not dominated  
by the drain field

as described by Poisson's  
equation

## Scaling to Molecular Dimensions

$$t_{\text{dielectric}} \lesssim L$$

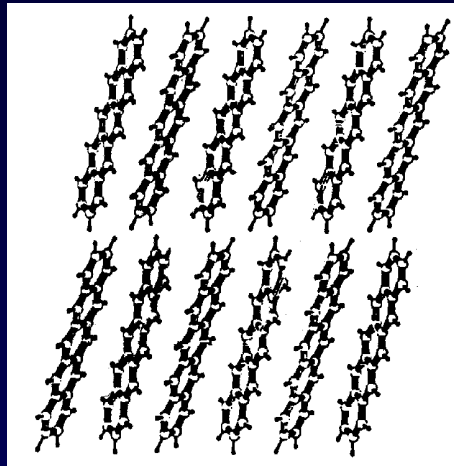
yet  $t_{\text{dielectric}}$  cannot be leaky

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

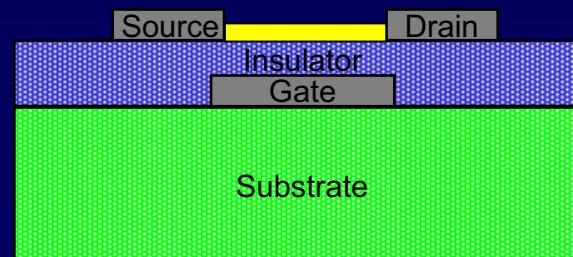
**Many mechanisms for  
molecular switching may  
be envisioned but the device  
electrostatics must work**

# Organic Thin Film Transistors

## Intermolecular Charge Transport

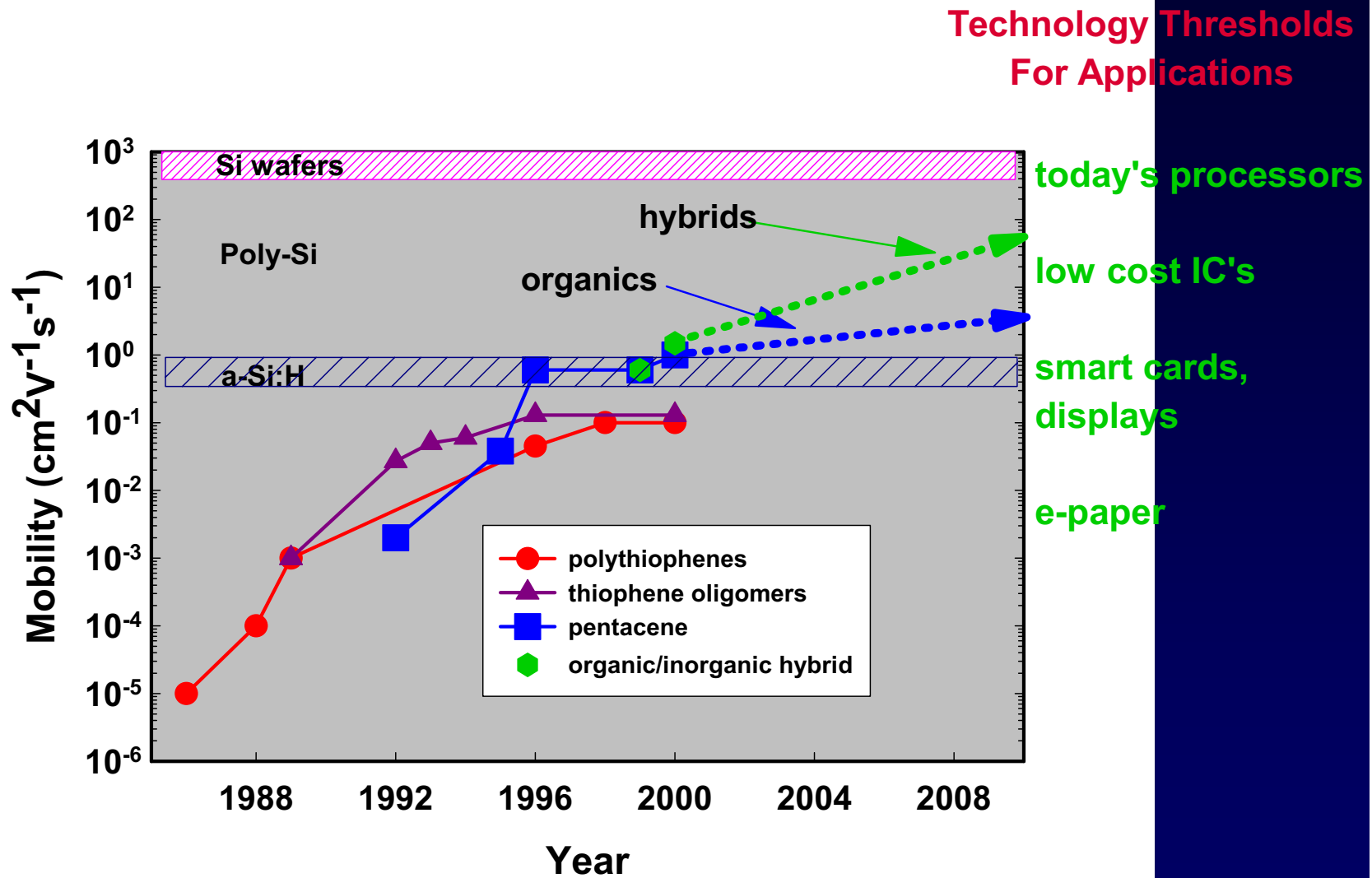


Collective property of molecules



Channel Lengths  $\sim \mu\text{m}$

# Organic Semiconductor Performance Trends



# Where New Materials May Impact Technology



Head-mounted  
Display



IBM Watchpad



Palm Pilot



IBM ThinkPad



RFID Tags

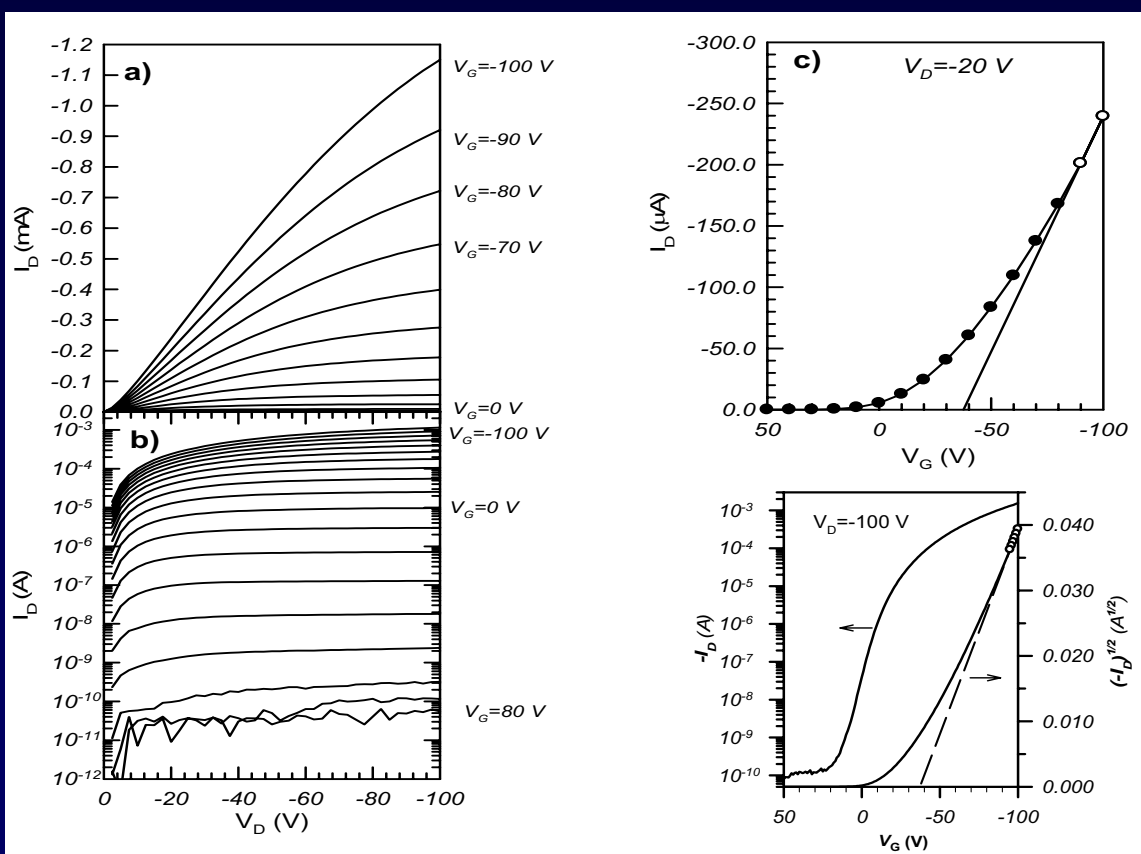
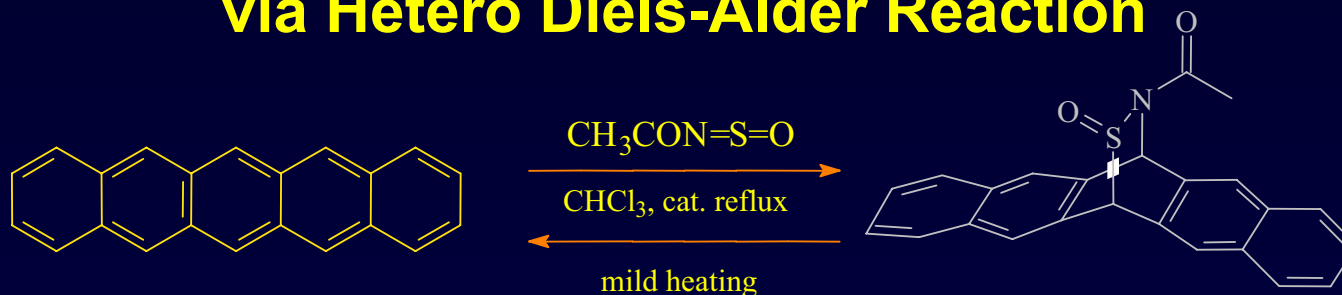


Smartcards



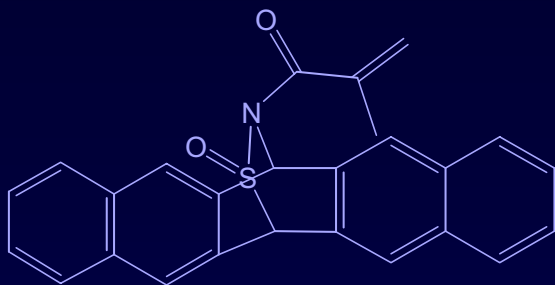
Electronic Newspaper  
R. Steinbugler, IBM

# Synthesis of a Pentacene precursor via Hetero Diels-Alder Reaction

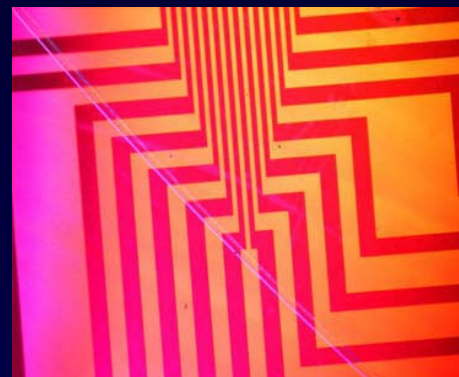


$\mu_{\text{sat}} \sim 0.5 \text{ cm}^2/\text{V-sec}$   
 $I_{\text{ON}}/I_{\text{OFF}} \sim 10^7$

# Device Stability of Photoimageable Pentacene Precursor

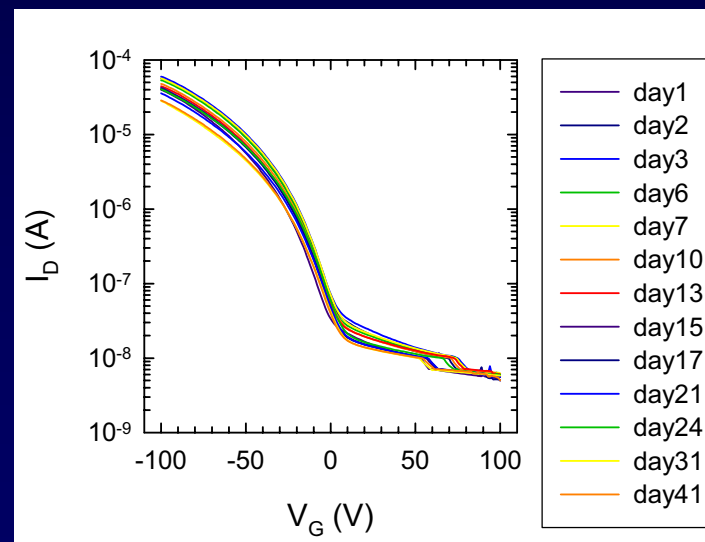
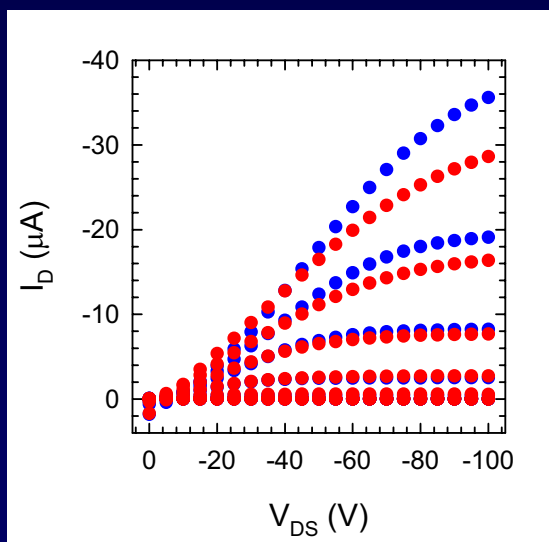


N-sulfinylmethylacrylamide  
pentacene adduct



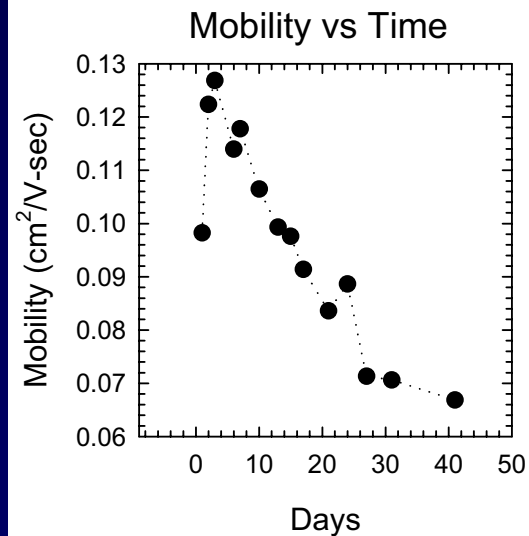
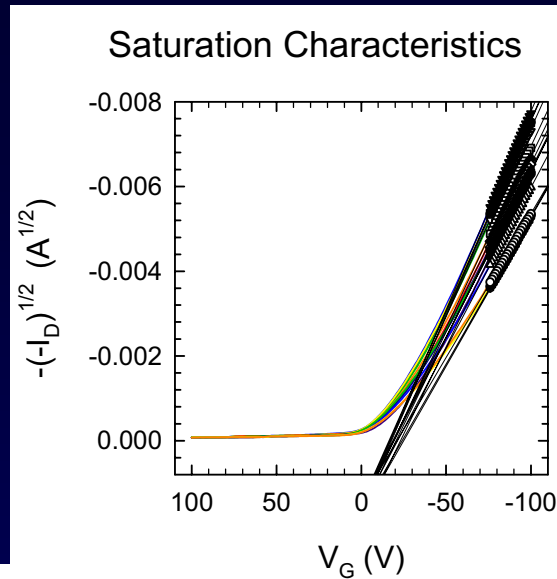
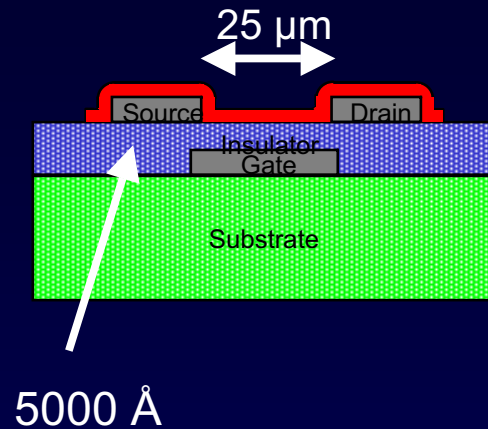
Photoimageable  
precursor

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

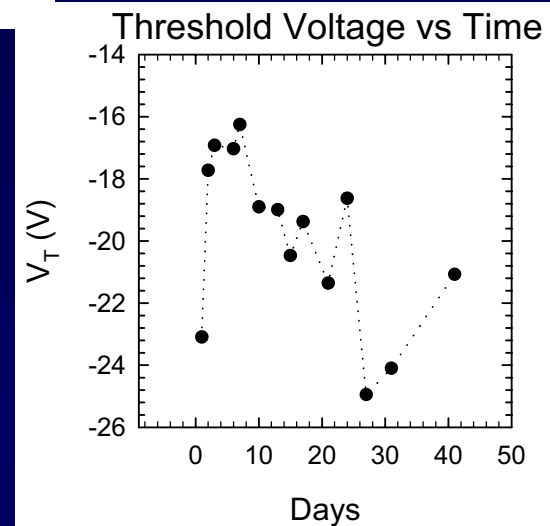


Device measured and stored in ambient

# Important Device Characteristics Beyond Mobility and On-Off Ratio

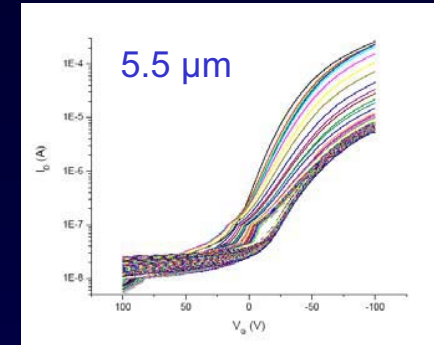
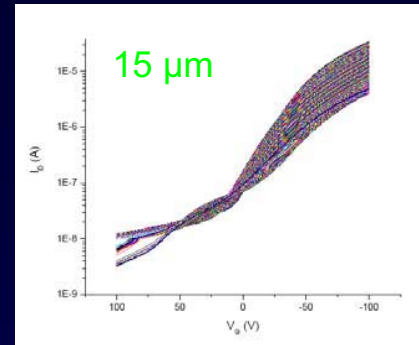
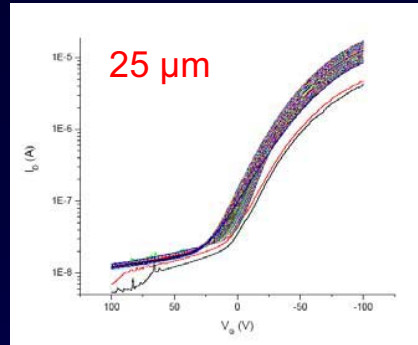
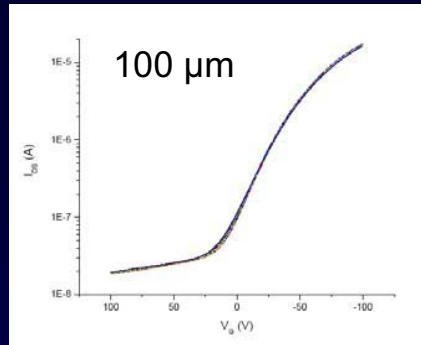


Mobility varies  
+/- 30%



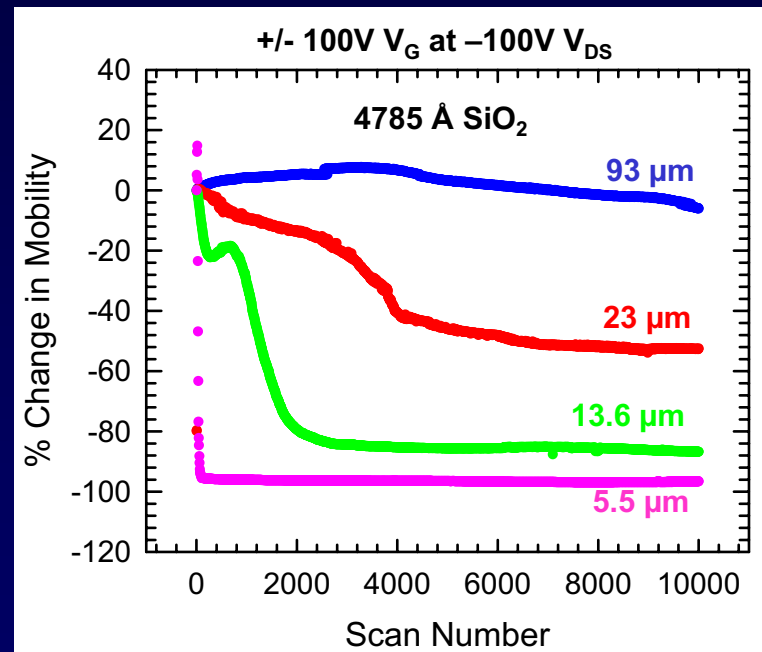
# Cycling Devices

## Channel Length Dependent Stability



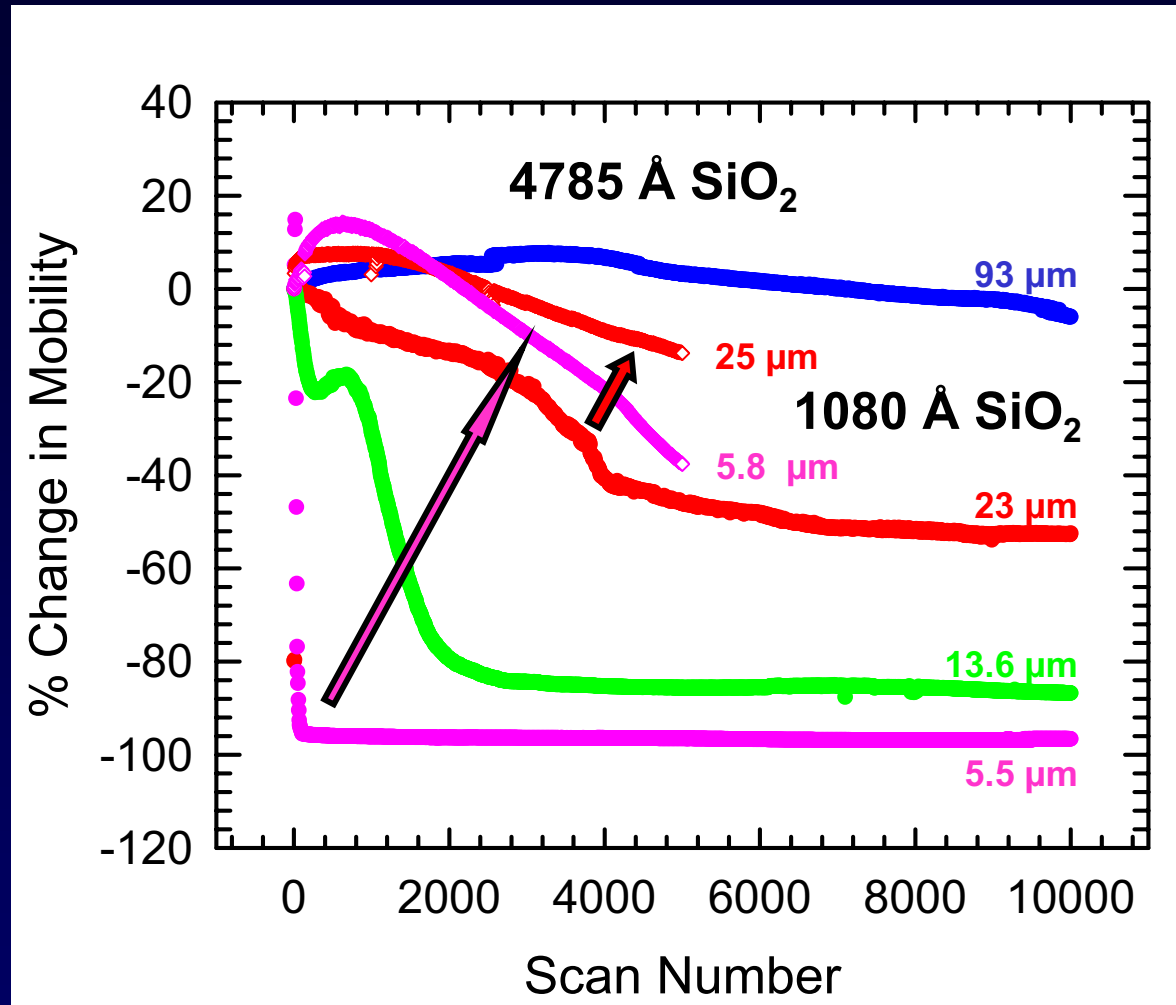
Cycle Devices 10001x

$V_G$   $\pm$  100V @ -100  $V_{DS}$



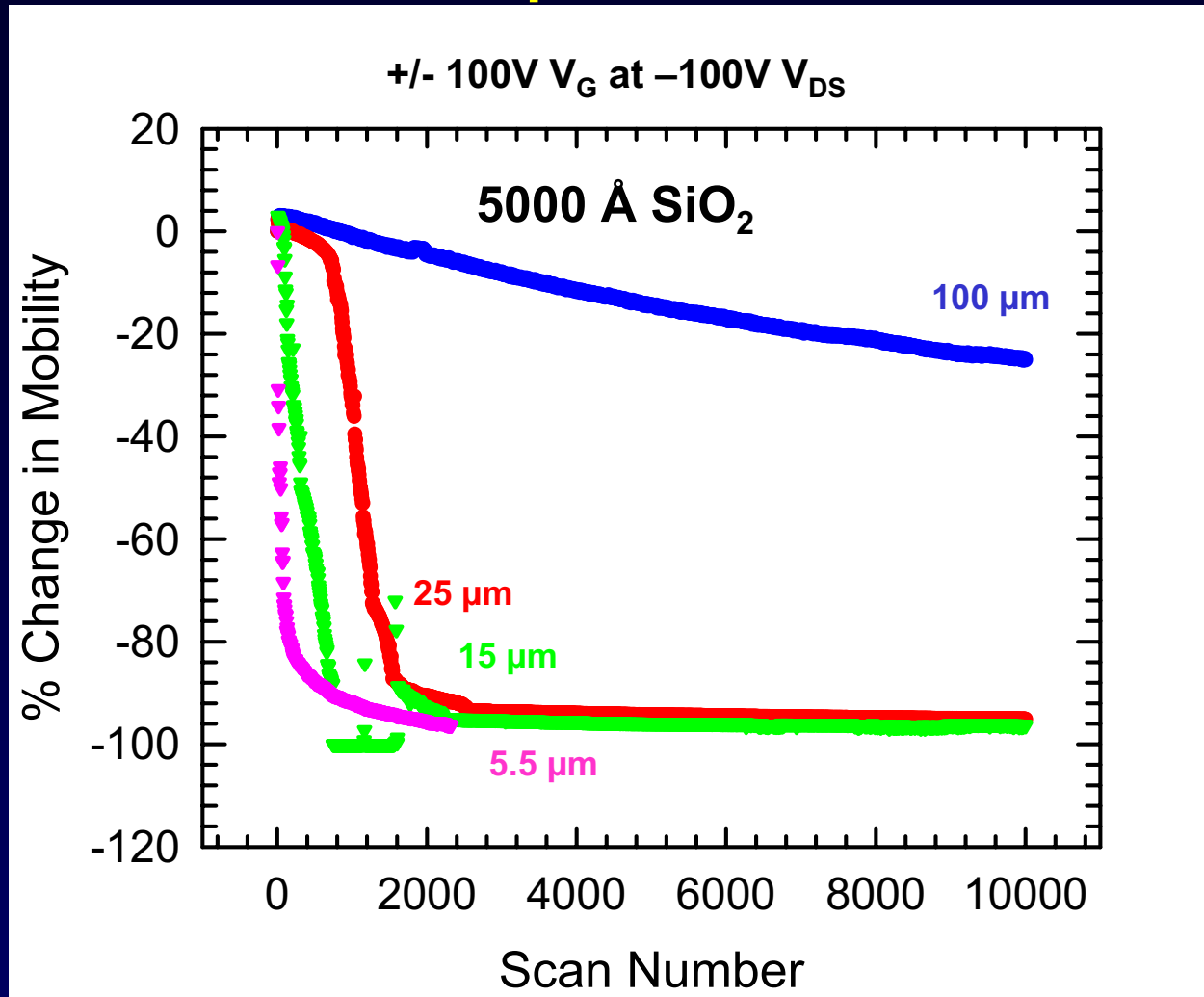
Mobility drops dramatically with decreasing channel length  
Mobility varies between  $\sim 0.015$ - $0.06$   $\text{cm}^2/\text{V}\cdot\text{sec}$  in these devices

## Oxide Thickness Dependence of Carrier Mobility



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

## Vacuum Evaporated Pentacene

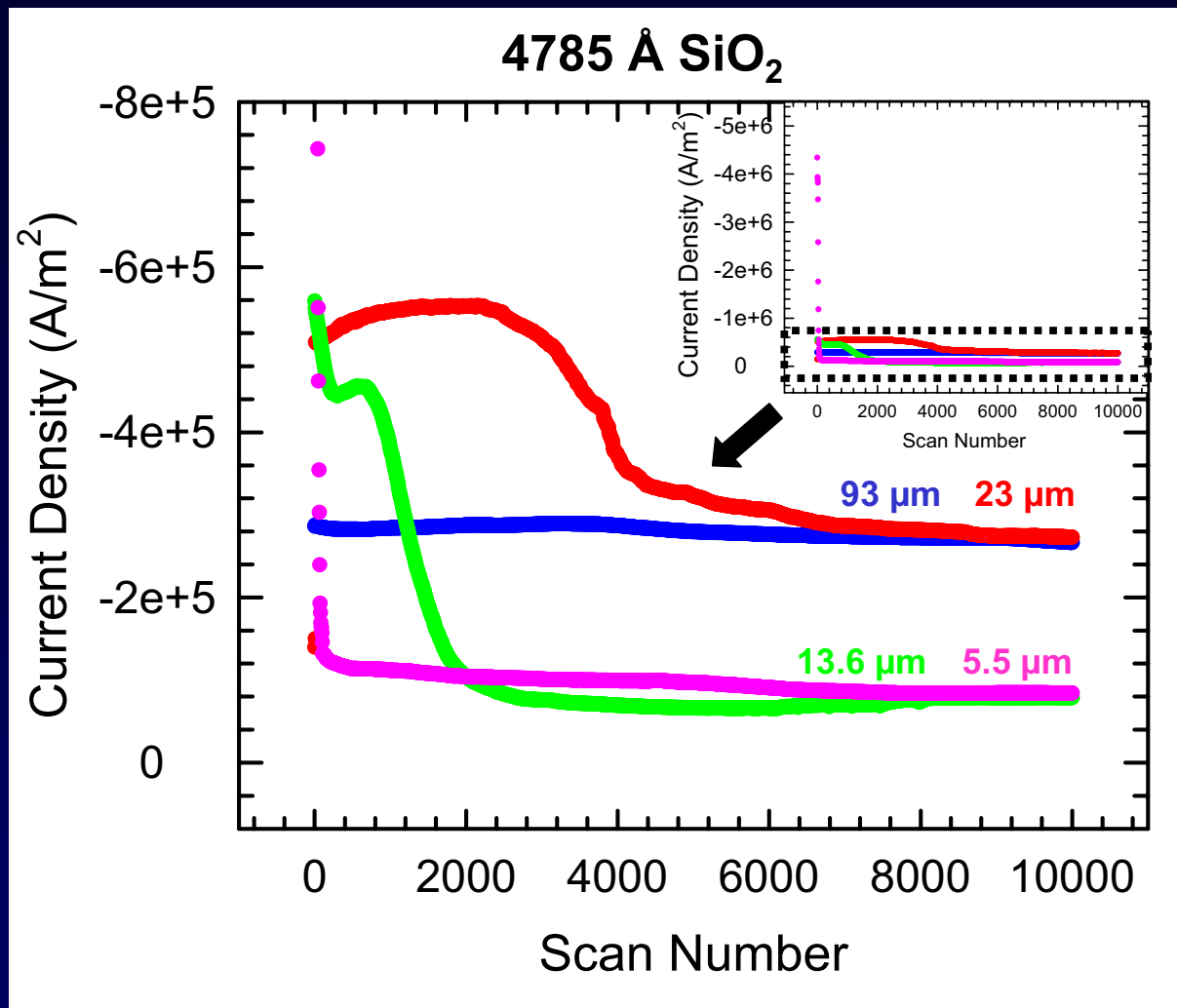


Mobility of solution deposited films 0.015-0.06  $\text{cm}^2/\text{V}\cdot\text{sec}$

Mobility of vacuum deposited film 0.6  $\text{cm}^2/\text{V}\cdot\text{sec}$

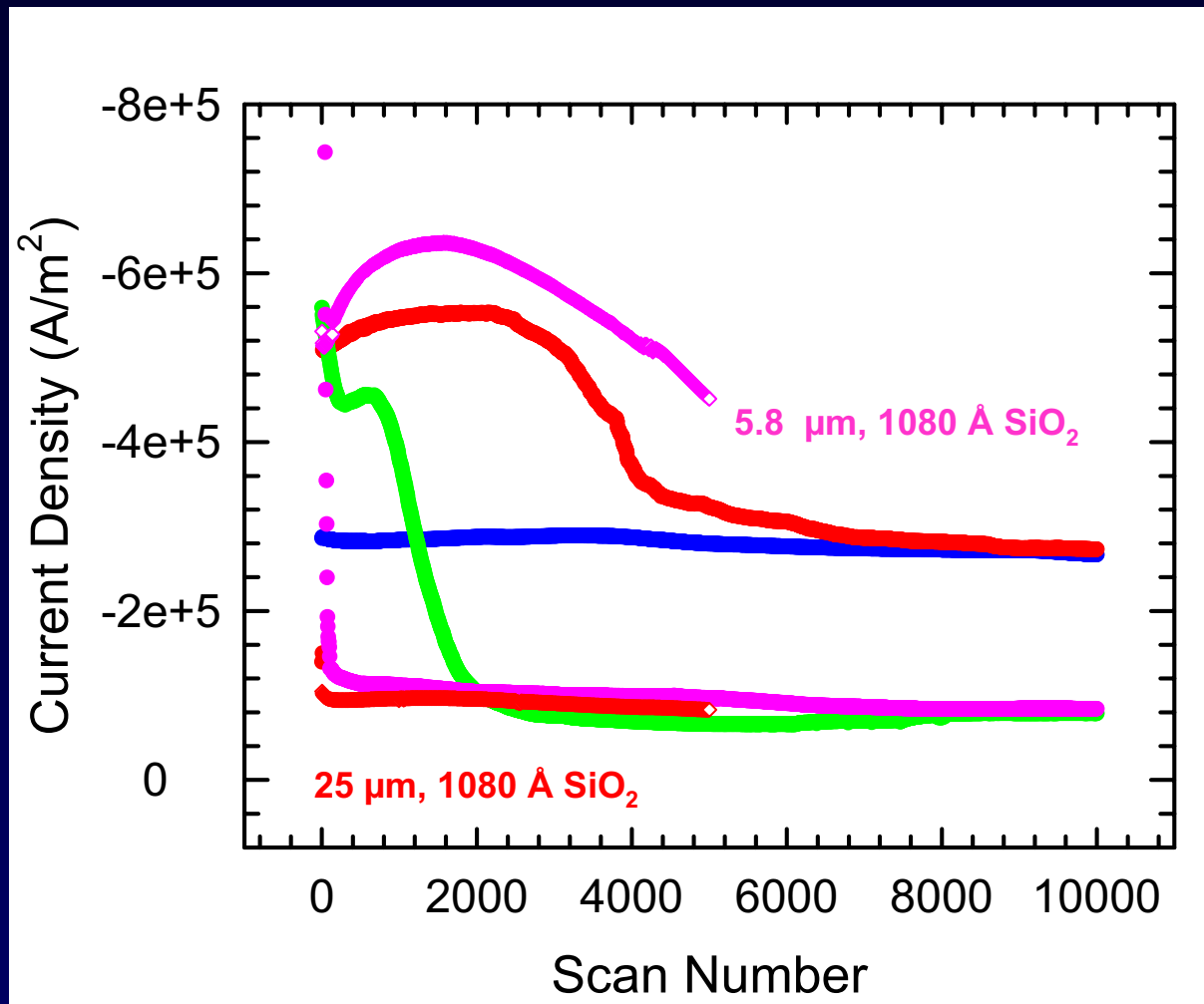
Vacuum deposited film less stable – power density limitation of evaporated film or chemical stability/morphology of soluble precursor

## Channel Length Dependent Current Density



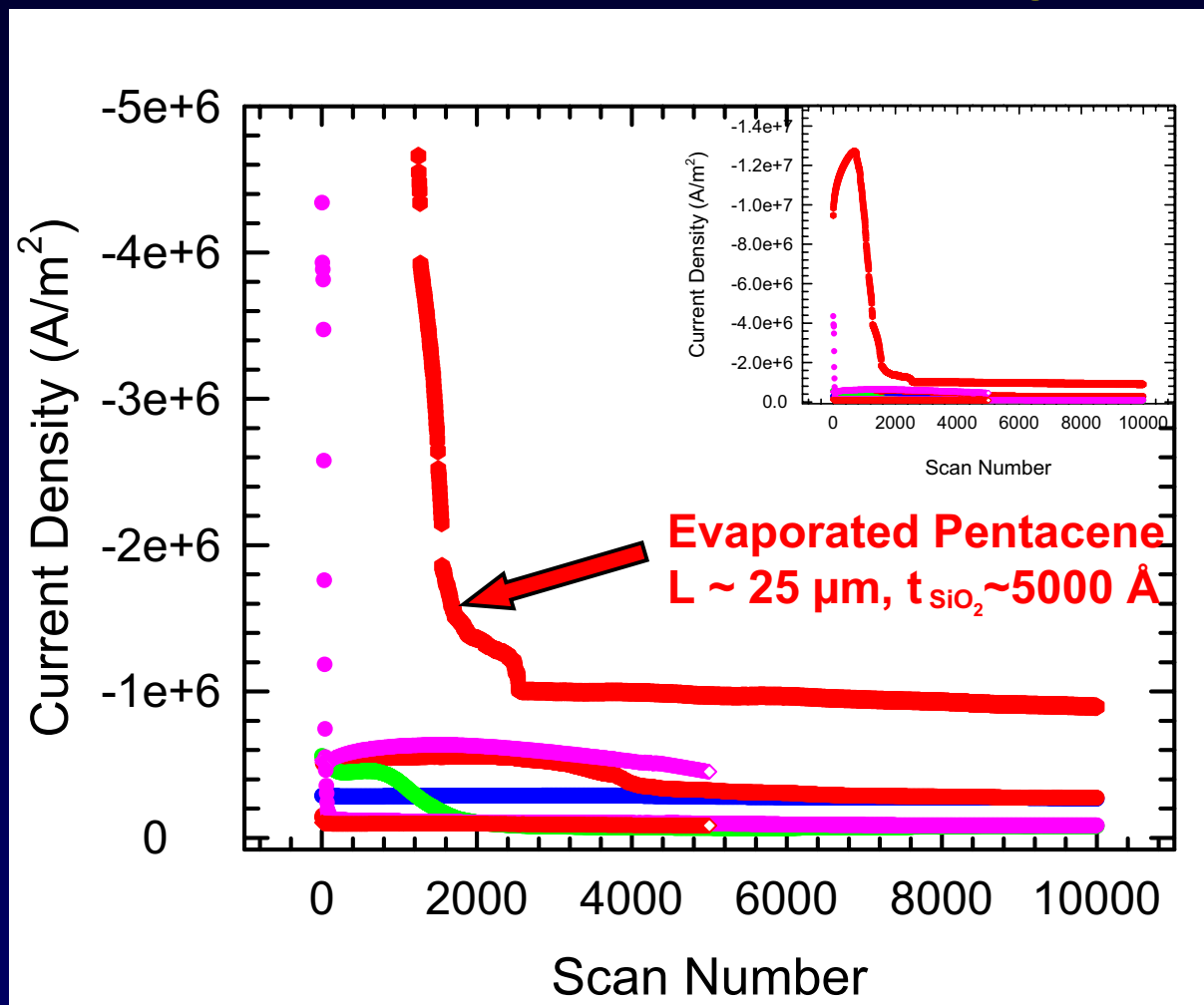
At same voltages (various source-drain fields), higher current densities not maintained  
As number of scans increased current density drops and plateaus

## 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