

# Molecular Electronics For Fun and Profit(?)

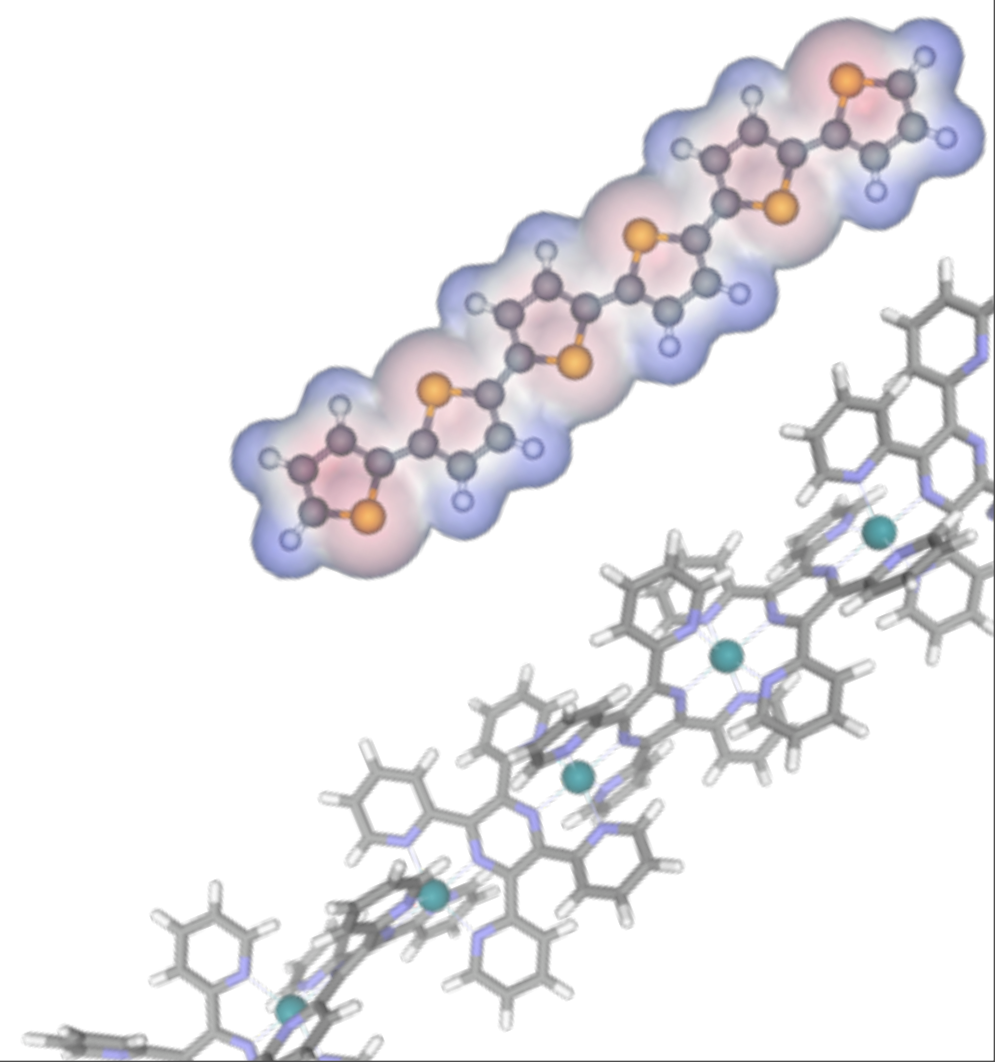


**Prof. Geoffrey Hutchison**

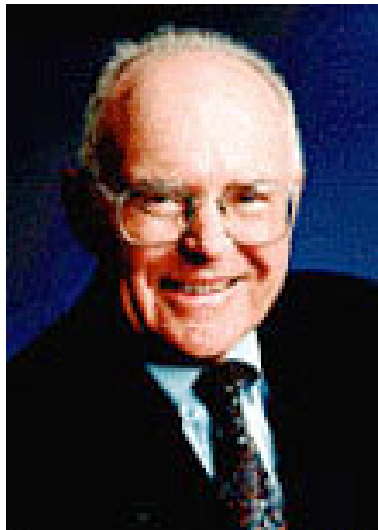
Department of Chemistry  
University of Pittsburgh  
geoffh@pitt.edu

July 22, 2009

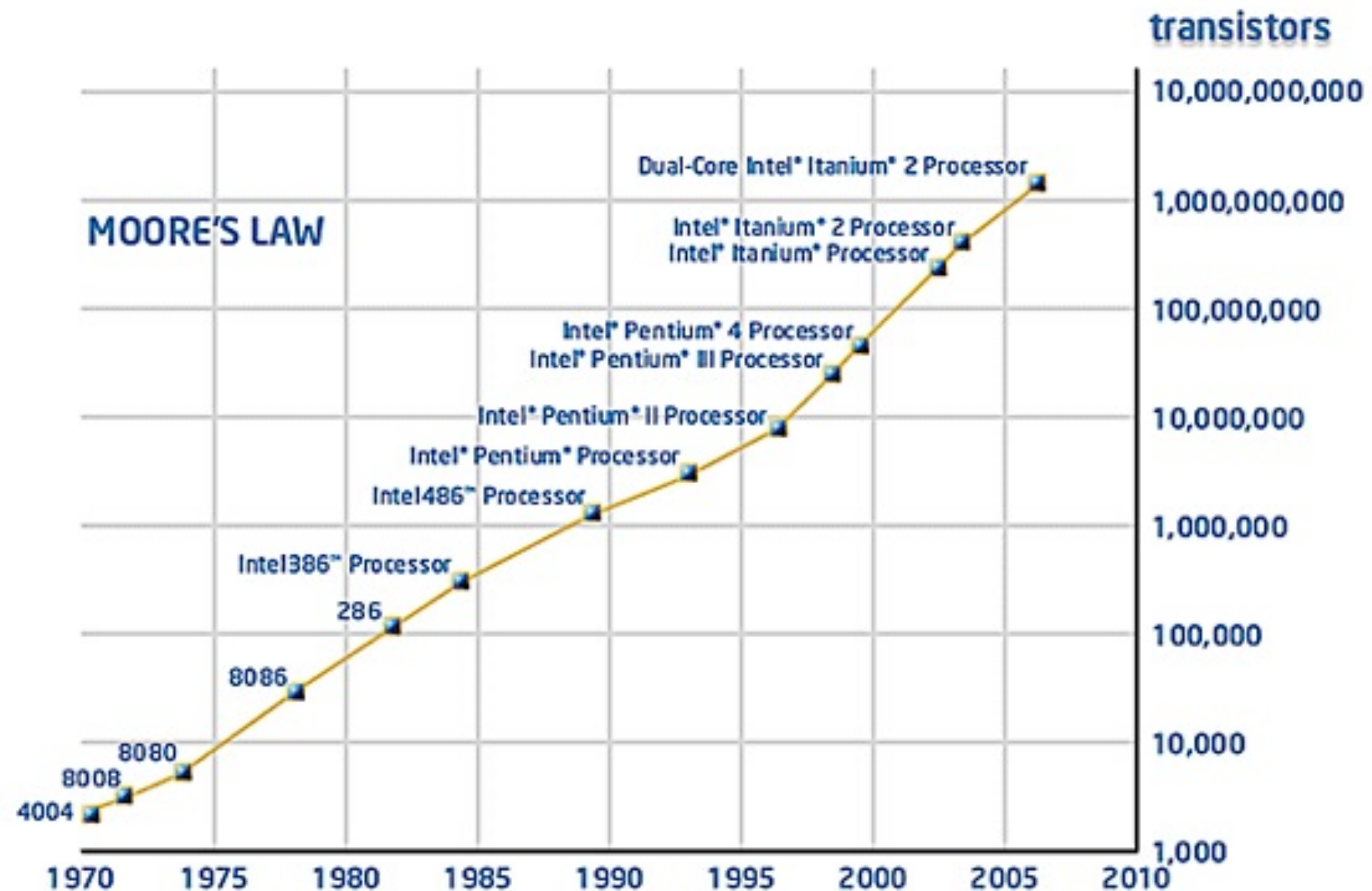
<http://hutchison.chem.pitt.edu>



# Moore's "Law:" Transistor Count Doubles Every 18 Months



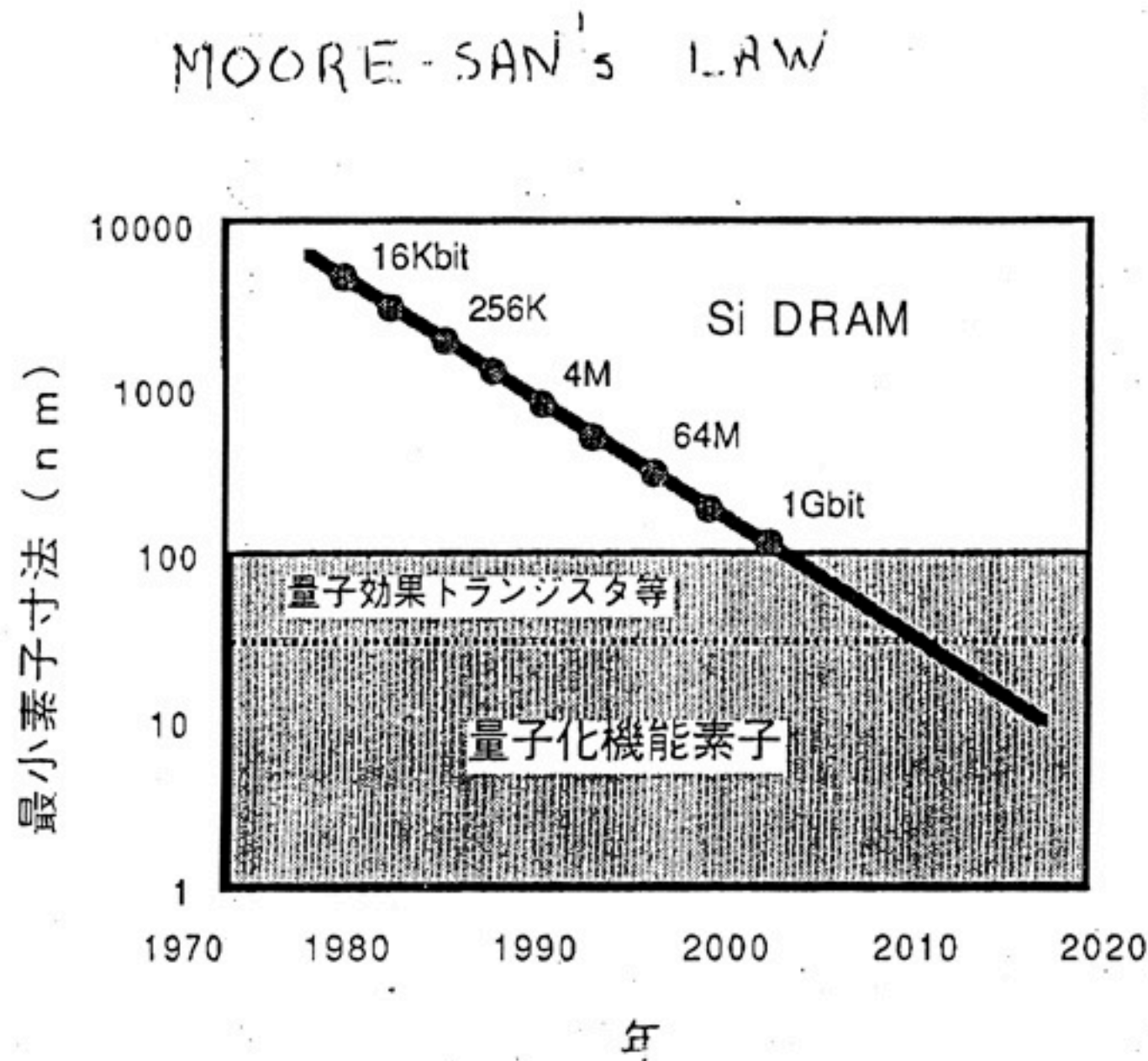
Gordon Moore:  
Co-founder of Intel



*From Intel Corp. circa 2007*

**Similar trends observed in chip performance,  
price per performance, etc.**

# Moore-San's Law

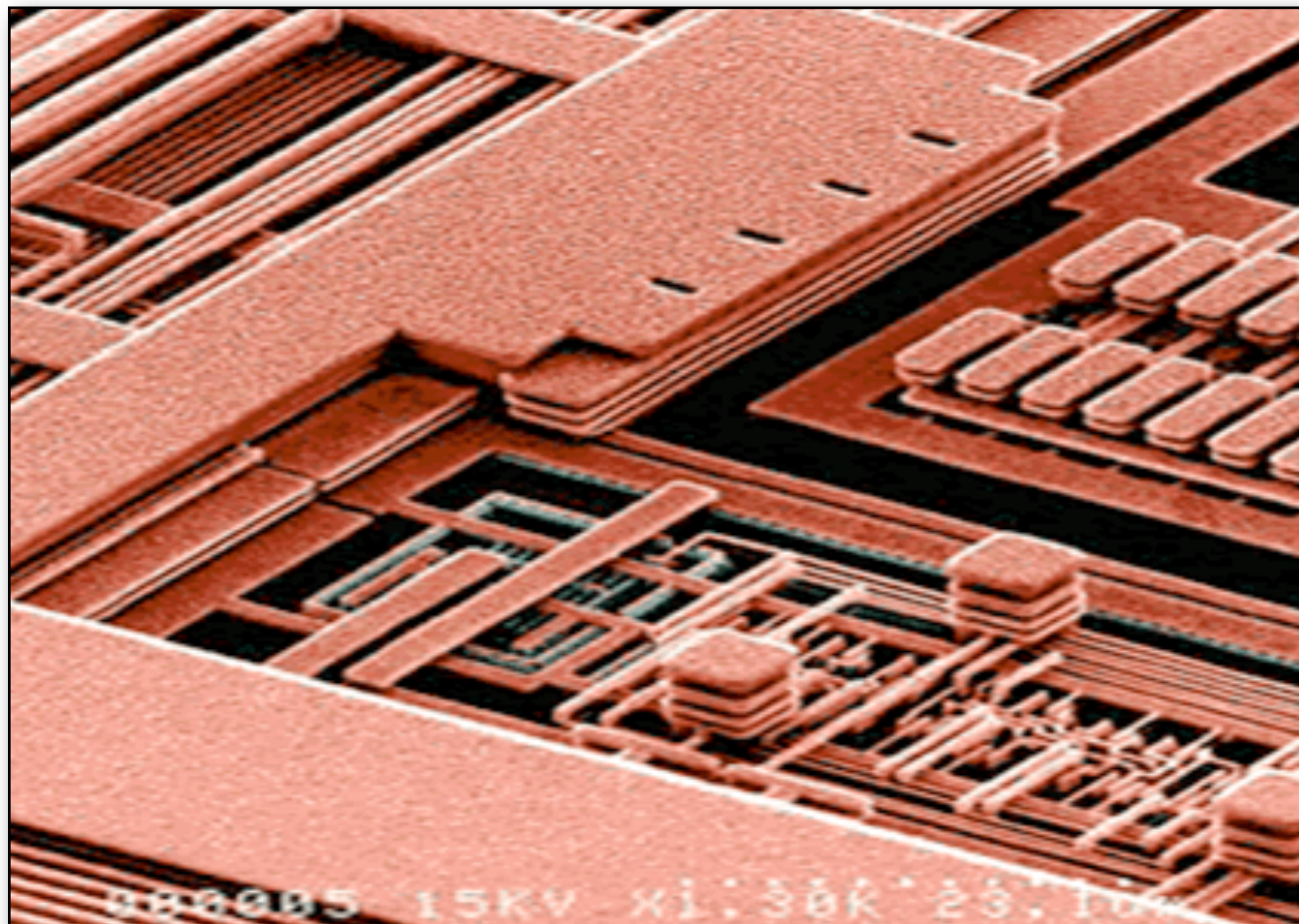


- 1) 微細化限界
- 2) デバイス限界  
ex. トンネルリーク
- 3) 集積化限界  
ex. 配線遅延

Image courtesy M. Ratner



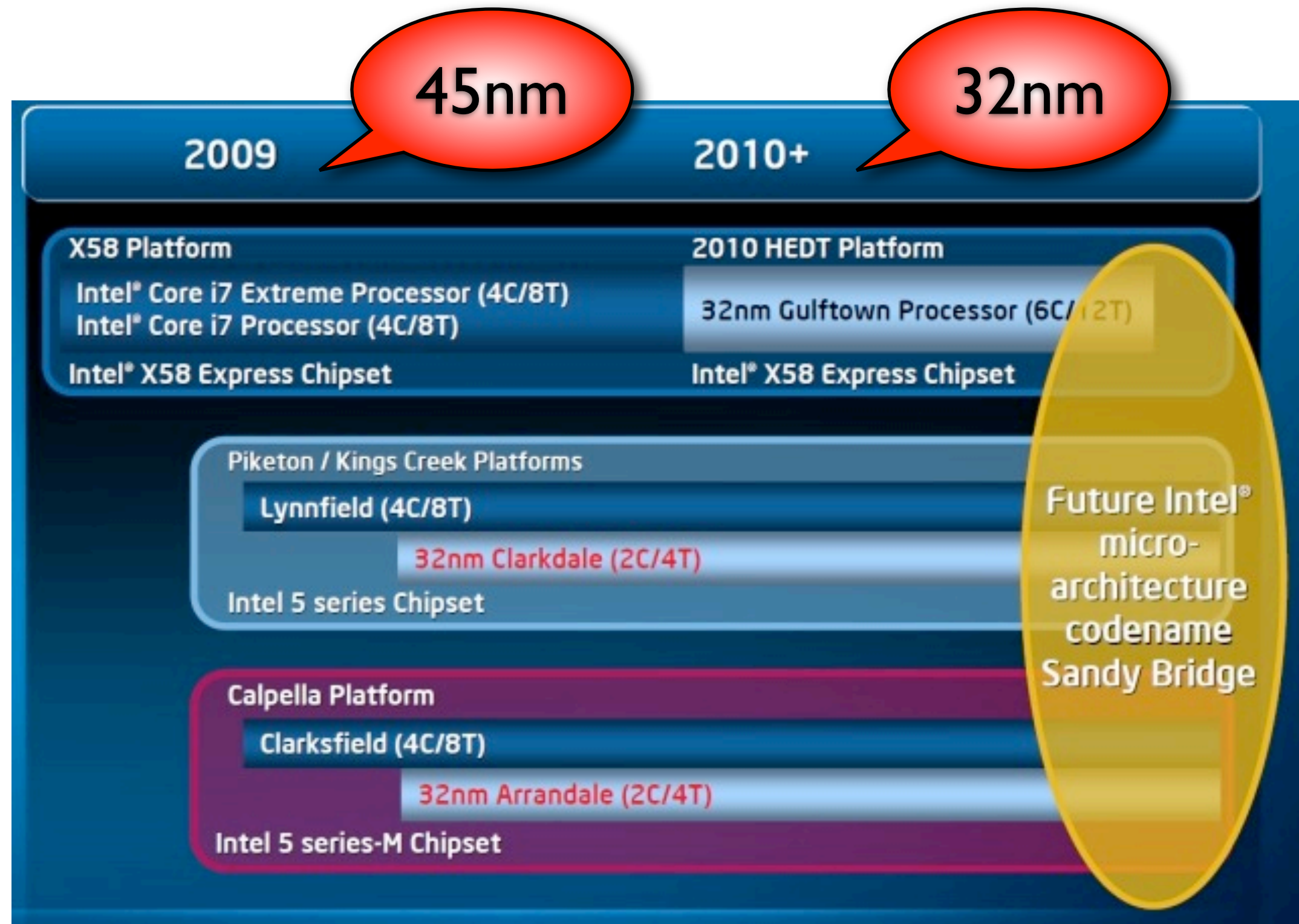
# Don't Underestimate Silicon...



**Actually, these are from 1997(!)**

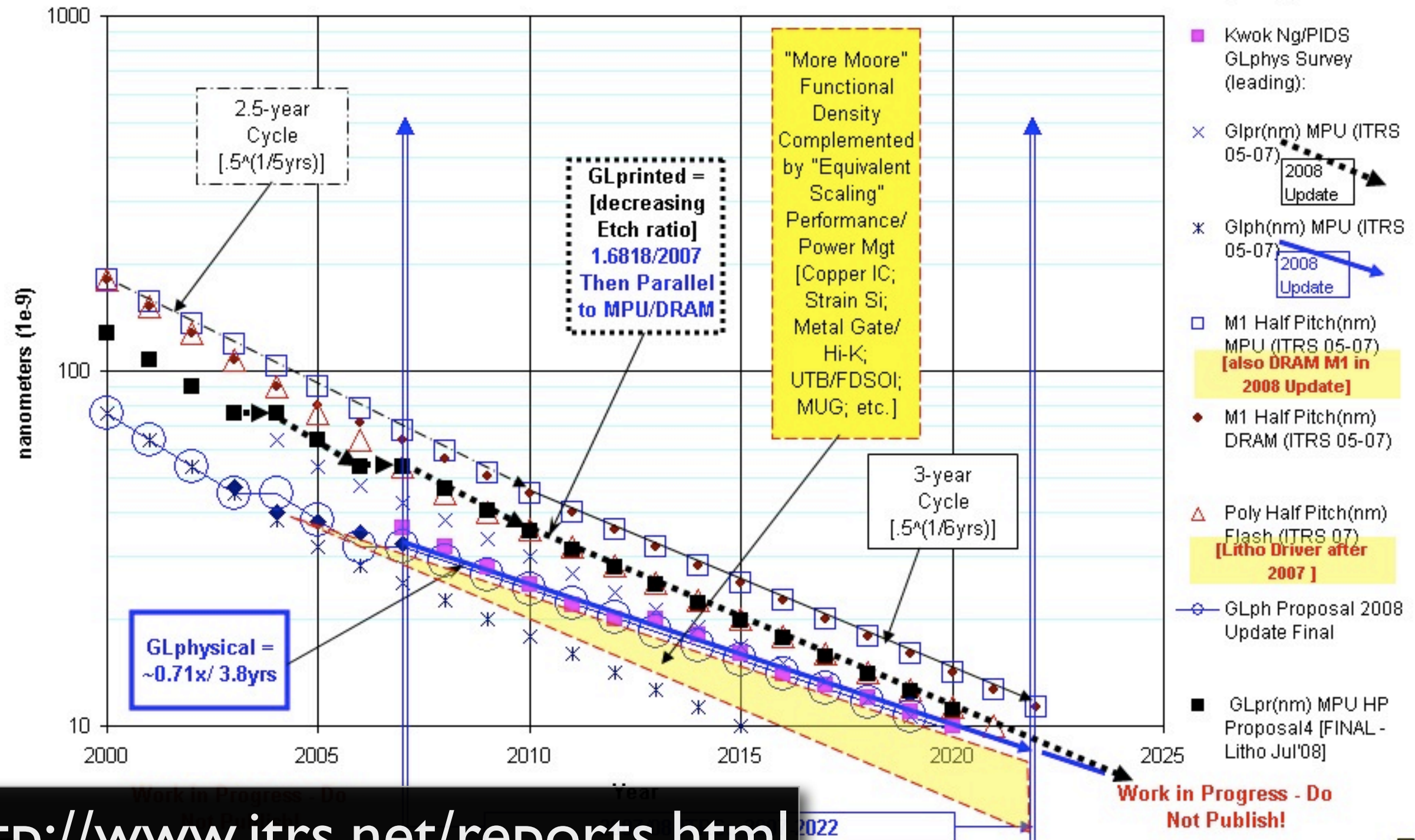


# Current Intel Roadmap



# International Technology Roadmap for Semiconductors (ITRS)

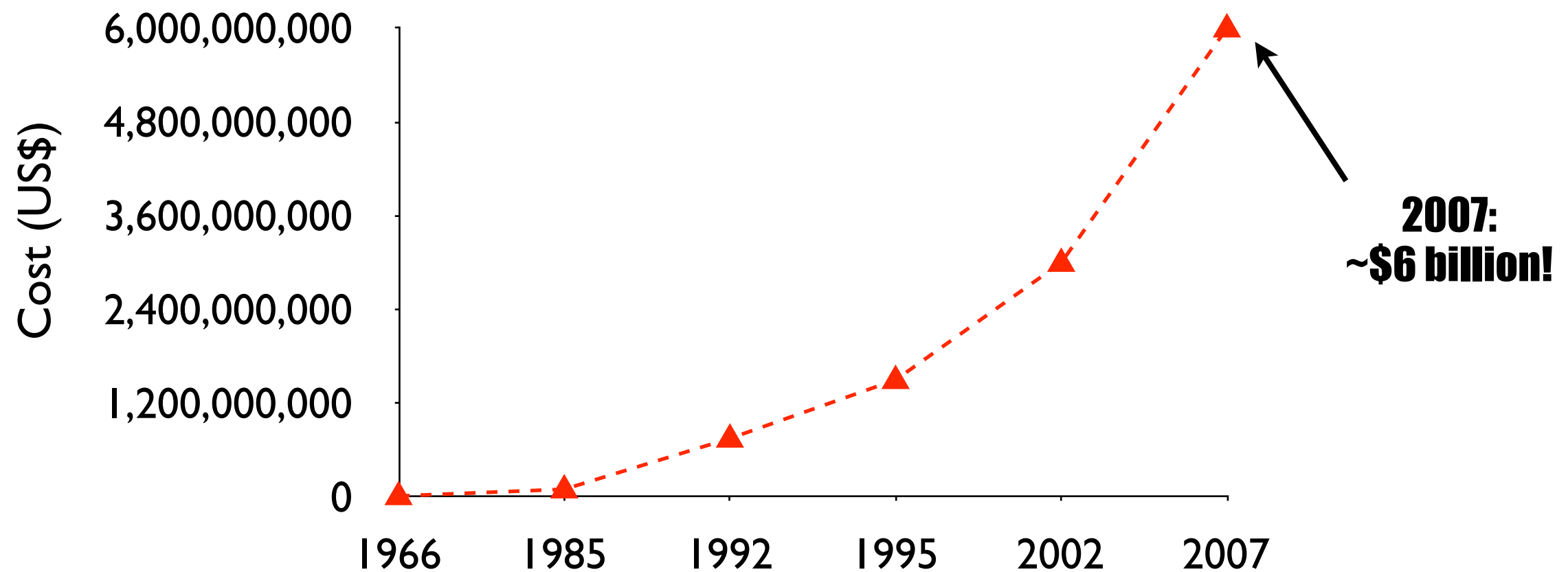
2008 ITRS Update - Technology Trends vs Actuals and Survey  
[including Final Litho Printed Gate Length Proposal]





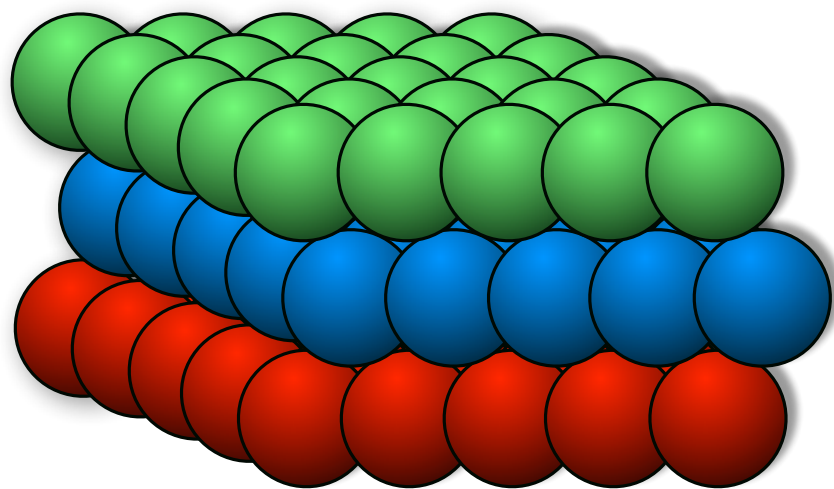
# Moore's Second Law: Exponential Economics

Cost of a building a new fabrication plant  
**doubles** every 3-4 years:

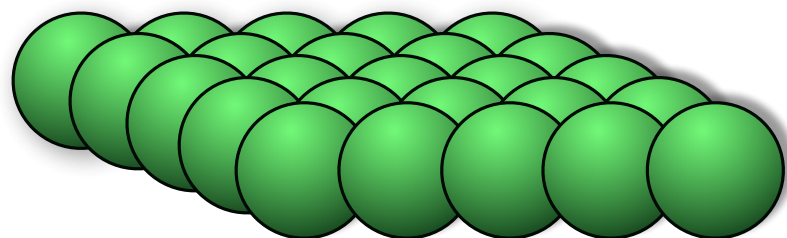


**Advances in conventional lithography  
are quickly becoming cost-prohibitive!**

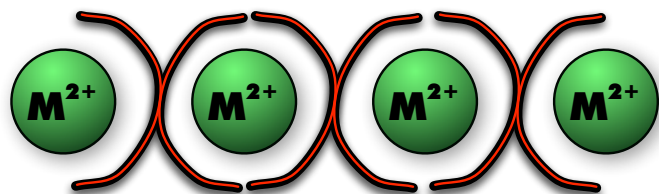
# Molecular Electronics: Just Nanoscale?



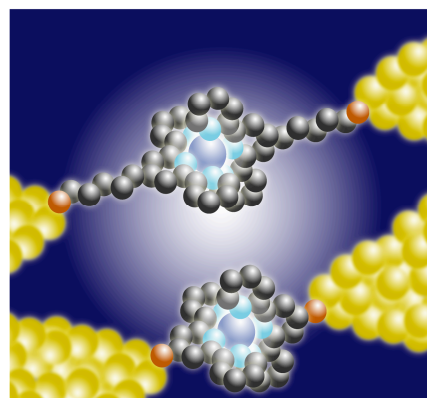
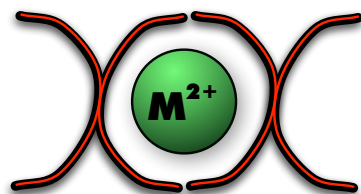
**3D: Bulk Films**



**2D: Monolayer**



**1D: Chains**



**0D: Individual Molecules**



# Why Organic Electronics?

## Relative to Inorganic Materials:

### Pros

- Greater “tailorability” through synthetic chemistry
- “Wet” deposition
  - Wide-area
  - Inexpensive
- Flexible, lightweight
- Synthesis =  $6.02 \times 10^{23}$

### Cons

- Lower electron mobility
- Slower switching speeds
- Hard to obtain complementary *p/n* logic
- Integration into industry?

# Broad Applications for Molecular Electronic Materials

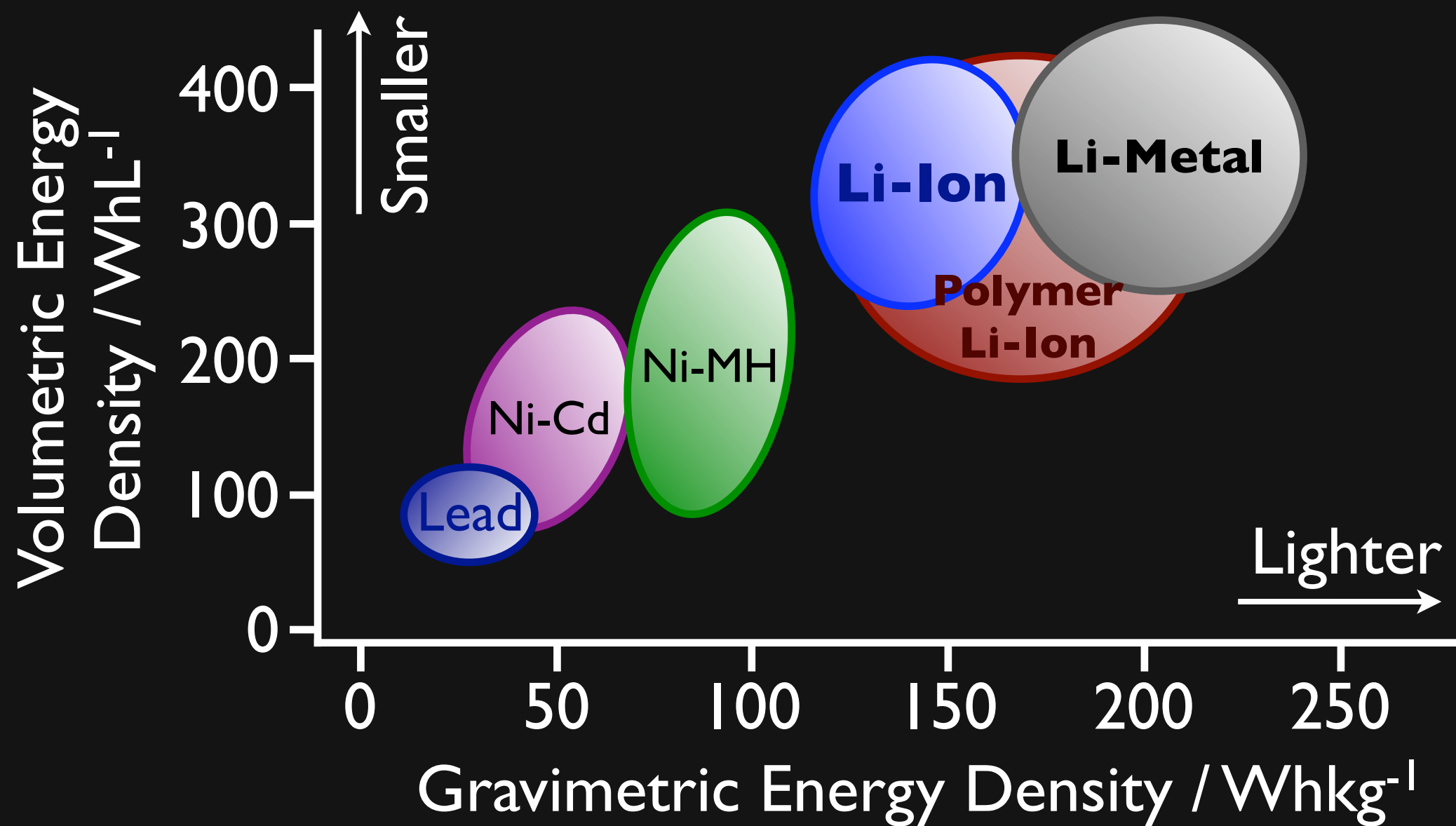


- **Light-Emitting Diodes**
  - *Hole transport layers*
  - *Flexible anodes*
- **Photovoltaic Devices**
- **Thin-Film Transistors**
  - *Flexible circuits*
- **“Smart” Windows**
  - *Fast color changes*
- **Anti-Static Films**
  - *Device fabrication*
  - *Photographic film*

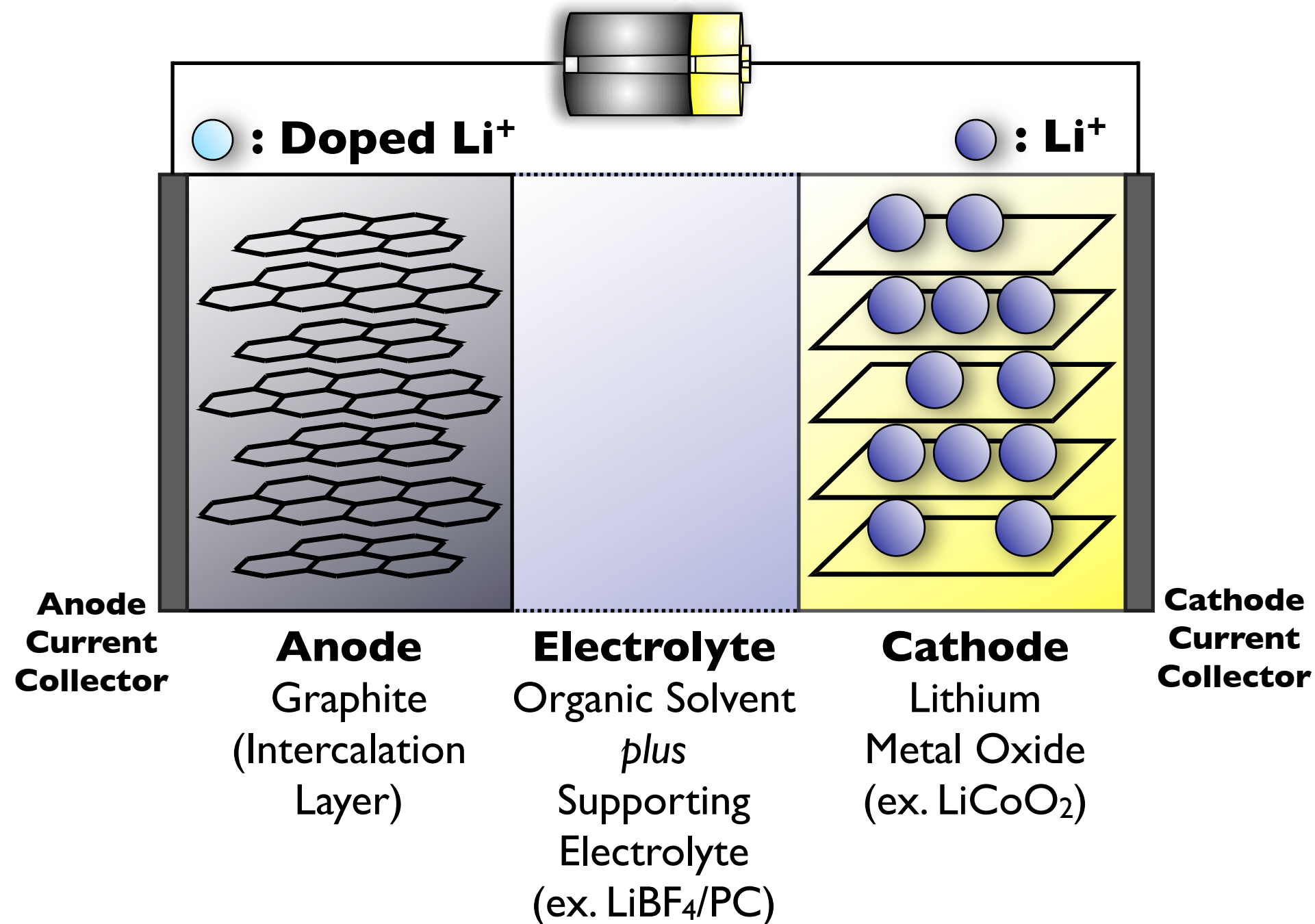


# Batteries: Not Just Inorganics...

## Energy Density for Secondary Batteries

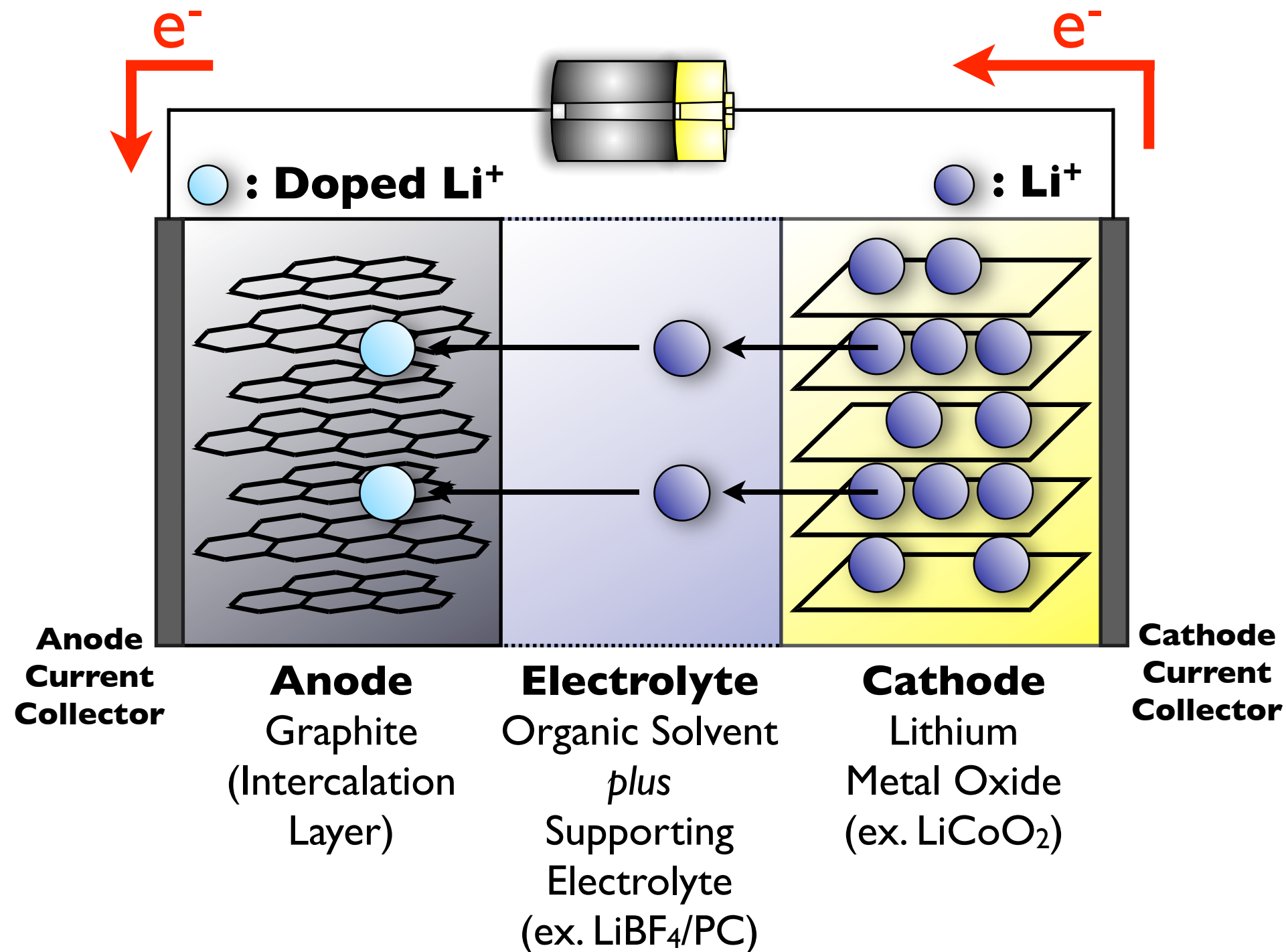


# Reaction Mechanism for LIBs



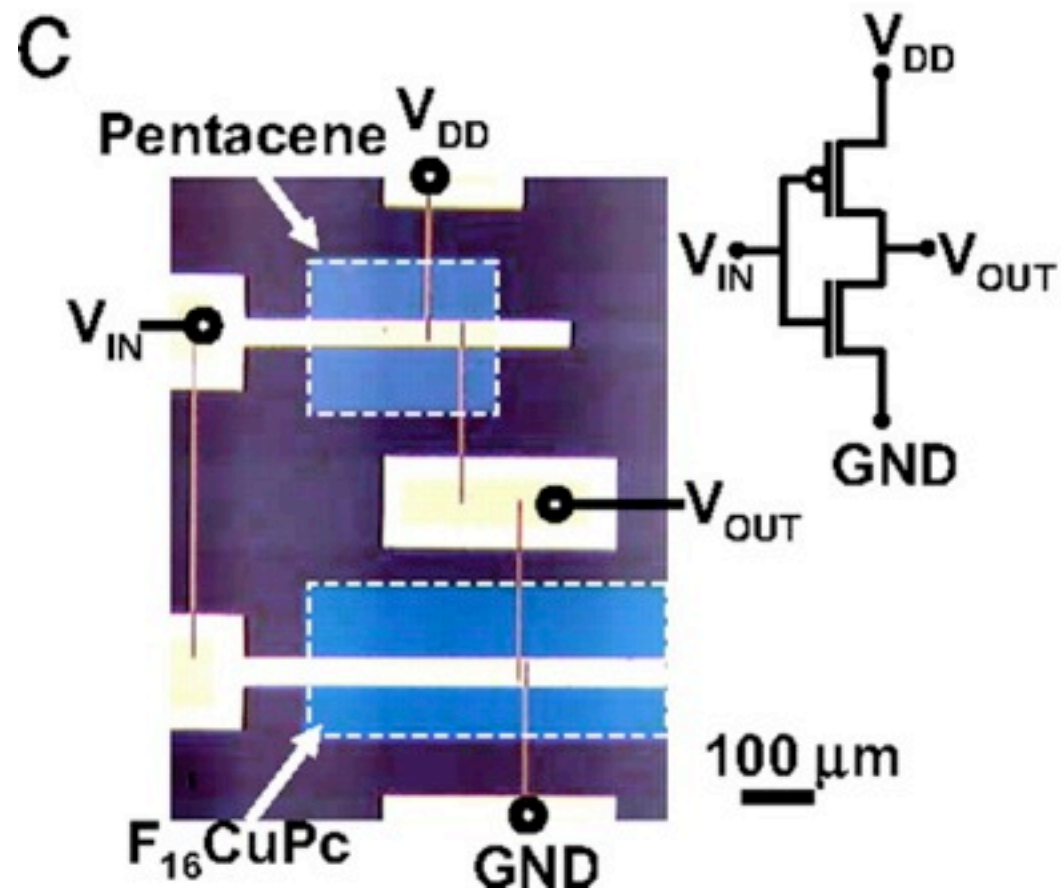


# Reaction Mechanism for LIBs



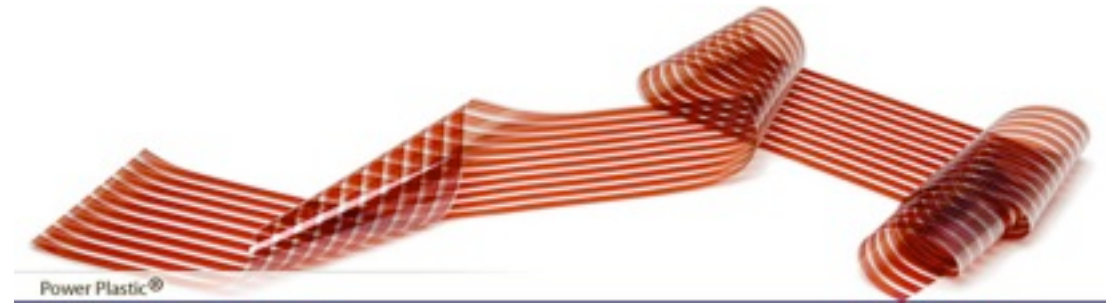
# Ink-Jet Printing of Organic Electronics

## Ink-Jet Printing Transistors

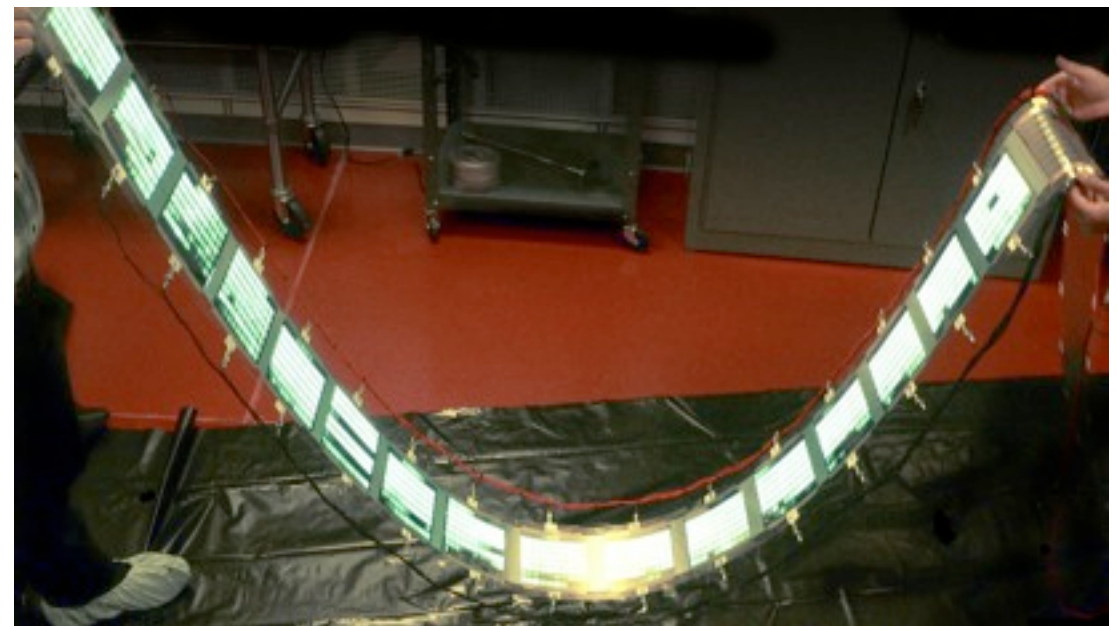


Sekitani et al. *PNAS* **2008** p. 4976

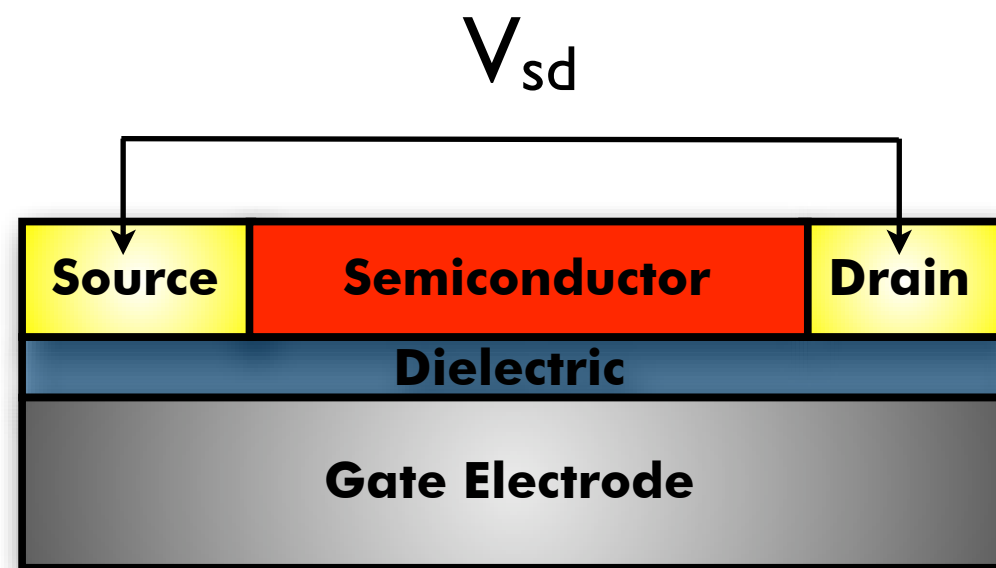
Konarka: Ink Jet Printing for Solar Cells  
Mar. 4, 2008



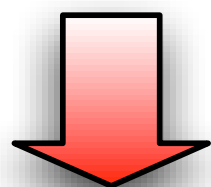
GE: Ink Jet Printing for Displays  
Mar. 11, 2008



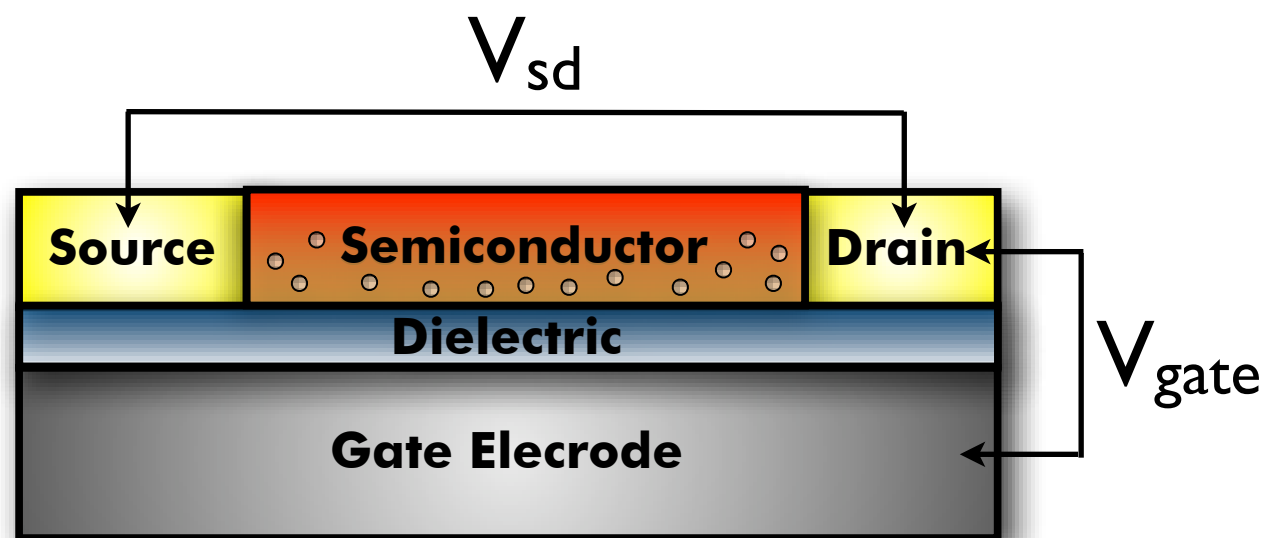
# Organic Field-Effect Transistors



$$I_{sd} \sim 0.0 \text{ A} \text{ "Off"}$$



**Applied Gate Potential**

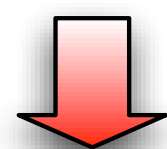
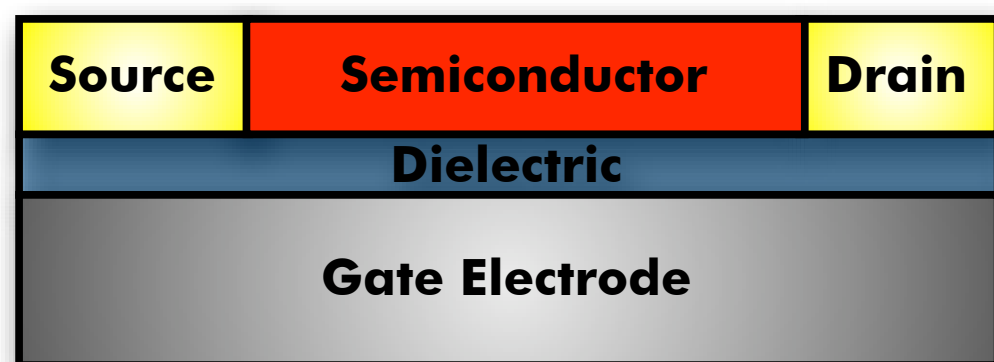


$$I_{sd} = 10^{\times} \text{ A} \text{ "On"}$$

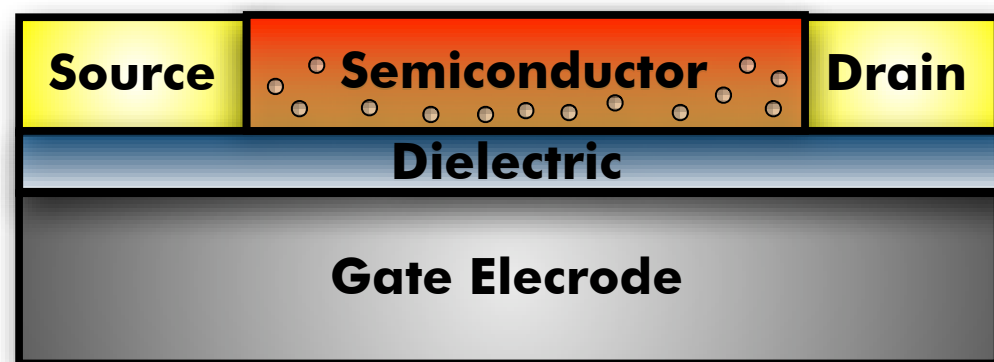


# Organic Field-Effect Transistors

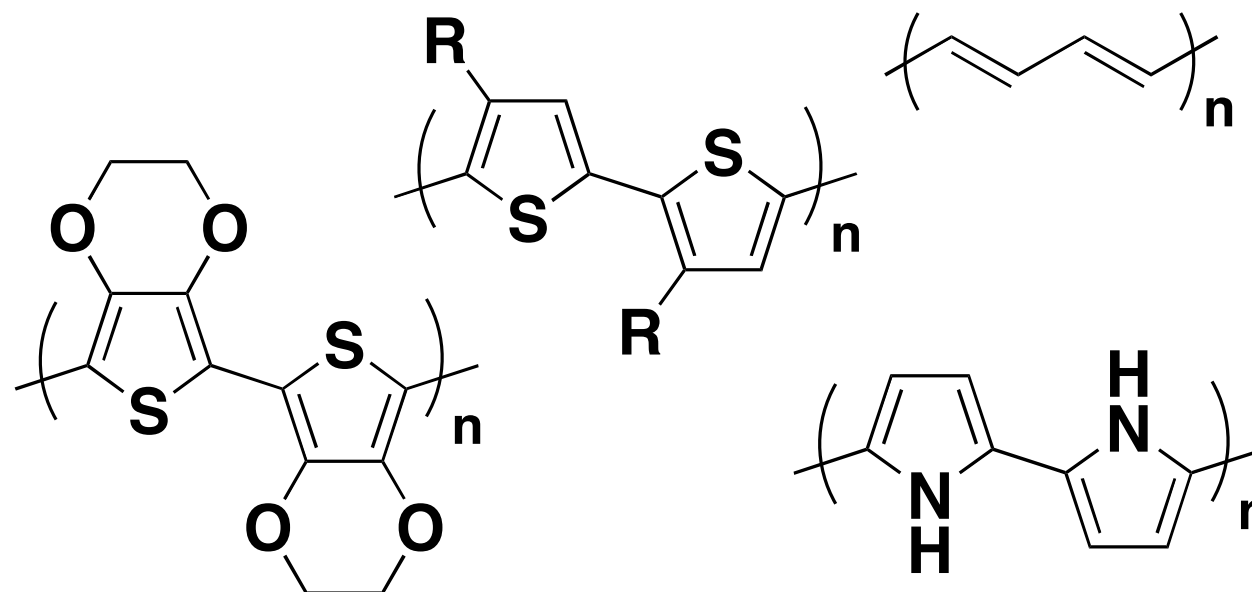
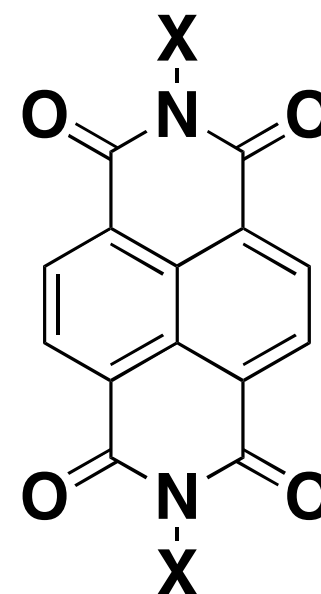
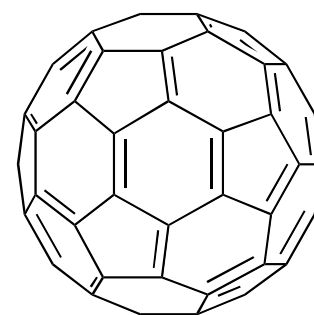
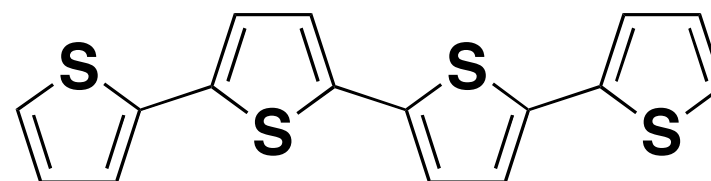
## Operation of an Organic Field-Effect Transistor



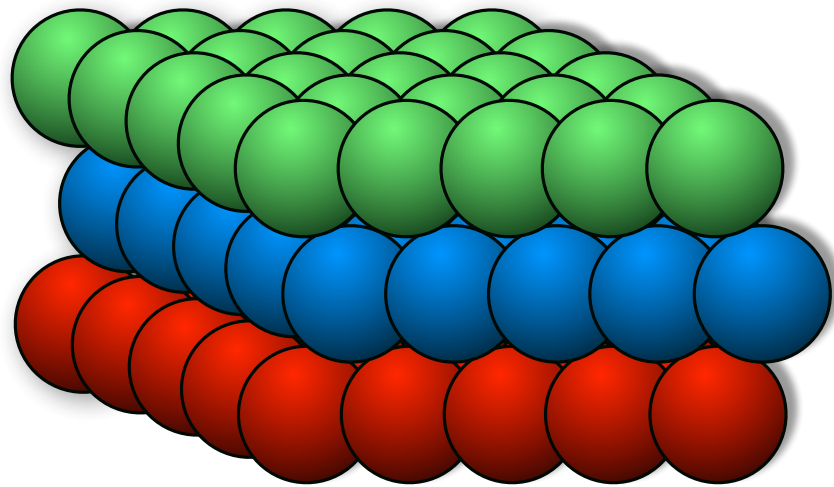
**Applied Gate Potential**



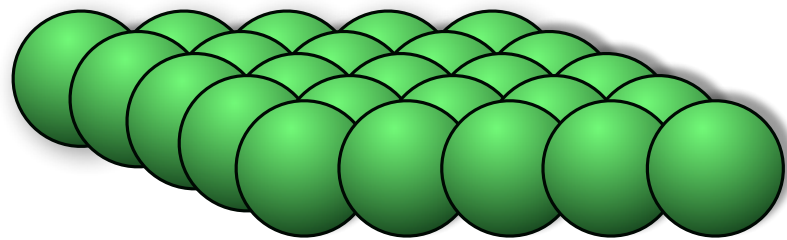
## Example Organic Semiconductor Materials



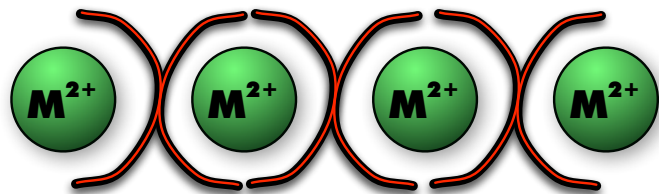
# Back to the Nanoscale...



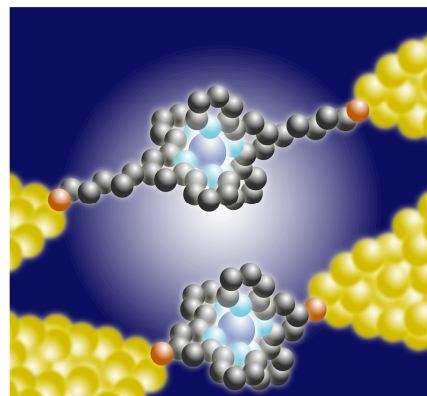
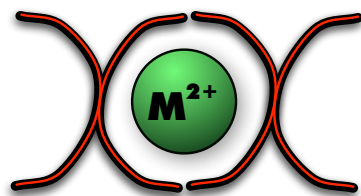
**3D: Bulk Films**



**2D: Monolayer**



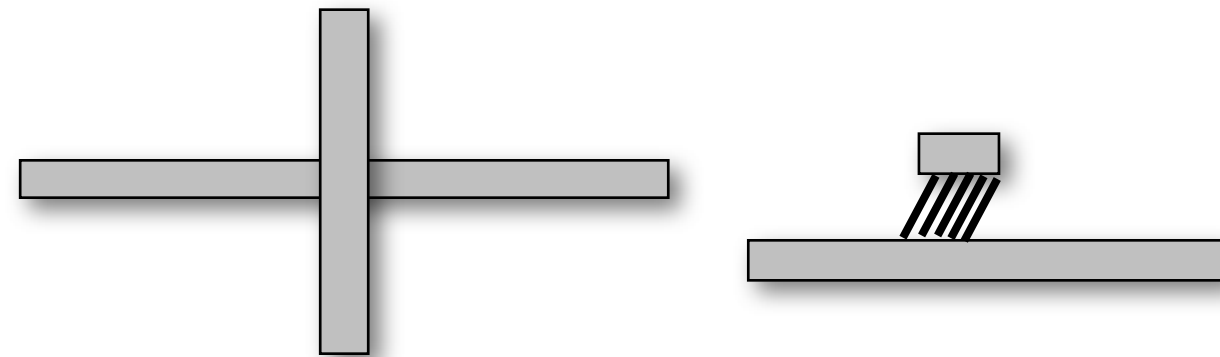
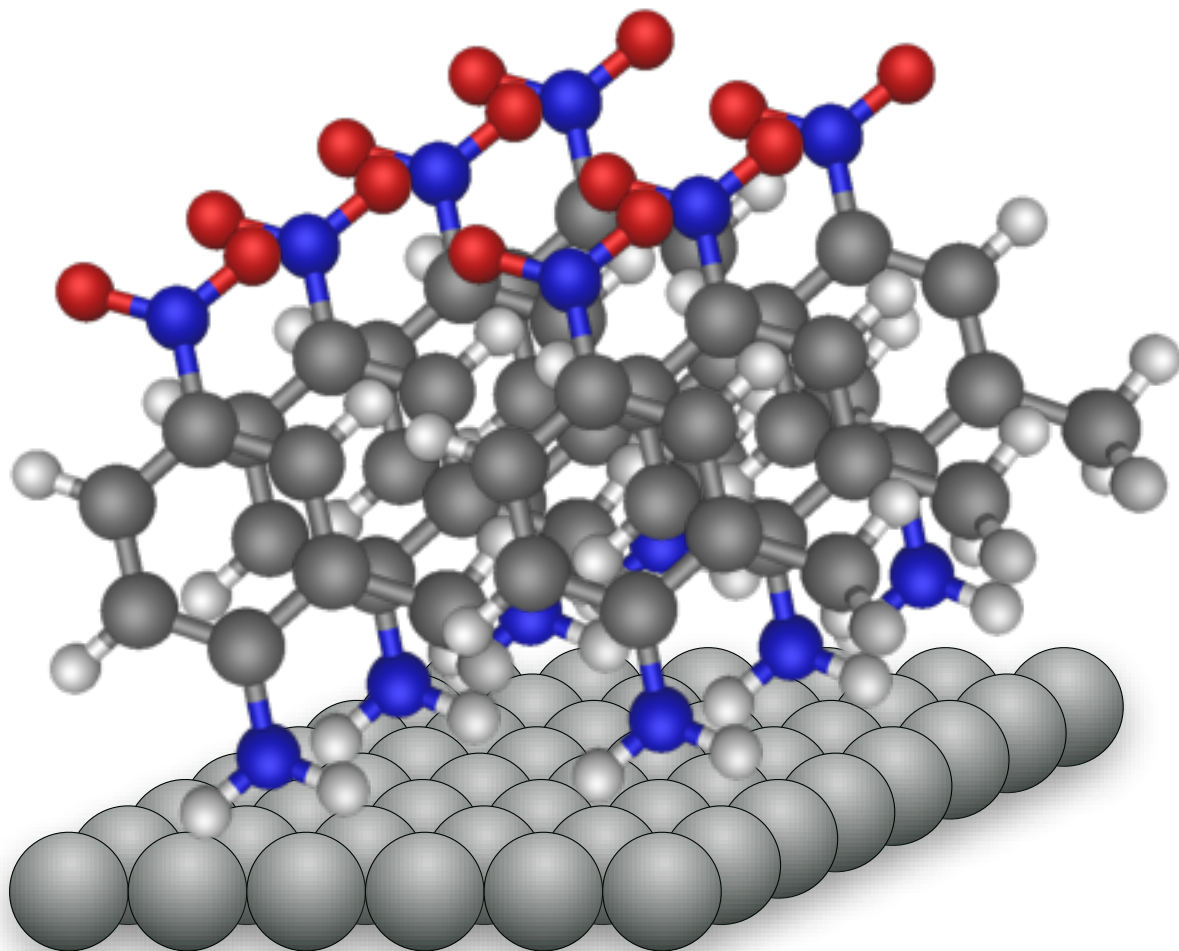
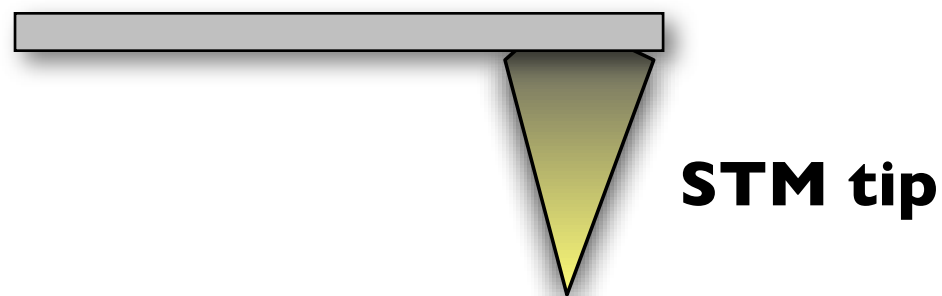
**1D: Chains**



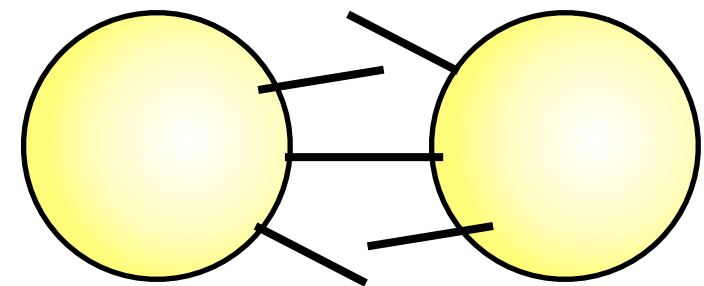
**0D: Individual Molecules**

# Enough Bulk Conductivity: How Do You Wire Up a Molecule?

**Many, Many Methods...**



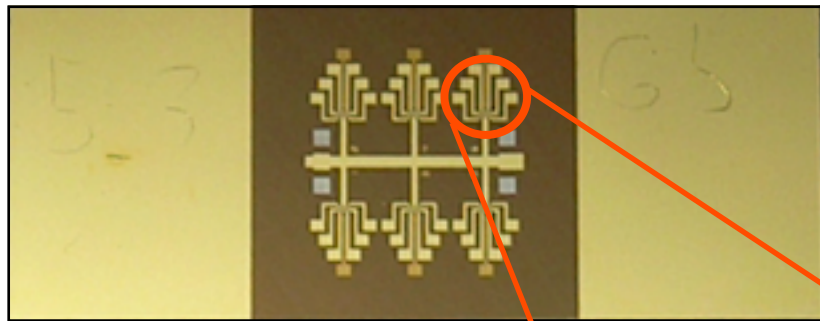
**Crossbars**



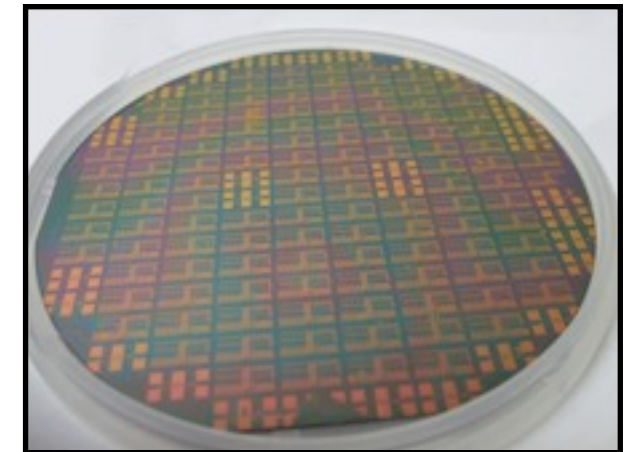
**Break Junctions**



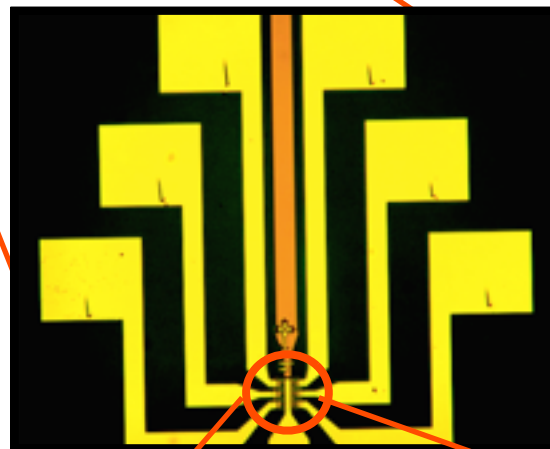
# Example: Device Fabrication



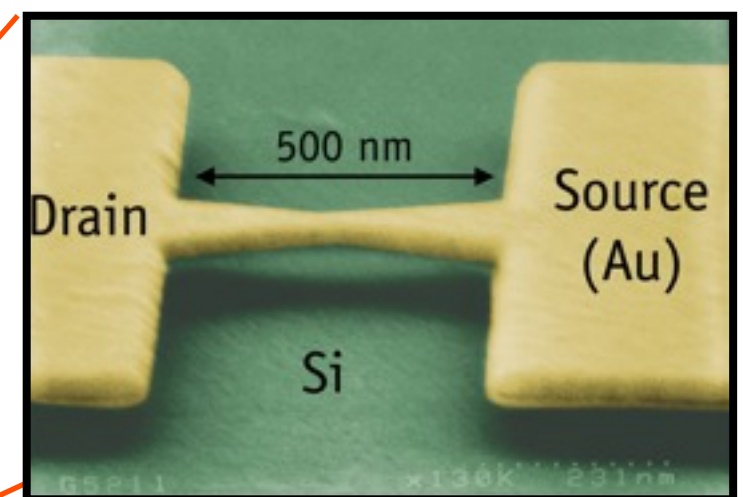
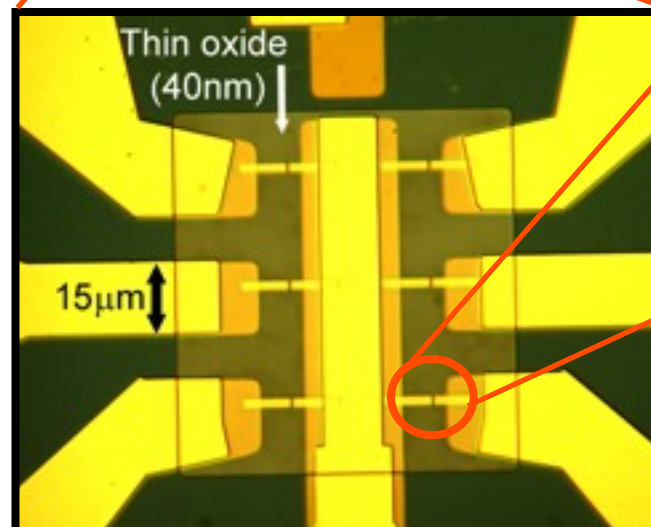
Sixty 15 mm x 6 mm chips are fabricated on a thin (200  $\mu\text{m}$ ) Si wafer.



Bonding pads are defined by photolithography.

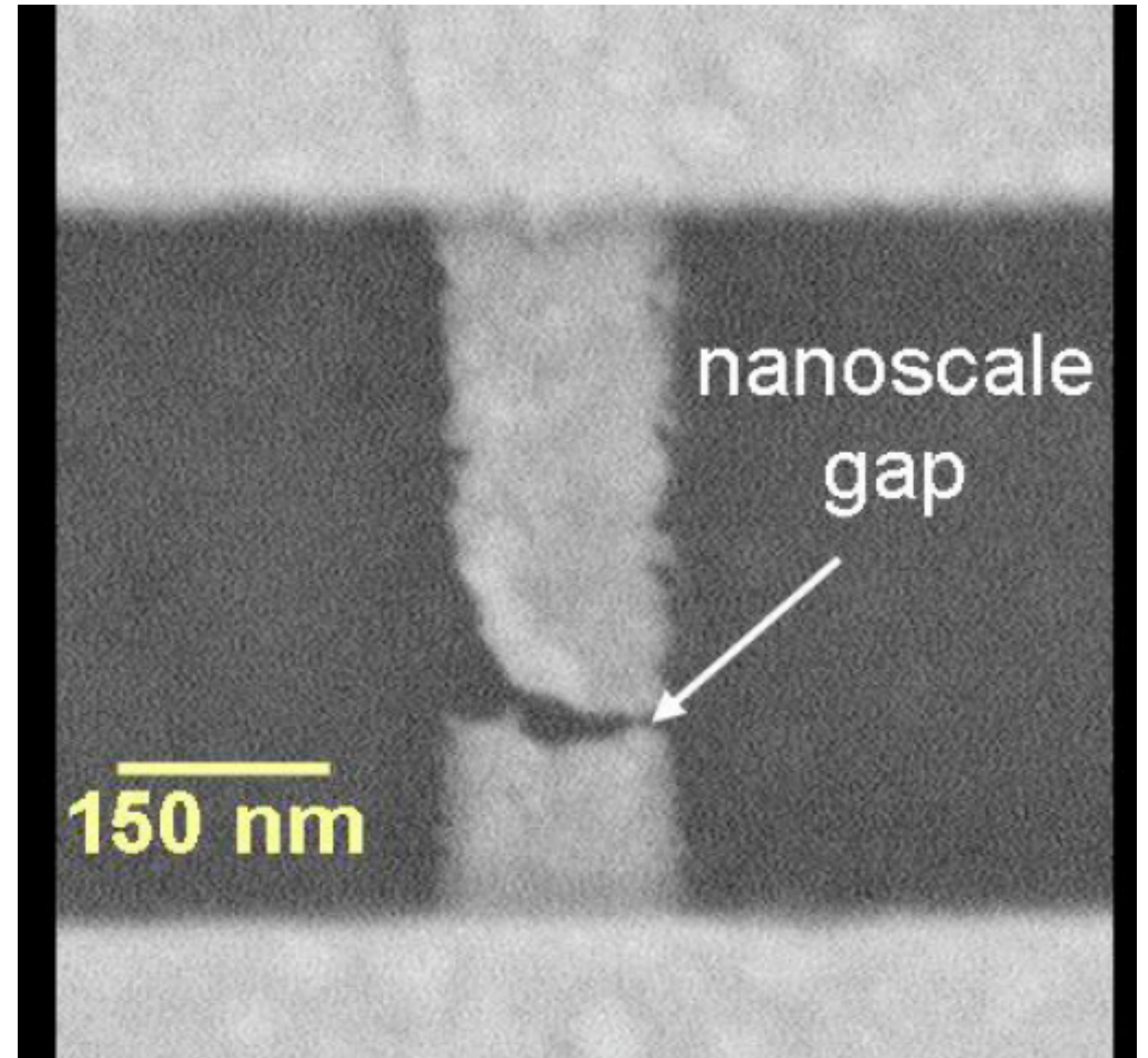
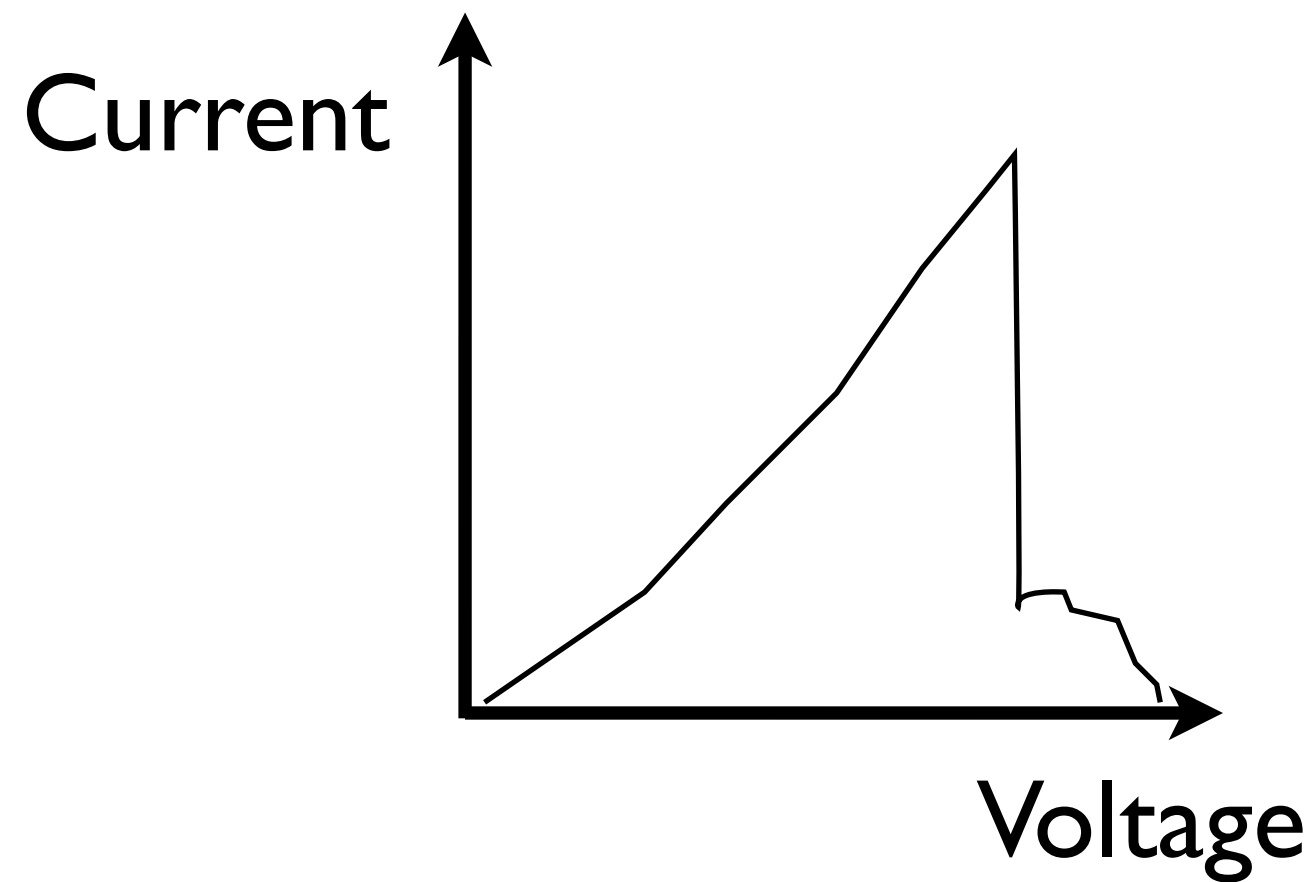


Critical features are defined by e-beam lithography.



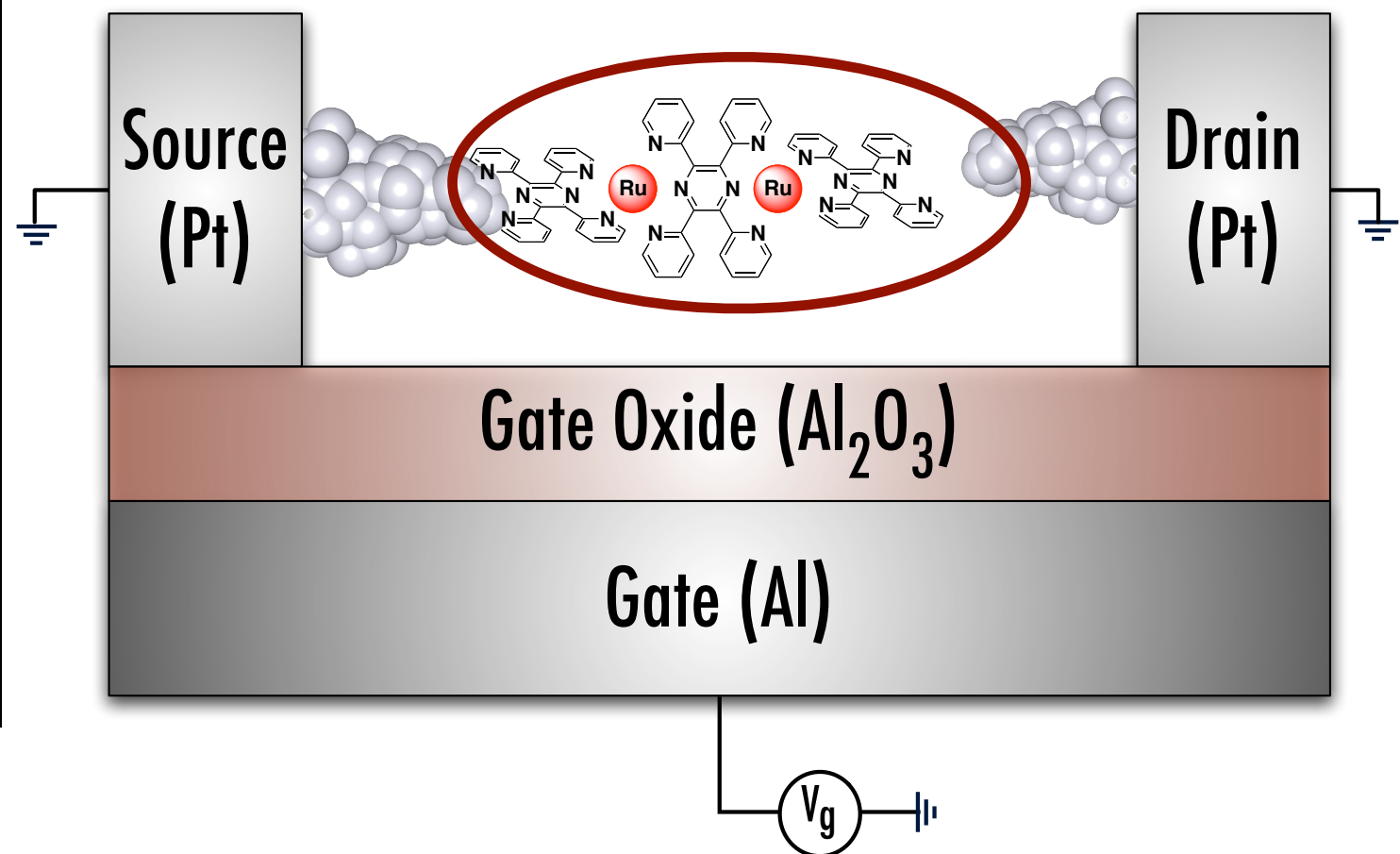
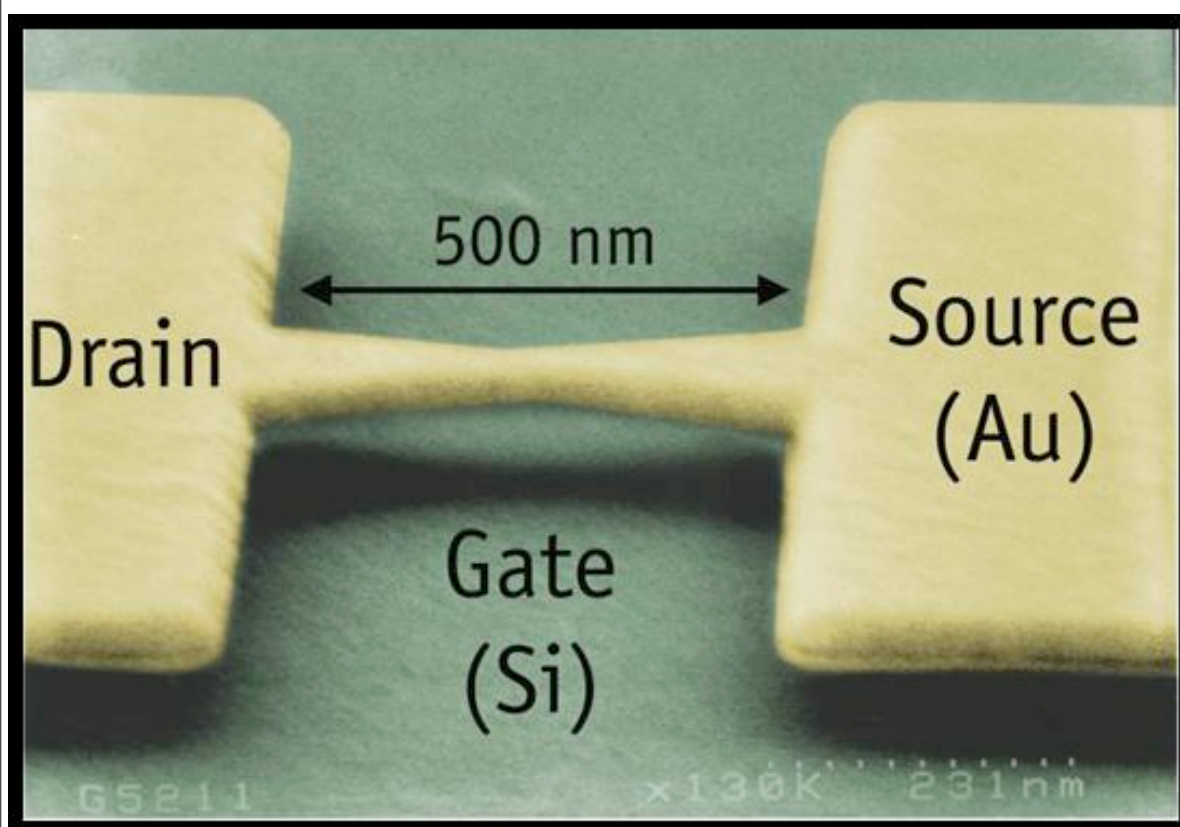
A timed etch is used to suspend the junctions.

# Electromigration: Making a 1-3nm Gap



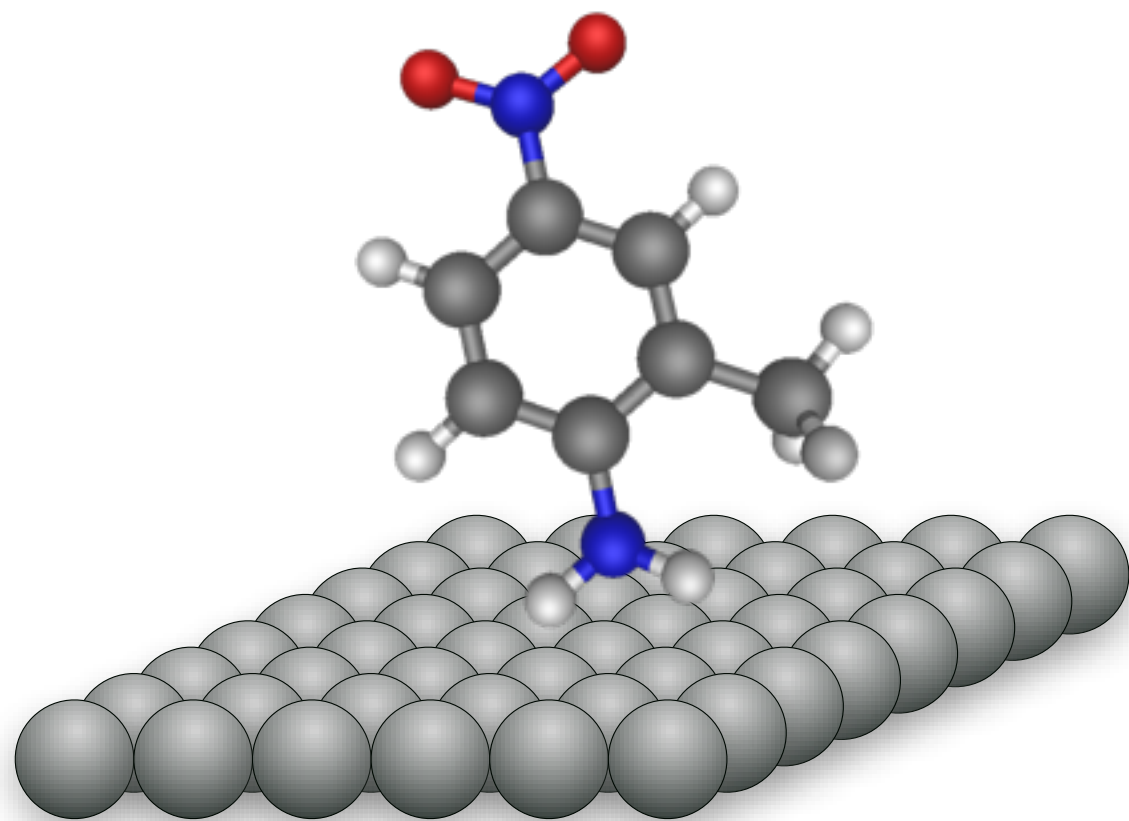
# Single Molecule Transistors

**Note: No Guarantee of 2 Connections**

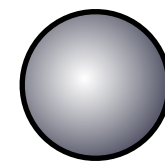




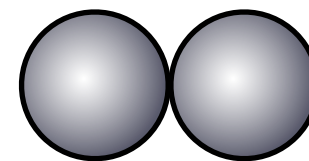
# Metal / Molecule Interface



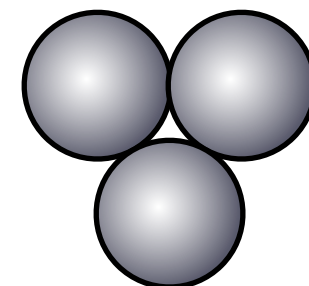
## Coordination



One-Site



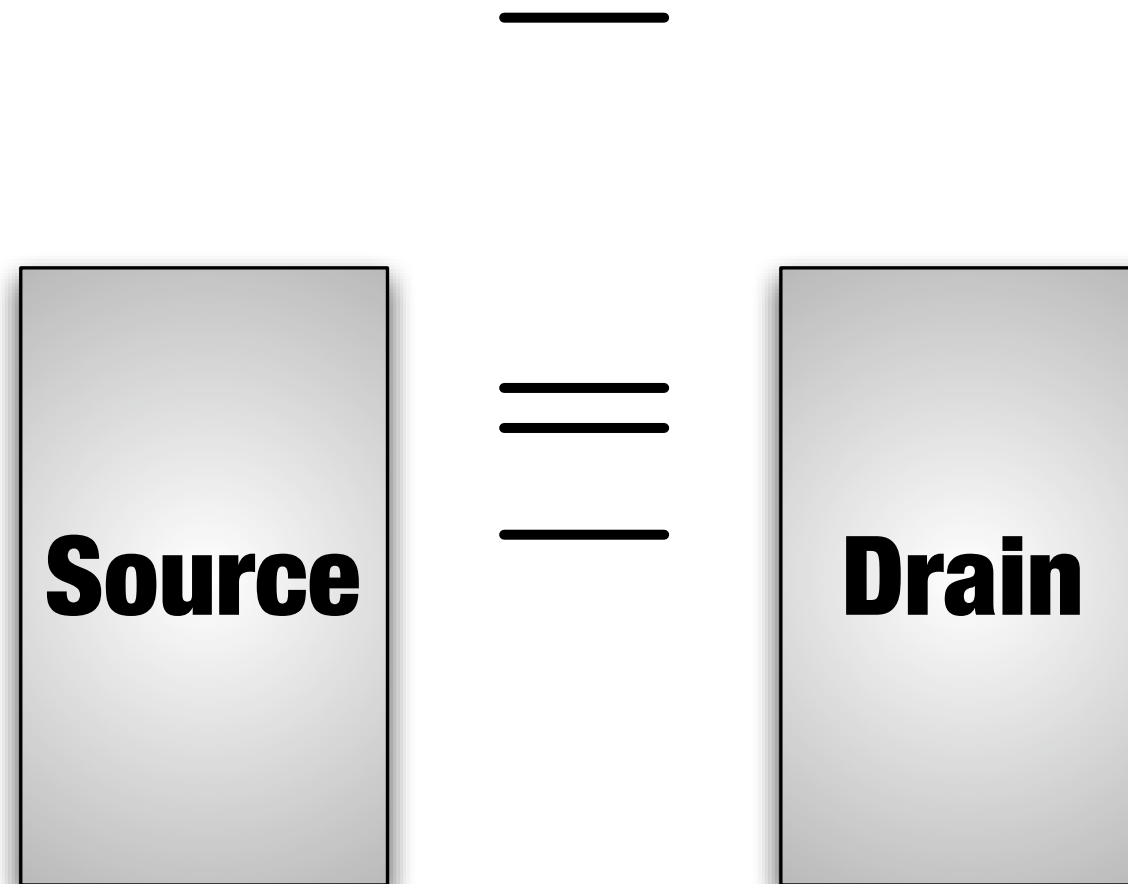
“Bridging”



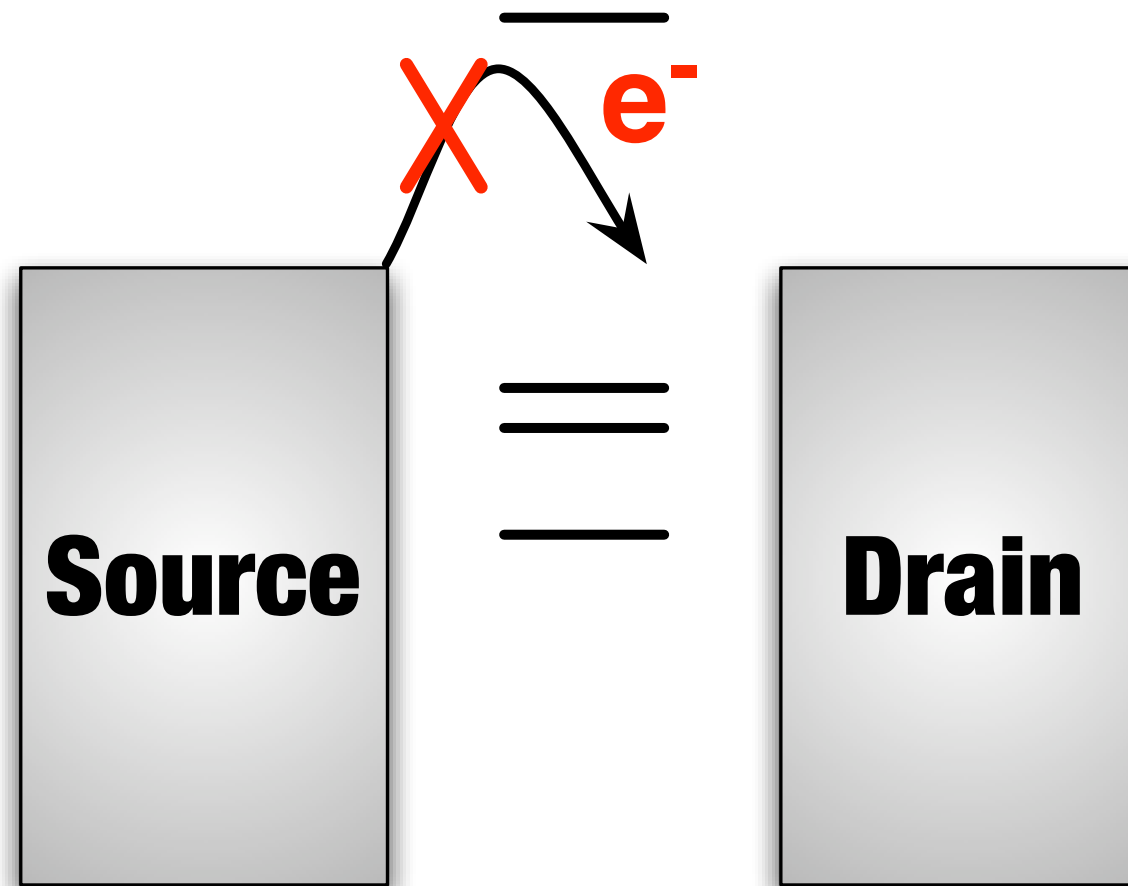
Three-Site

**WARNING: PowerPoint Science!**

# “Coulomb Blockade”

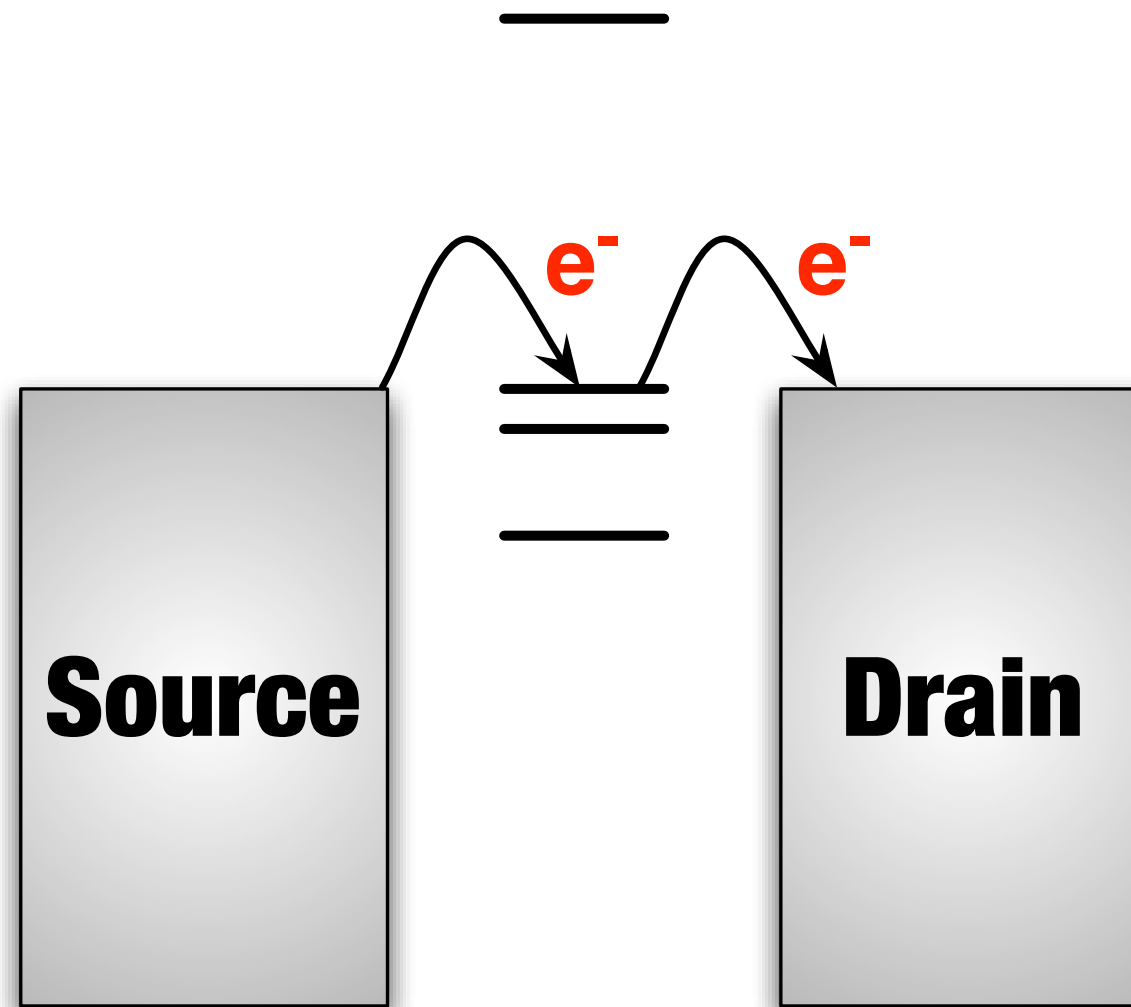


# “Coulomb Blockade”

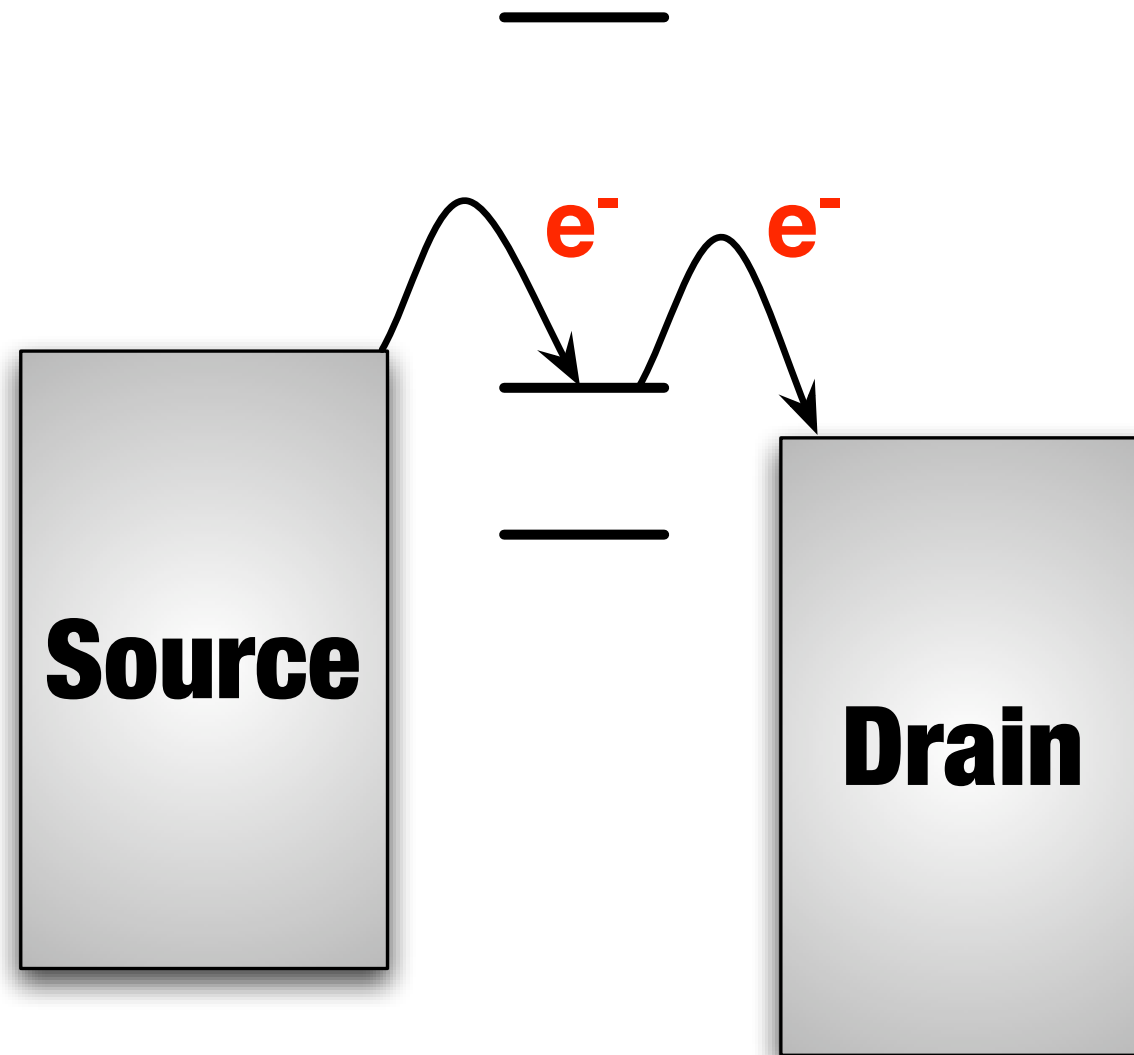




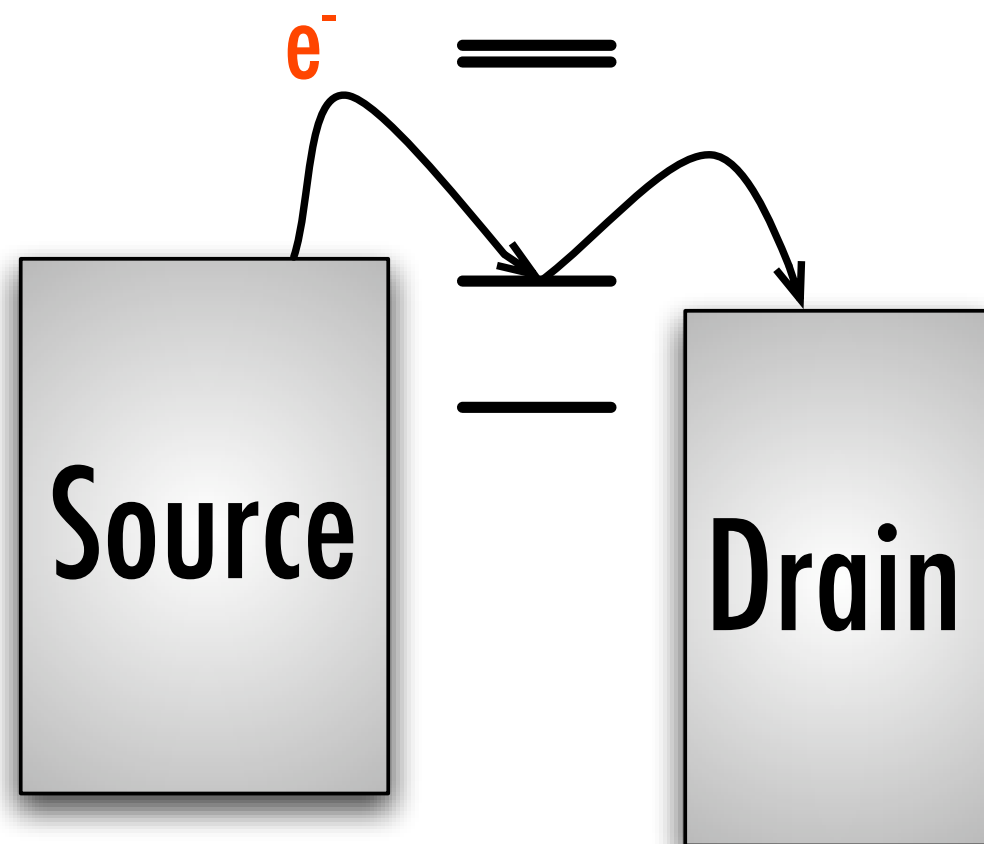
# “Coulomb Blockade”



# “Coulomb Blockade”

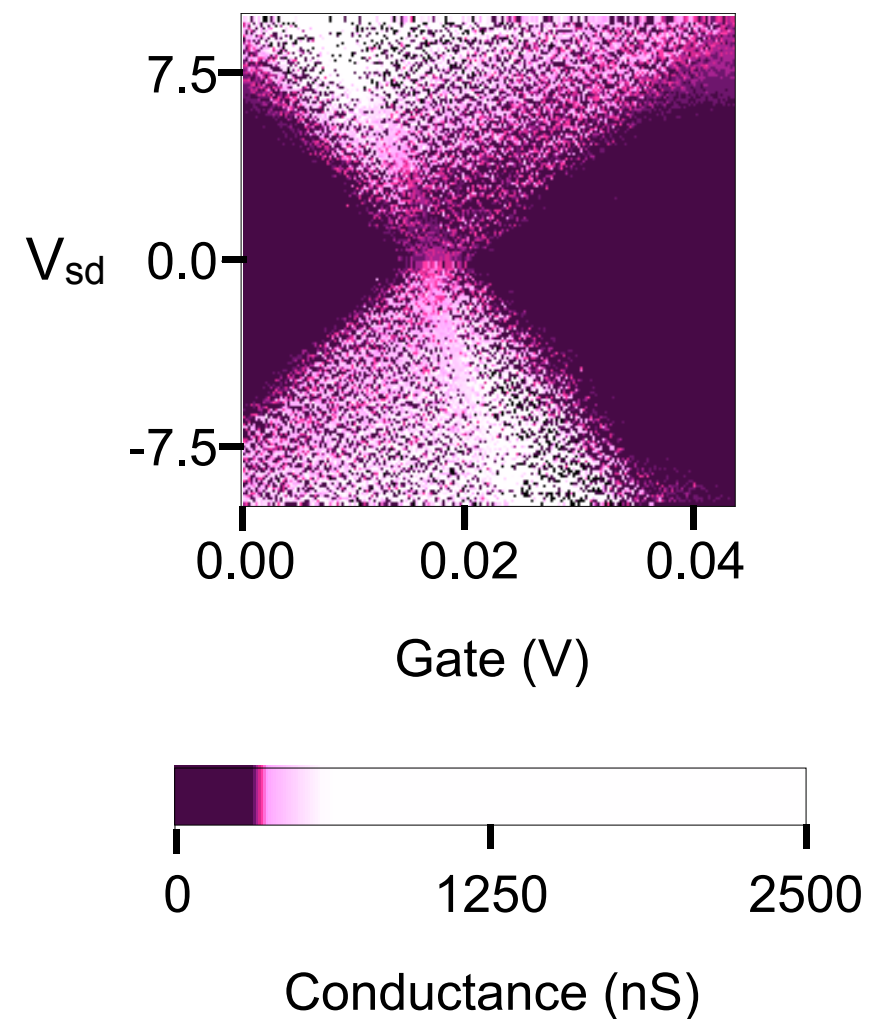


# Coulomb Blockade in $[\text{Ru}_2(\text{tppz})_3]^{+4}$



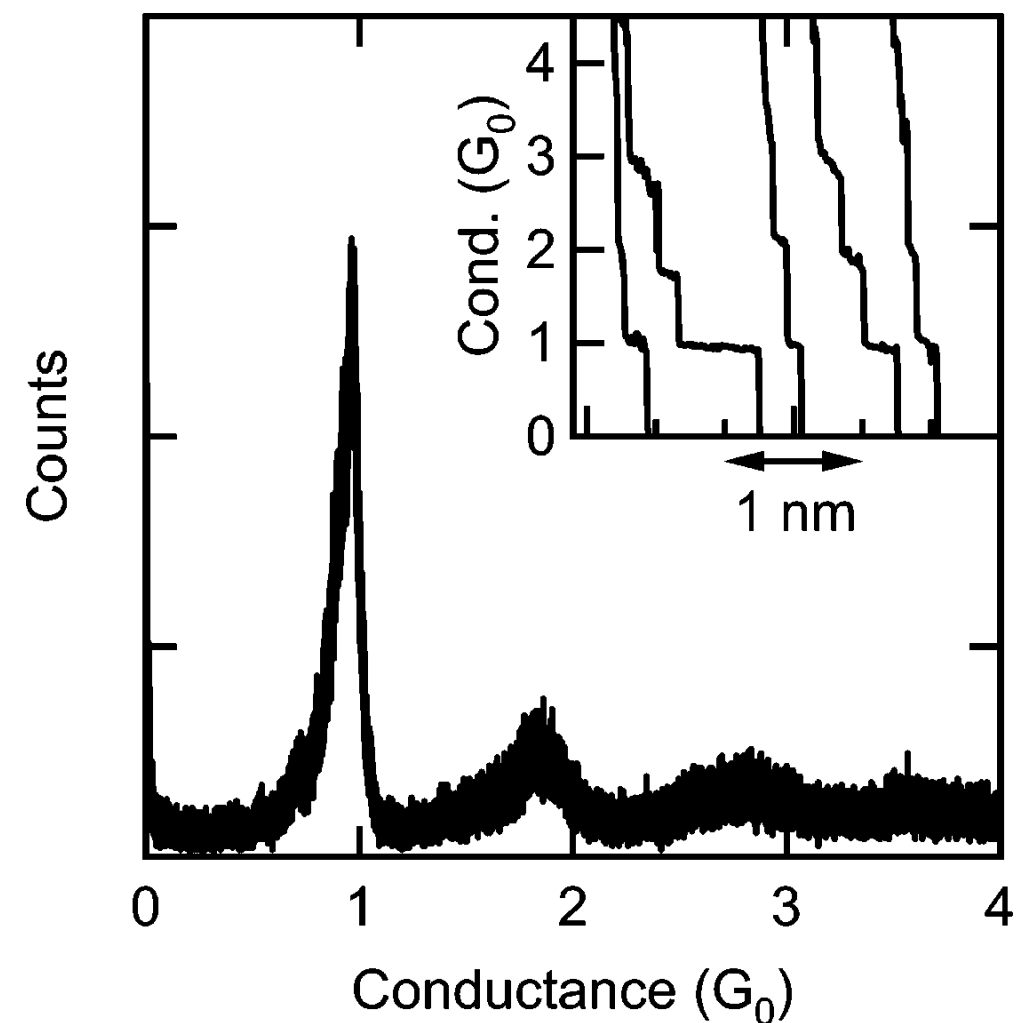
Charge passes when source, drain  
and molecule bridge electronic  
states are aligned

## 4K Temp. Single-Molecule Coulomb Blockade Transistor



# Is it Really Single-Molecule?

- You must do statistics....
- You must do statistics...
- Careful controls (“no molecules”)
- Dilution Experiments





# Is it Really A Molecule?

- Is it a nanoparticle?
- What are molecular “signatures?”
- What are control experiments?
- What are our statistics?

**WARNING: Be Skeptical!**  
**We can do theory...**  
**But what's the real experiment?**

# Prospectus

- Statistics, Statistics, Statistics!
- Charge Transport Mechanisms
- More Charge Transport
- Ensembles & Dynamics
- Solar Energy:  
Where things get (more?) complicated