

Simulations of nanomaterials

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- I. Introduction to nanoscience and nanotechnology**
- II. Nanotubes – a nanoscale laboratory**
 - The strongest material known**
 - Quantum transport in nanodevices**
- III. Ferroelectric polymers**
- IV. Optical signatures of surface structures – helping Moore's law**
- V. The multiscale and time-evolution challenge**
- VI. Future outlook and summary**

Collaborators: C. Brabec, M. Buongiorno Nardelli, W. Lu, A. Maiti, V. Meunier, S. Nakhmanson, D. Orlikowski, C. Roland, W. G. Schmidt, S. Wang, Q. Zhao, B. Yakobson, S. Iijima

Introduction to nanoscience and nanotechnology

- **Richard Feynman, ~ 1959 “There’s plenty of room at the bottom”**
 - Nanoscience will not teach fundamental physics (no new particles or interactions)
 - More like solid state physics – strange phenomena in complex situations
 - Would have an **enormous number of technical applications**
- **Some of Feynman’s examples**
 - A speck of dust can store all books in the world – (125 atoms/bit)
 - **DNA** uses 50 atoms per bit
 - **Small memories** could be write once – negligible waste of material
 - A **wire** should be 10-100 atoms in diameter
 - **Computers** with billions of connections could **“think”**
 - **Power consumption** in a nano computer would be negligible, speed would be much higher
 - Weight and inertia will be negligible, relative strength will be much greater
 - **Nano magnets** will be single domain
 - Effective viscosity would be higher, but lubricant may not be needed due to rapid cooling.
 - **Resistance on small scale** will be different (he did not see ballistic conduction)

Intro to nanoscience and nanotechnology, cont...

- **Some of Feynman's applications**
 - Automated factory making very small **computers**
 - A million of machines $1/4000$ of the original size will need only 2% of original weight
 - **New materials** designed with atomic level control
 - **Nano machines** in blood stream doing surgery
 - **Bio-inspired** chemical **machinery**
 - High intensity light beams from **nano antenna arrays**

Experiments were too hard to realize Feynman's vision!

Current status of nanoscience

- **Recent experimental breakthroughs (MBE, STM, CBE, AFM, self-assembly, etc) enable nano science and technology**

- **Nanoscale experiments open new exciting avenues, but are v. difficult: results are hard to achieve and reproduce**

Theory and simulations can help

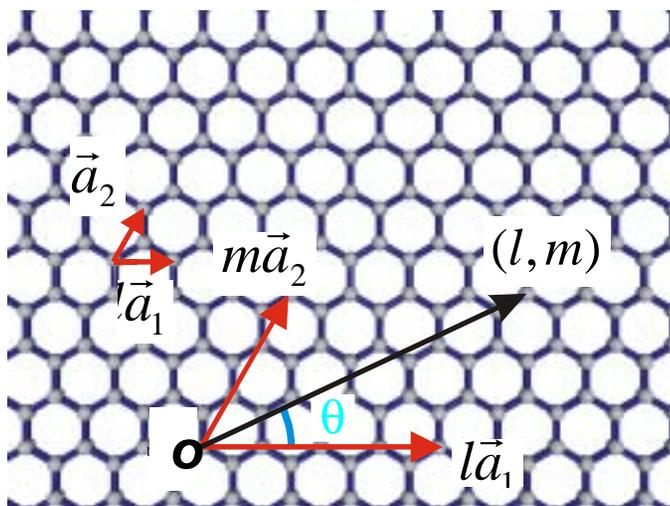
- **Role of theory and simulations**

explain experimentally observed phenomena

predict properties of nanomaterials

help in designing *new* or *artificially-structured* materials

Introduction to nanotubes



	Properties	(l, m) relation
Geometric	radius	$R = \frac{\sqrt{3}d\sqrt{l^2 + m^2 + lm}}{2\pi}$
	chiral angle	$\theta = \arcsin \frac{\sqrt{3}m}{3\sqrt{l^2 + m^2 + lm}}$
Electronic	metal	$\text{mod}(l - m) = 3$
	semi-conductor	$\text{mod}(l - m) \neq 3$



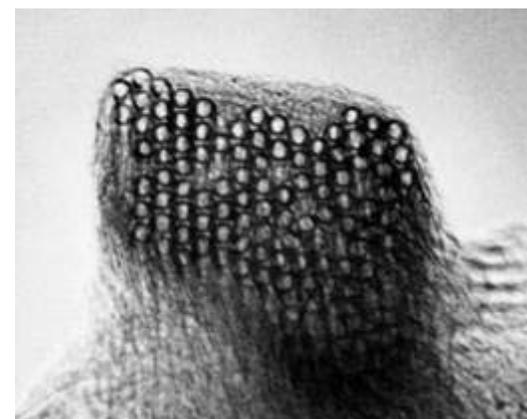
(12,0)
zigzag



(6,6)
armchair



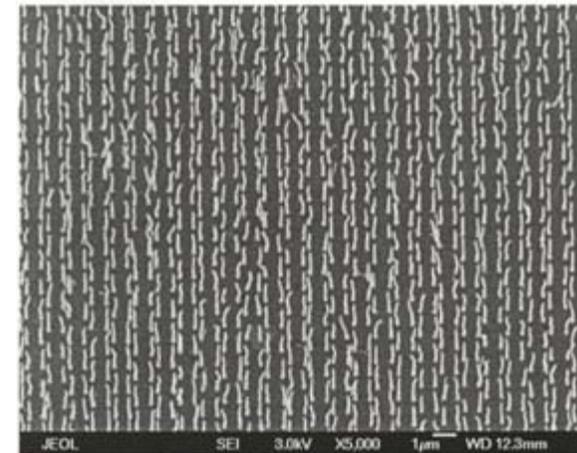
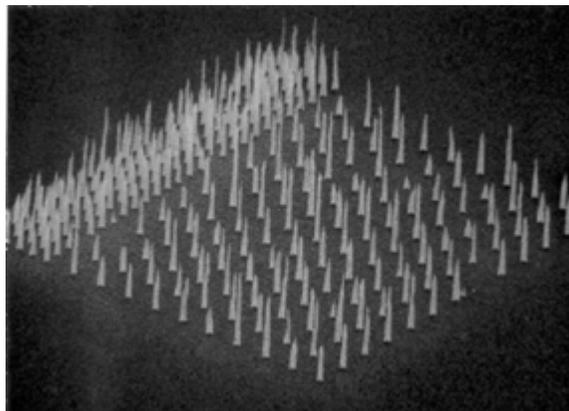
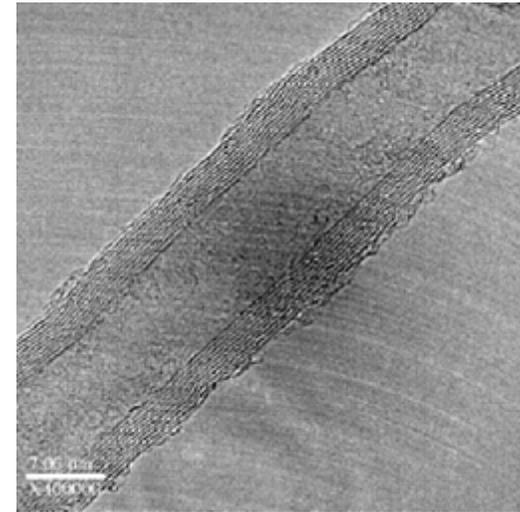
(6,4)
chiral



nanotube "rope"

Commercial sources

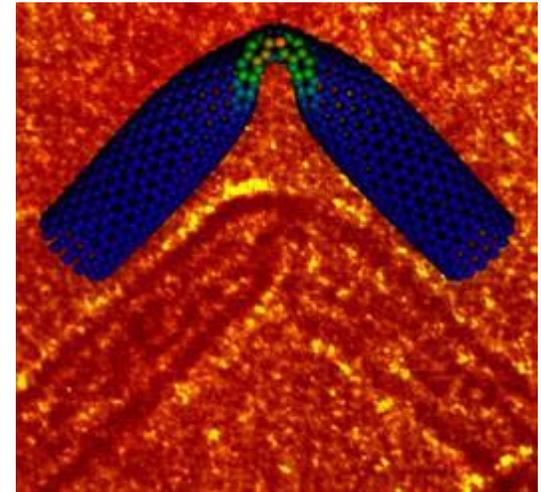
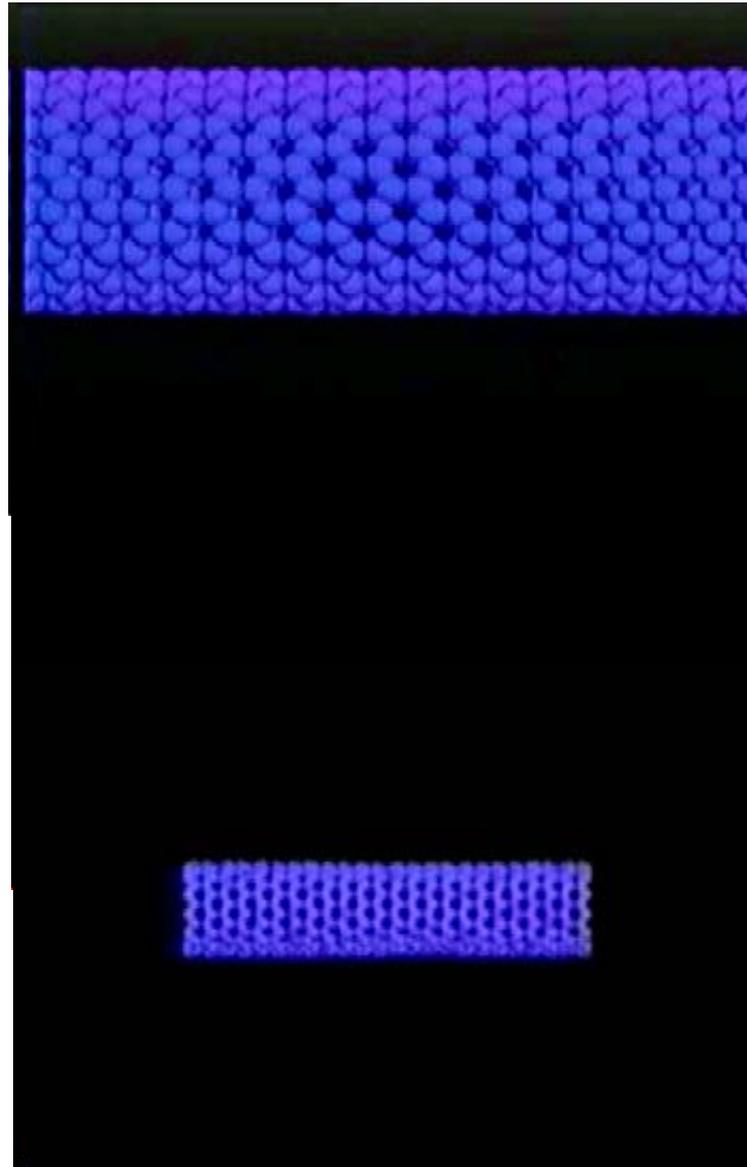
- 60\$-150\$/gram for SWNTs
- 100\$/gram for MWNTs
- >1000\$ for arrays or composites
 - <http://carbolex.com>
 - <http://www.flash.net/~buckyusa/>
 - <http://www.nano-lab.com/home.html>
 -many more...
 - promise of \$75/kg in 2004 (MWNT)



Elasticity and Breakage of Carbon Nanotubes

Bending

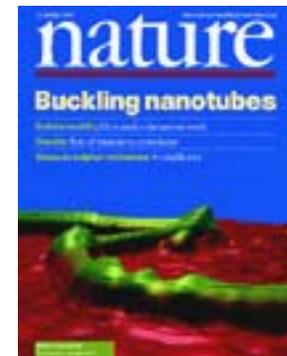
Iijima, Brabec,
Maiti, Bernholc
JCP 104, 2089 (1996)



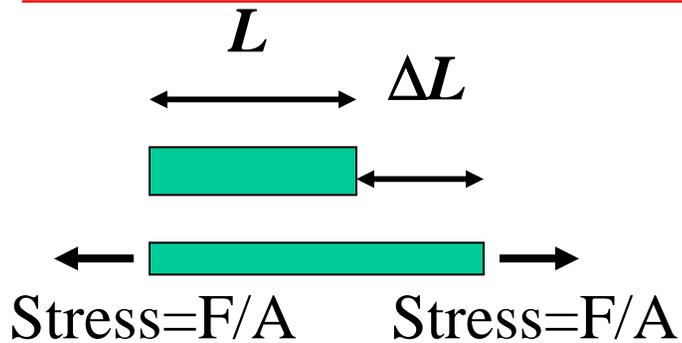
Compression

Yakobson, Brabec, Bernholc
PRL 76, 2511 (1996)

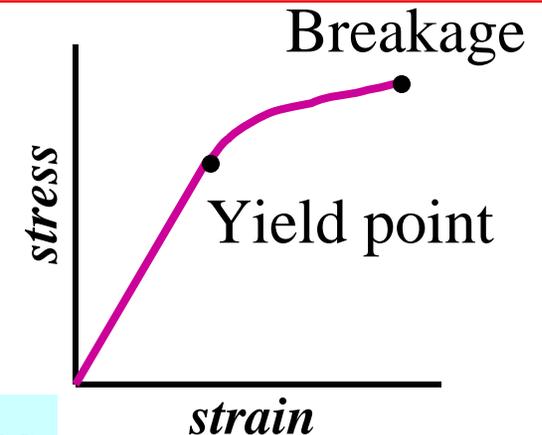
Tension



Introduction to strength of materials



$$\frac{F}{A} = Y \frac{\Delta L}{L}$$



Young's modulus determines stiffness

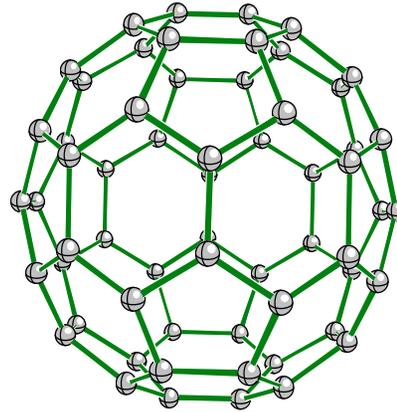
Material	Y [GPa]	Yield point [GPa]	Max $\Delta L/L$ [%]
Graphite	1080	31.3	2.9
Steel	220	4.2	1.9
Glass	168	3.6	2.2
Silicon	163	4.1	2.5

Most materials can be stretched by at most 3%.

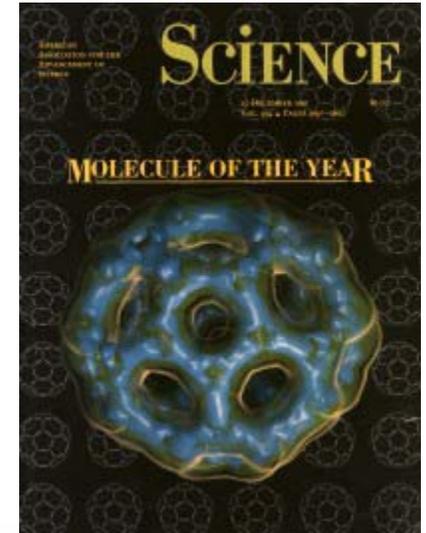
Early simulation of C₆₀ solid

solid C₆₀ geometry optimization
no symmetry constraints
fcc structure, a=14.2 Å (from exp.)

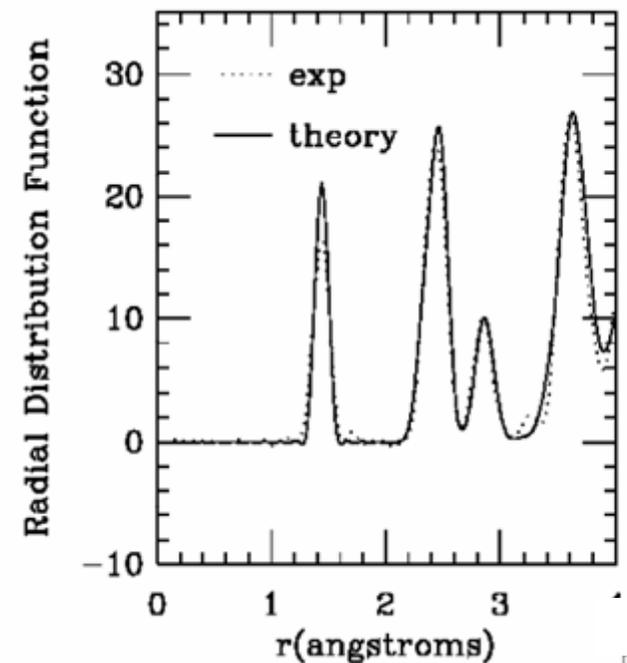
	C-C distance [Å]	
	Double	Single
CP (35 Ry)	1.40	1.45
CP (26 Ry)	1.41	1.45
exp (NMR)	1.40	1.45



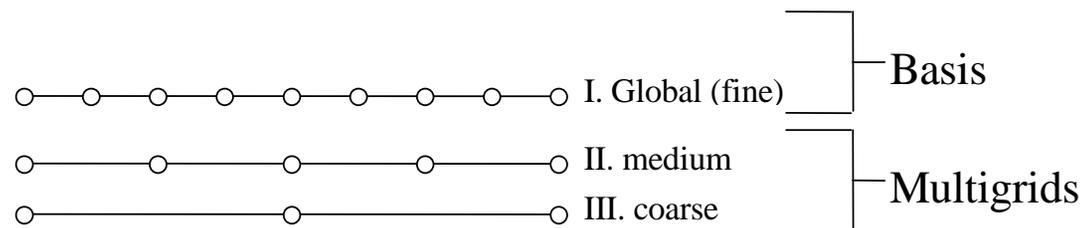
Zhang, Yi,
Bernholc, PRL 91



excellent agreement with photoemission
(Weaver et al), EXAFS (Cox et al), NMR,
and also with subsequent neutron diffraction data
(Li, Lannin, et al)

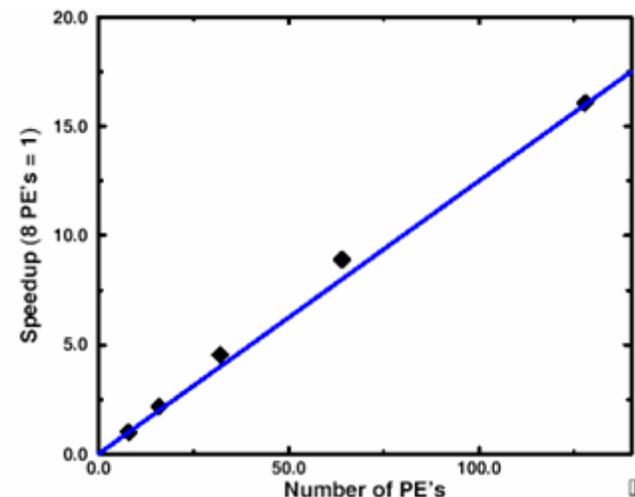


Multigrid method for quantum simulations



- Density functional equations solved directly on the grid
- Multigrid techniques remove instabilities by working on one length scale at a time
- Convergence acceleration and automatic preconditioning on all length scales
- Non-periodic boundary conditions are as easy as periodic
- Compact “Mehrstellen” discretization
- Allows for efficient massively parallel implementation

See *E. L. Briggs, D. J. Sullivan and J. Bernholc Phys. Rev. B 54, 14362 (96).*

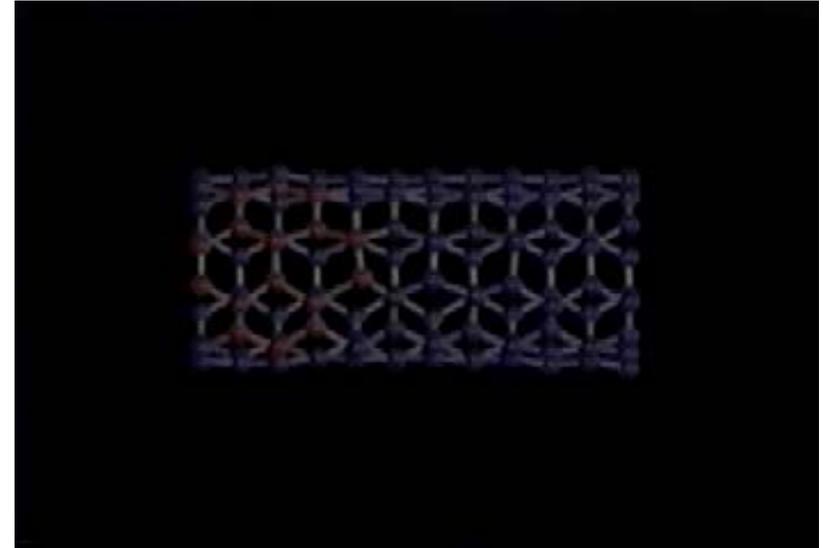
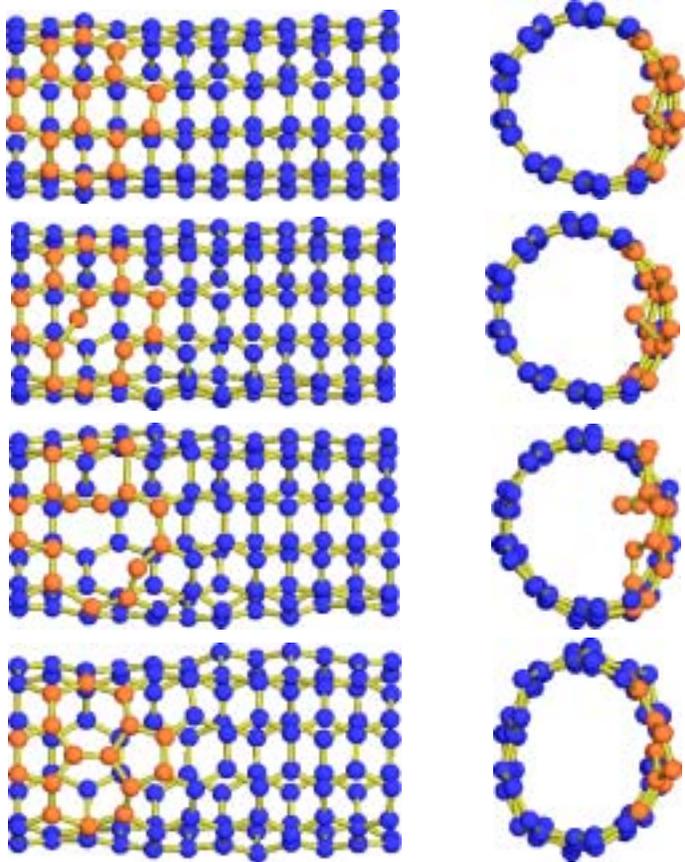


Speedup on Cray T3E with number of processors

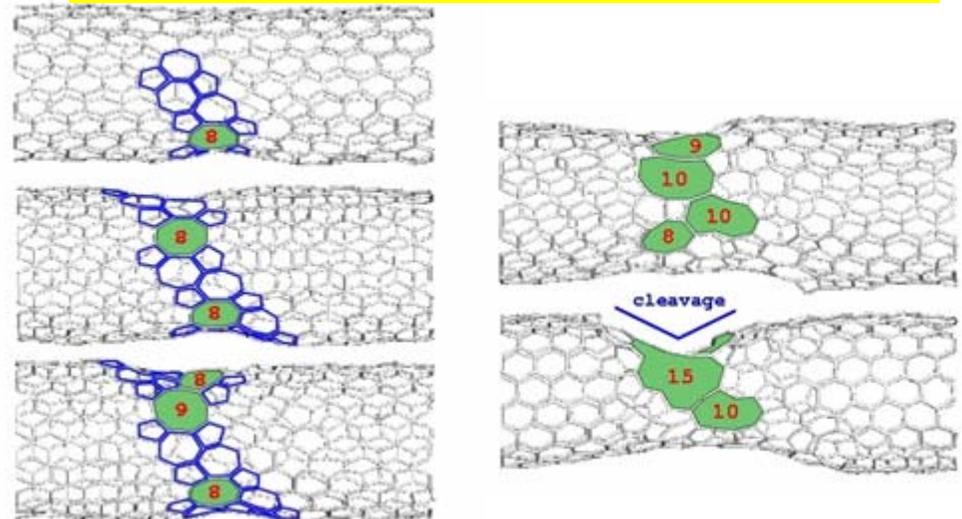
Runs also on IBM SP, Origin 2000 and Linux clusters

Breakage of nanotubes

Nanotubes break by first forming a bond rotation 5-7-7-5 defect.

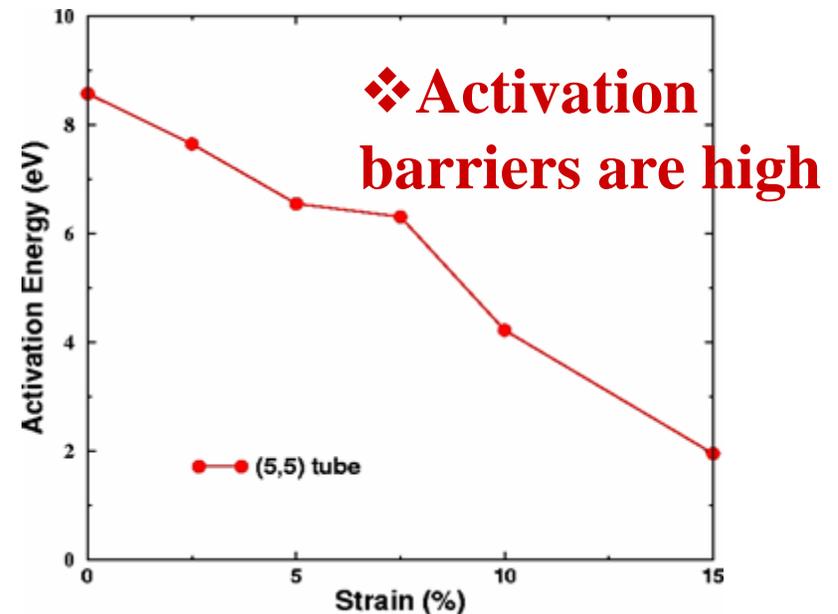
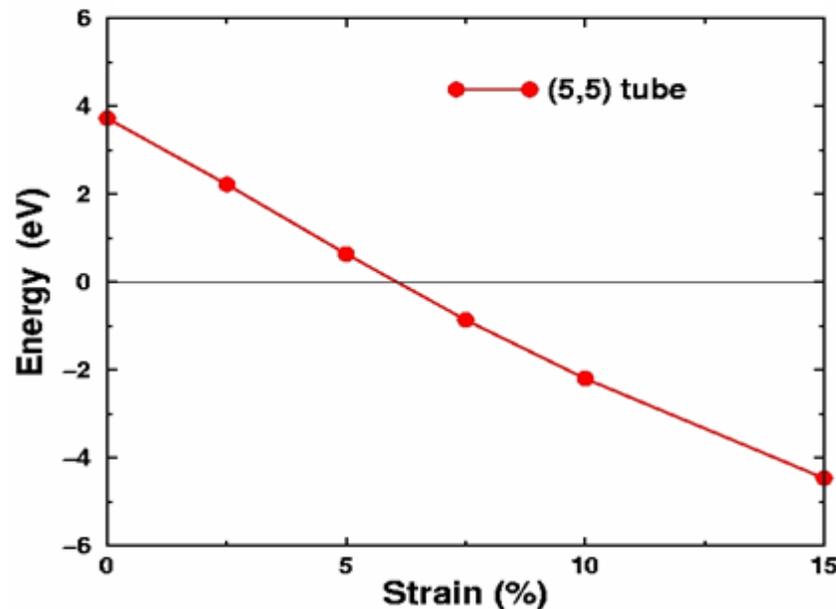


Additional bond rotations lead to larger defects and cleavage.



Buongiorno Nardelli, Yakobson, Bernholc
PRB 57, R4277 (1998).

Formation and activation energies of 5775 defect in (5,5) nanotube (*ab initio* results)

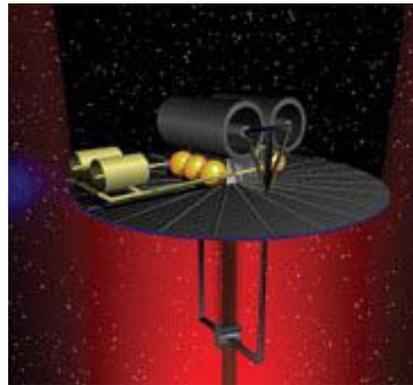


- ❖ Formation and activation energies decrease with strain
- ❖ 5775 defect is favored for strains above ~ 6%
- ❖ Experimentally, tubes break at around 5-6% strain (Walters, Smalley et al APL, 1999; Yu, Ruoff et al PRL, 2000)
- ❖ Nanotubes are kinetically stable up to ~ 17% at room T.
- ❖ The measured tubes likely contained defects.

Space elevator

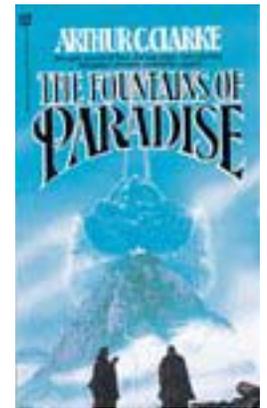


Oct 5, 2002



Eiffel tower to space
K. Tsiolkovsky, Russia (1895)

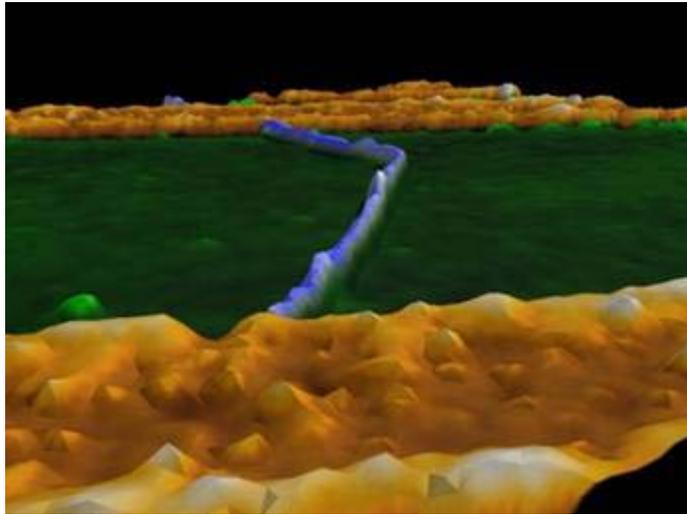
*If the laws of celestial mechanics make it possible for an object to stay fixed in the sky, might it not be possible to lower a cable down to the surface and so establish an elevator system linking earth to space? —Arthur C. Clarke, 1978, *The Fountains of Paradise**



Estimated cost \$7-10B (2000)

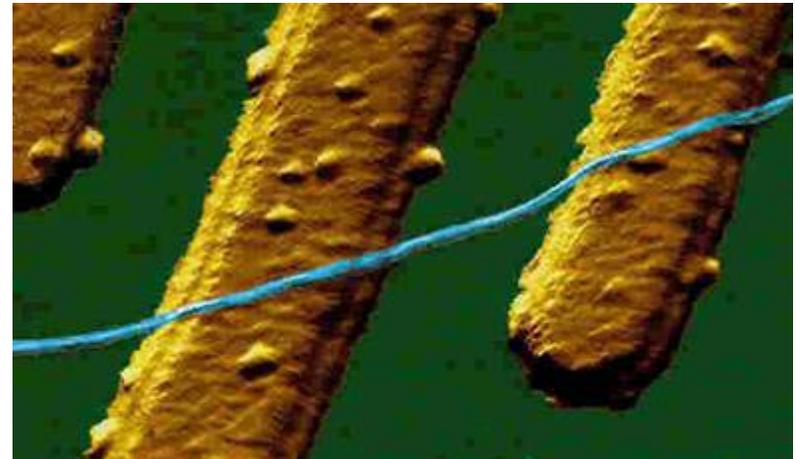
<http://www.highliftsystems.com/> Dr. Brad Edwards

Design of novel nanoscale electronic devices



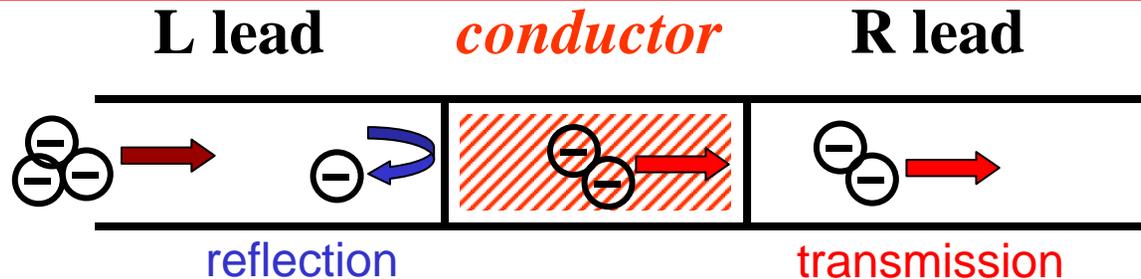
Manipulation and positioning of nanotubes as active circuit components leads to strong modifications of the physical properties of nanotubes

Strain, bending, substrate and doping will influence the electronic properties and tune the characteristics of the device

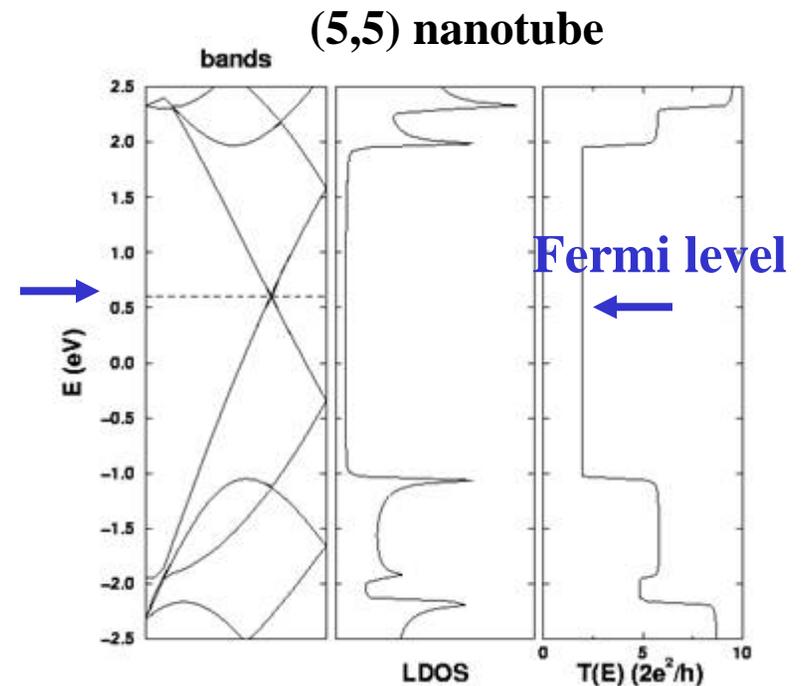


(C. Dekker, Delft)

Introduction to quantum conductance



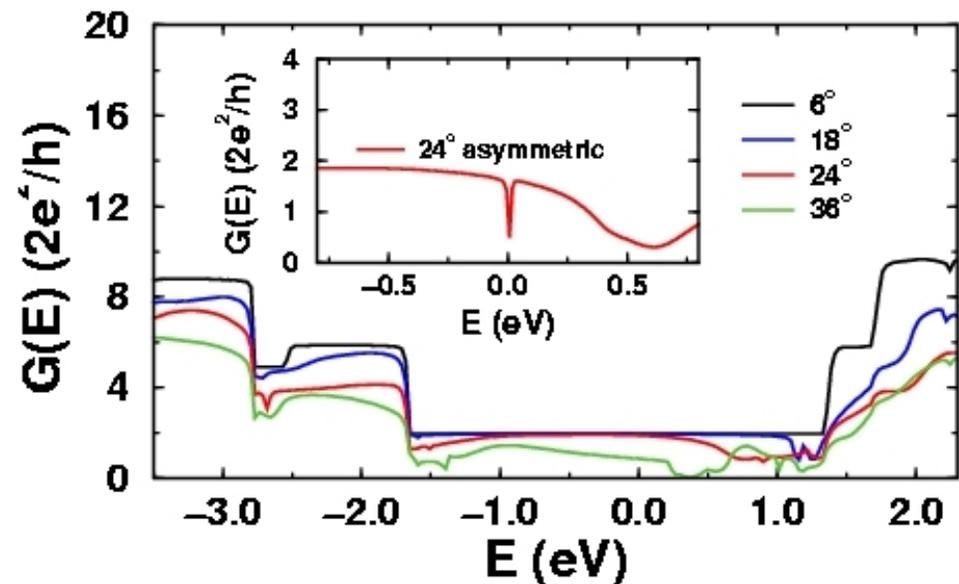
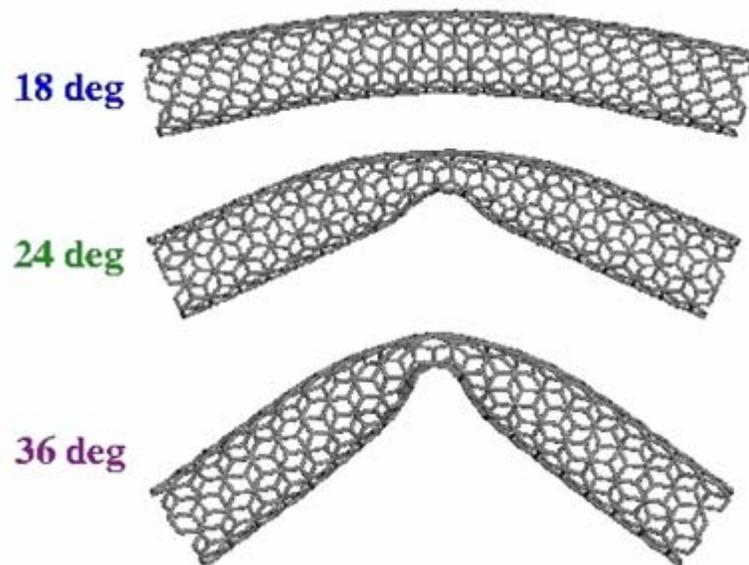
- In general, the quantum conductance measures the number of electron channels extending through the conductor *and* the leads, each contributing $2e^2/h$.
- For a perfect metallic nanotube and perfect contacts, both bands at the Fermi level contribute equally.
- For a disordered nanotube or for poor contacts, the conductance is much less.
- Conductances computed using a new, very efficient method (Buongiorno Nardelli PRB 1999; Buongiorno Nardelli and Bernholc, PRB RC 1999, Buongiorno Nardelli, Fattebert, Bernholc, PRB 2001)



Two bands cross at the Fermi level
 \Rightarrow Conductance $\equiv T(E_F) = 2$
Units of $2e^2/h \approx (12.9 \text{ k}\Omega)^{-1}$

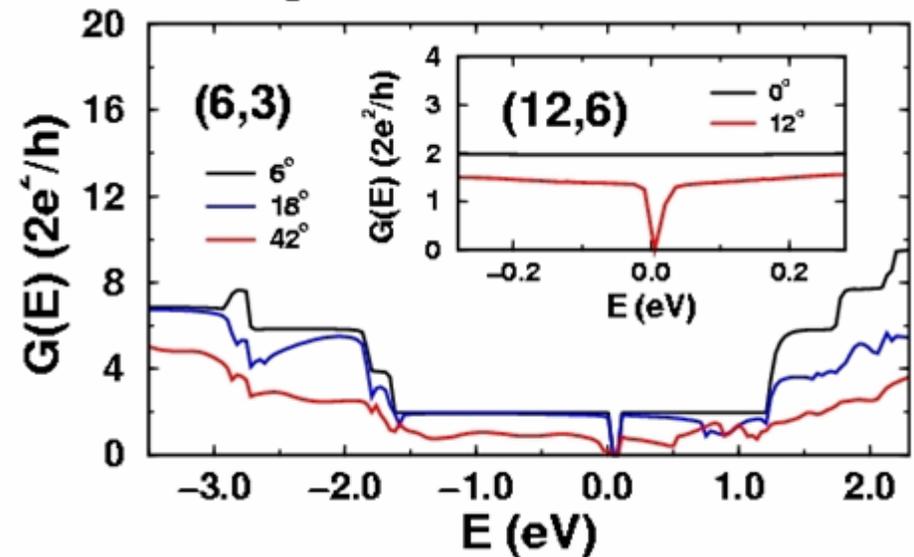
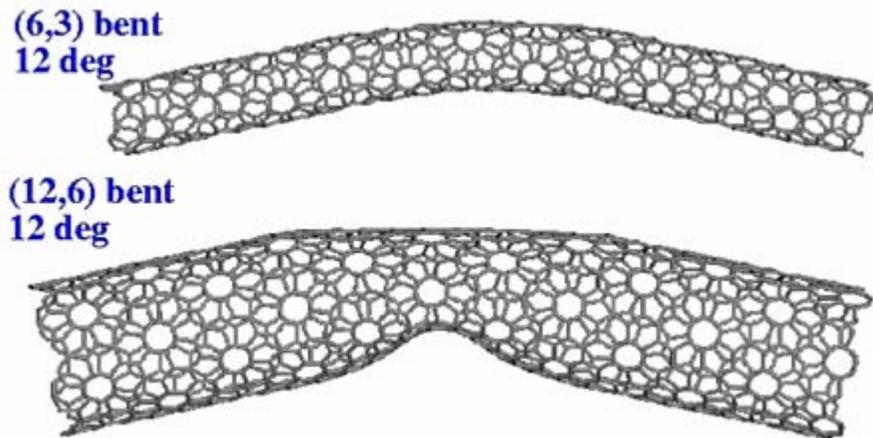
Conductance of bent armchair nanotubes

Armchair nanotubes remain conducting at fairly large bending angles (kinks). Only in very small diameter, asymmetrically bent nanotubes, a small pseudo-gap will occur.



Conductance of bent chiral nanotubes

Small diameter chiral tubes are small gap insulators. Large diameter ones are metallic when $n-m=3k$, but bending opens a sizable pseudo-gap. This may explain the results of experiments in Dekker's group, PRL 80, 4036 (1998).

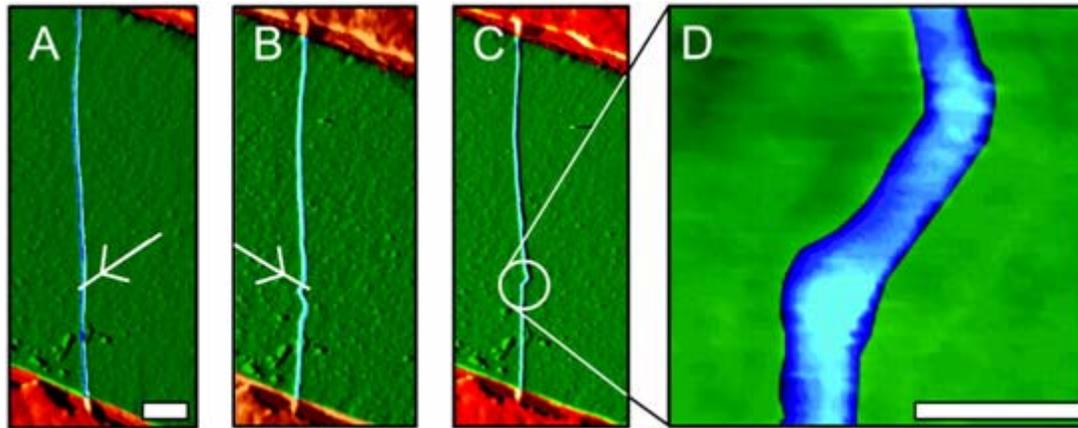


Applications

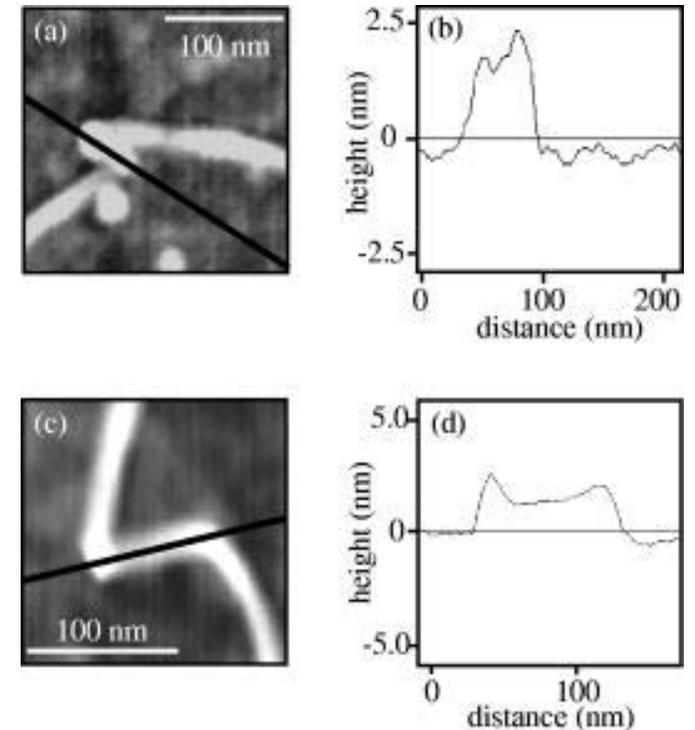
- * flexible ballistic conductors → armchair NT
- * nanostrain sensors → chiral metallic NT
- * high bending angles break conductance

M. Buongiorno Nardelli & J. Bernholc PRB 60, R 16 338 (1999), Postma et al, Science 2001

Single Electron Transistors and Dots From Kinks



Single electron quantum dot-based transistor operating at room temperature
Postma et al, Science 2001



Quantum dot up to 165 K
Bozovic et al, APL 2001

Carbon nanotubes as chemical sensors

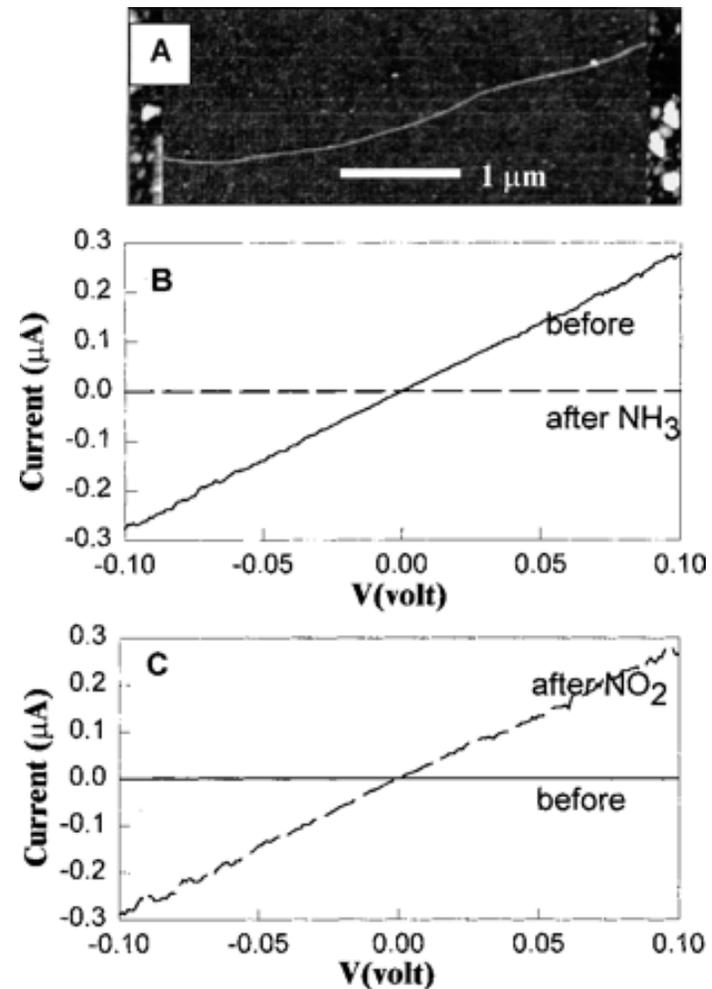
❖ Adsorption of chemical species on single wall nanotubes can induce changes in the electrical characteristics
(*Kong et al., Science 2000*)

Semiconducting SW-CNT before and after exposure to NO_2 and NH_3 :

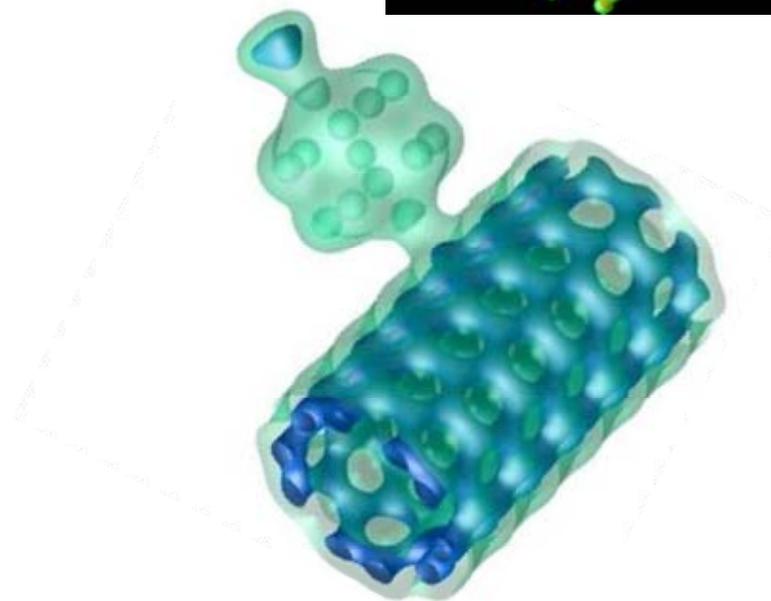
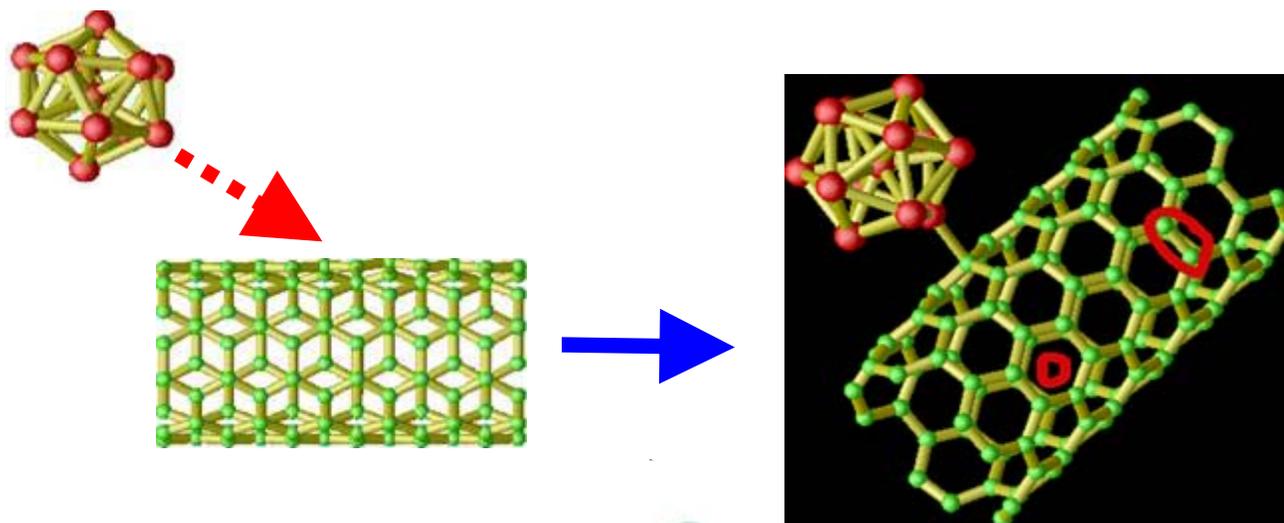
NO_2 binds to the SWNT

NH_3 does not bind directly:

- gating effect through substrate
- binding to adsorbed species



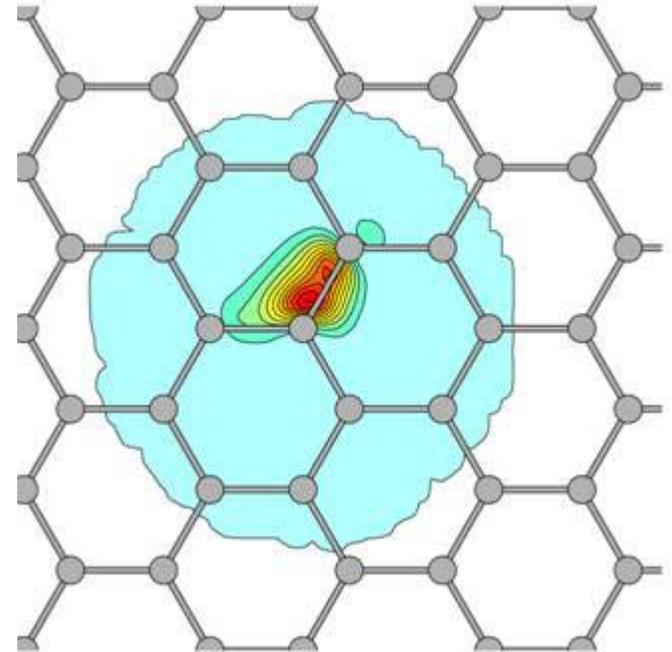
Nanotube/metal-cluster sensors



$\text{NH}_3 + \text{Al}_{13} + \text{nanotube}$

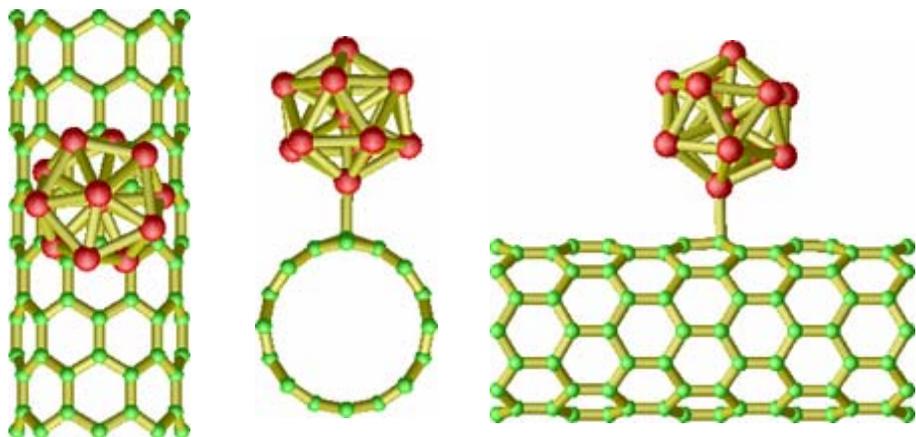
Ab initio $O(N)$ -like quantum transport calculations

- Expansion of the DFT total energy in *localized*, variationally optimized orbitals - – very few orbitals needed, e.g., 3-4 orbitals per carbon atom
- Same computational cost as in tight-binding models for computing conductances
- All operations performed on real-space grid with multigrid acceleration – fast convergence rate
- Main parts scale linearly with the number of atoms
- Unoccupied orbitals are essential (small $O(N^3)$ part)
- Fully parallel on Cray T3E, tested on > 1000 atoms
 - New code for IBM SP, Beowulf
- Forces, geometry optimization
 - Shape of an optimized orbital: valence bond function
 - Slice through a plane tangent to carbon nanotube, $R_c = 6$ a.u.

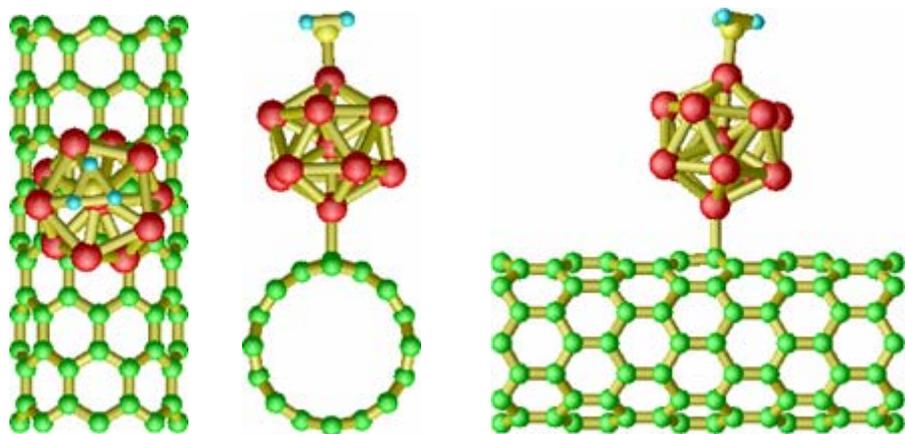


J.-L. Fattebert and J. Bernholc, Phys. Rev. B 62, 1713 (2000)

Semiconducting SWNT-metal assemblies

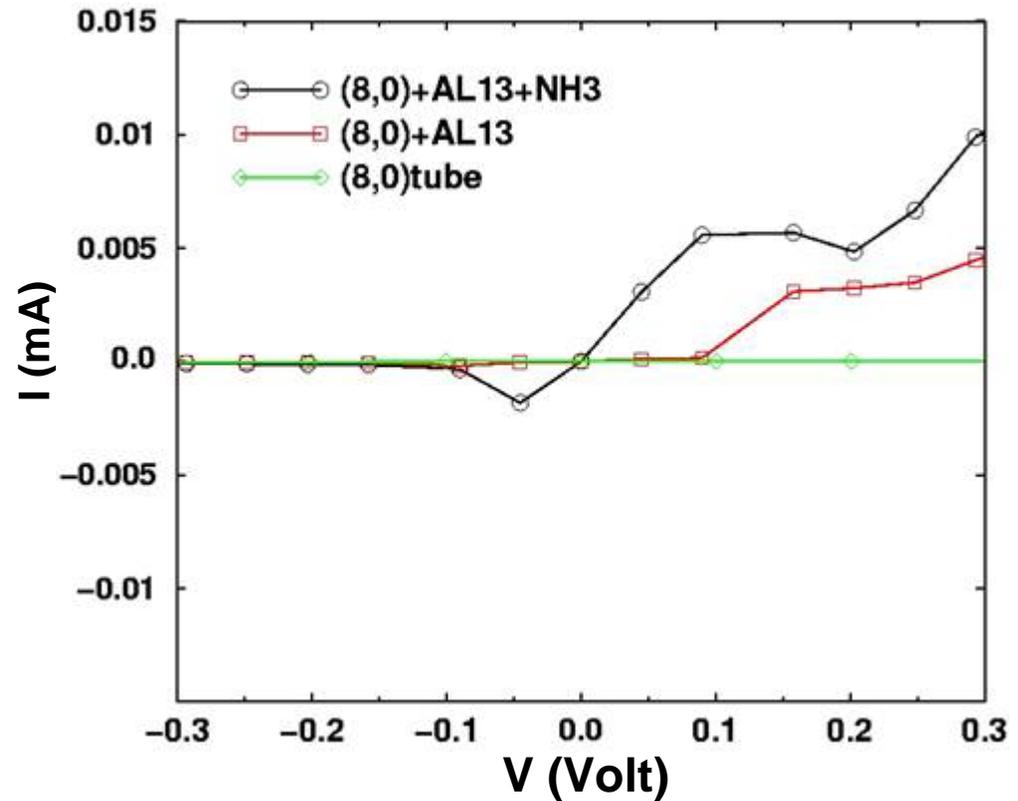
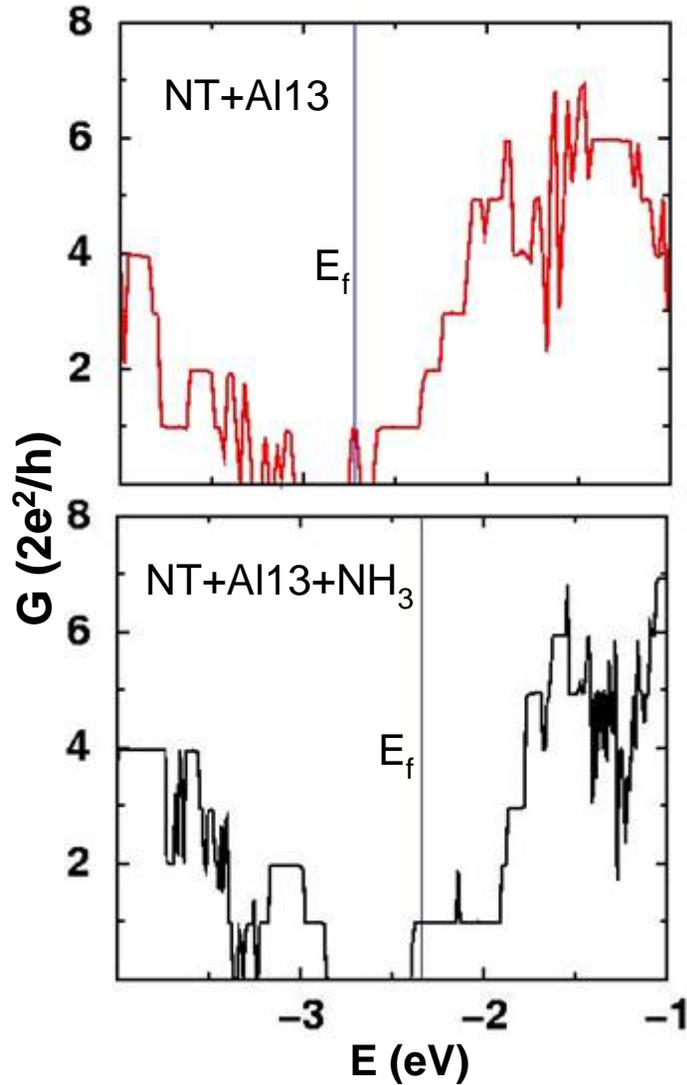


- ❖ (8,0)tube + Al_{13}
- ❖ More stable
- ❖ C-Al bond length: 2.15 \AA
- ❖ Formation energy: -0.7 eV



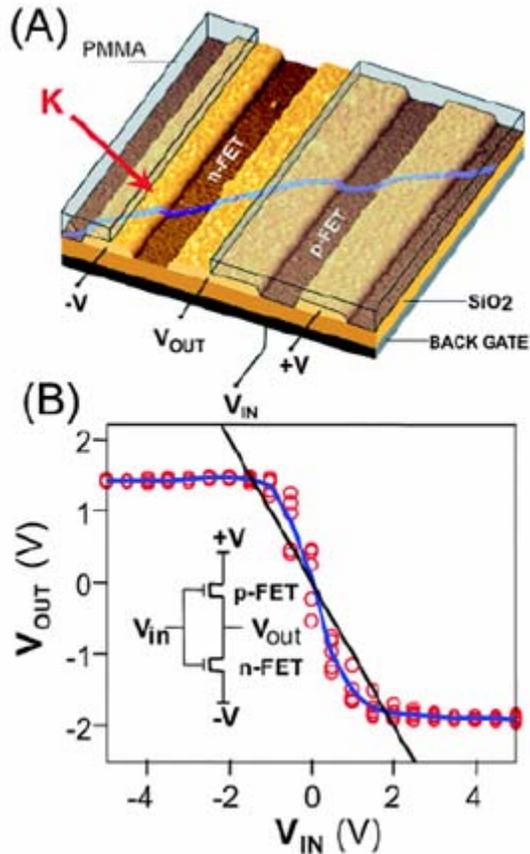
- ❖ (8,0)tube + Al_{13} + NH_3
- ❖ More stable
- ❖ C-Al bond length: 2.11 \AA
- ❖ Formation energy of the molecule complex: -1.8 eV

Quantum transport in semiconducting SWNT-metal cluster assembly

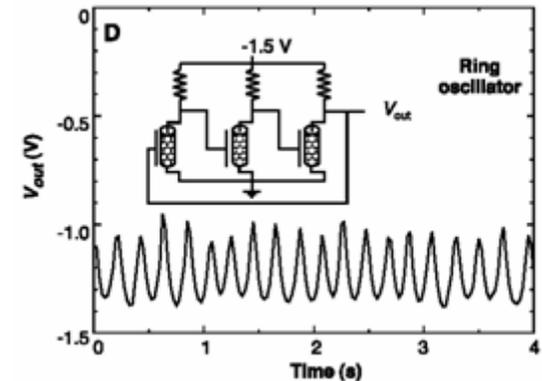
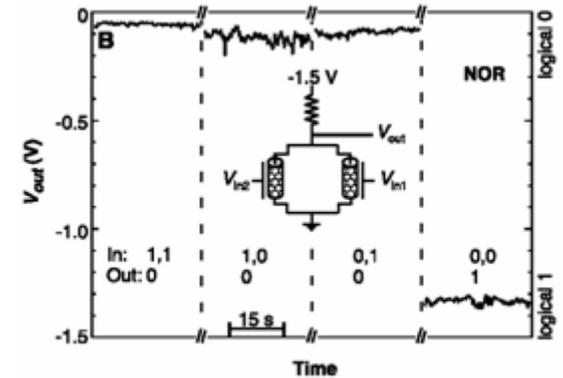
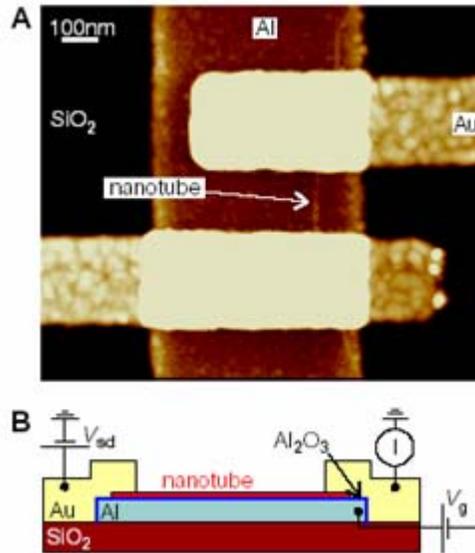


- ❖ $(8,0)$ tube-metal cluster assembly becomes conducting after NH_3 adsorption.
- ❖ SWNT-metal cluster assembly can be a good chemical sensor

Nanotube-based logic



NT-based inverter
 Derycke, Avouris et al
 Nano Letters 2001

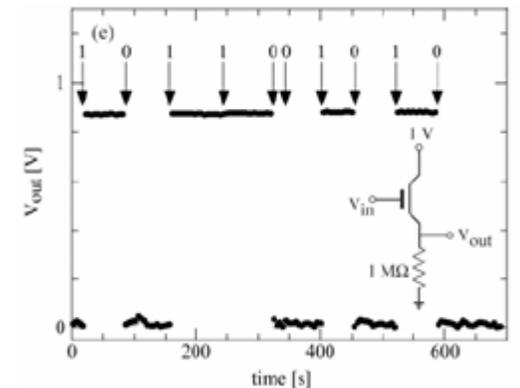
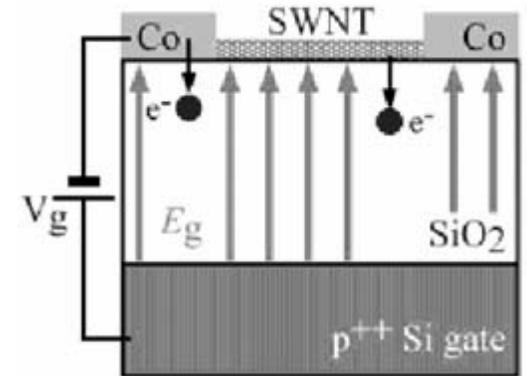
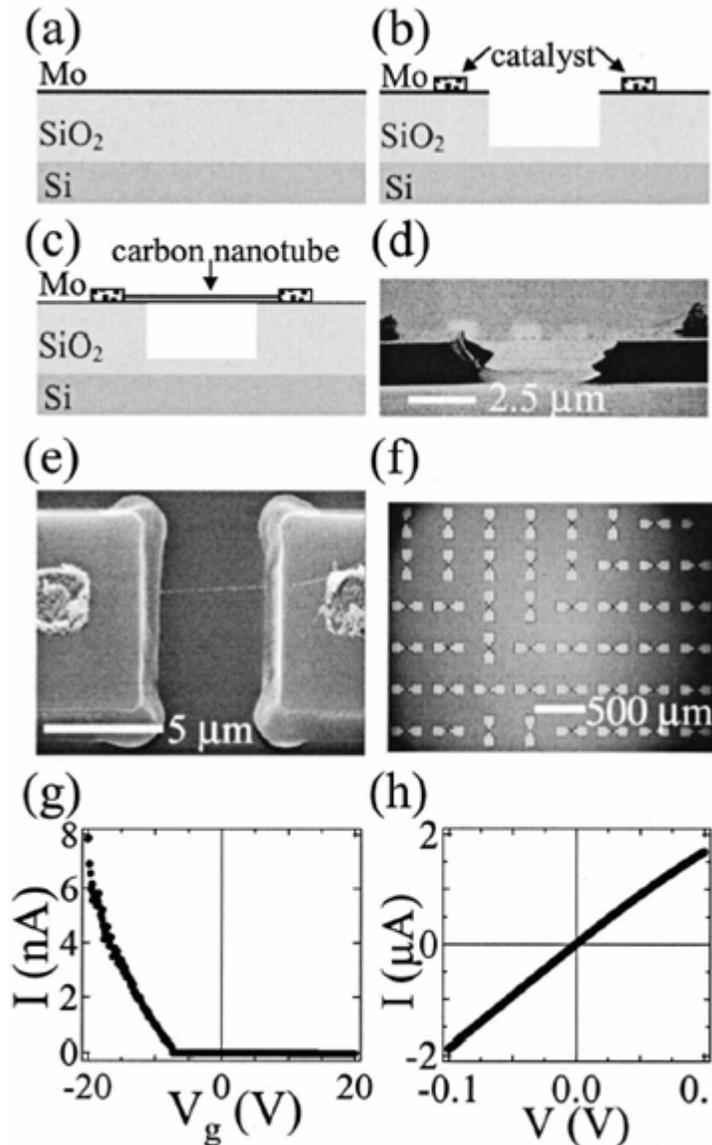


NT-based NOR and ring oscillator circuits
 Bachtold, Dekker et al
 Science 2001

Nanotube-based structures and memories

Electrically addressable suspended NT arrays

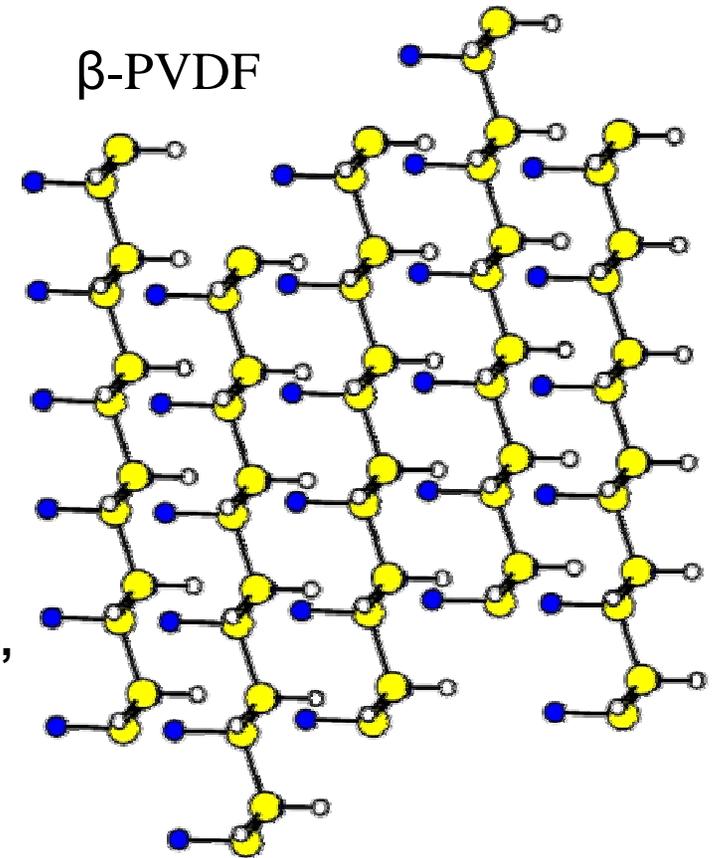
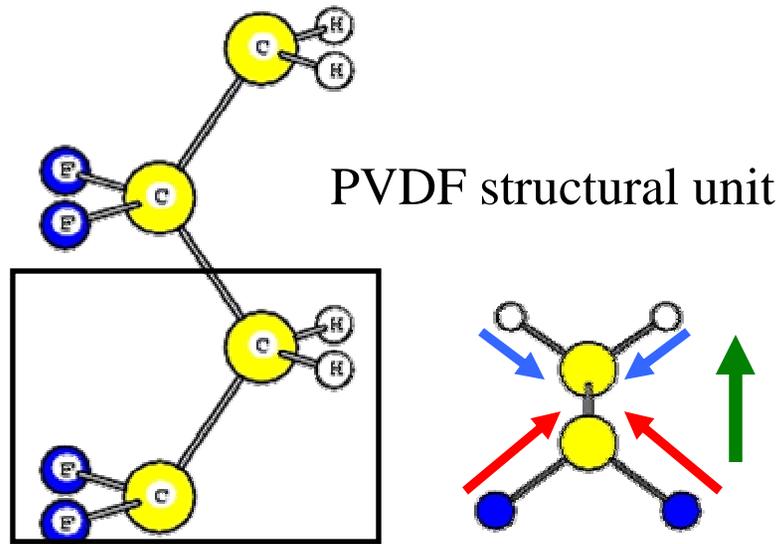
Franklin, Dai
APL 2002



Non-volatile NT-based memory

Radosavljevic, Johnson
et al 2002, Nano Letters

Ferroelectric polymers



Representatives: polyvinylidene fluoride (PVDF),
PVDF copolymers, nylons, etc.

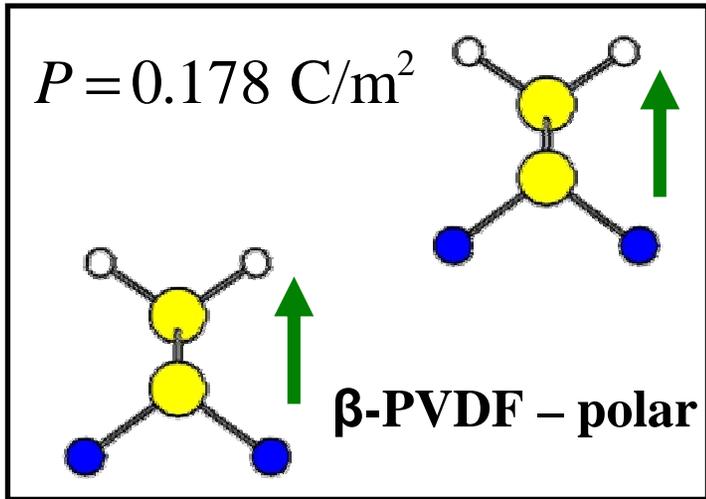
Spontaneous polarization: $0.1-0.2 \text{ C/m}^2$
Piezoelectric const (stress): up to 0.2 C/m^2

Mechanical/Environmental properties:

Light, flexible, non-toxic

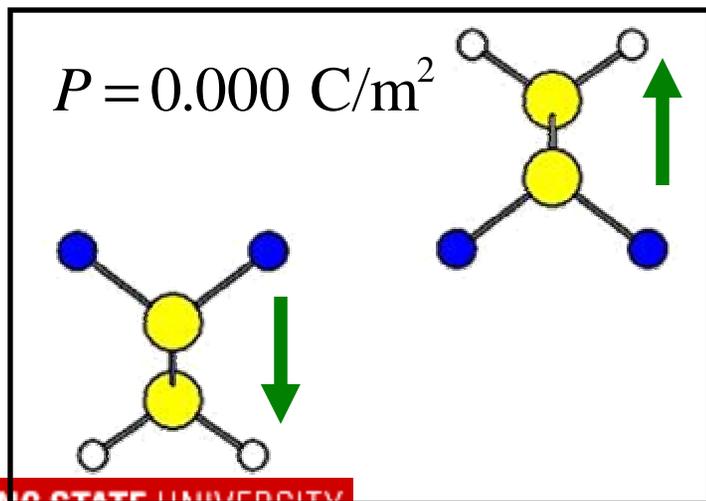
Applications: sensors, transducers, hydrophone probes, sonar

Polarization in β -PVDF from the first principles

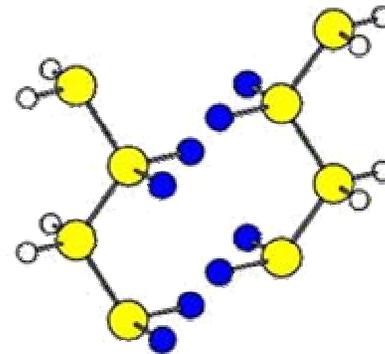
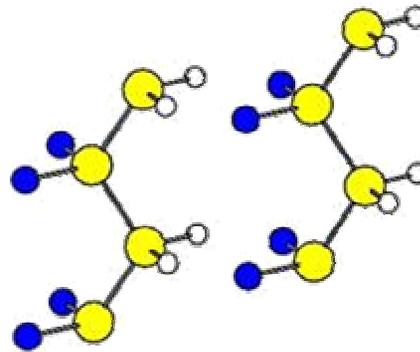


8.58 Å

non-poled PVDF – not polar



4.91 Å



Computations:

Berry phase method
with DFT/GGA

$\Delta P = 0.178 \text{ C/m}^2$

**crude estimate for 50%
crystalline sample:**

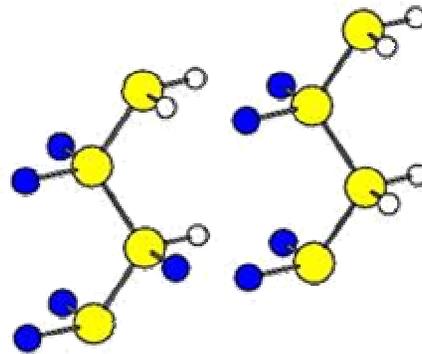
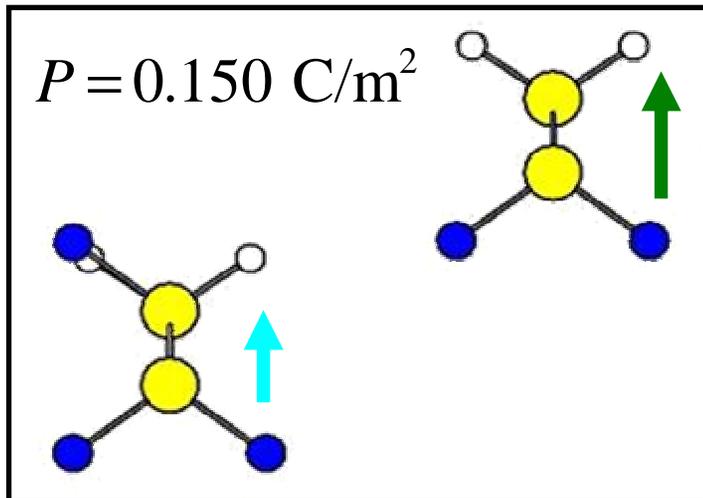
$P \approx 0.09 \text{ C/m}^2$

experiment:

0.05 – 0.076 C/m^2

Polarization in PVDF copolymers

P(VDF/TrFE) 75/25 copolymer



Comparison with experiment:
very crude predictions for
73/27 P(VDF/TrFE) copolymer
projected to 100% crystallinity

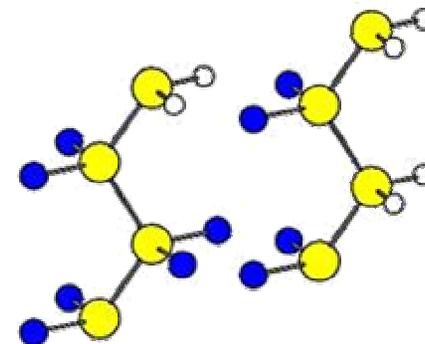
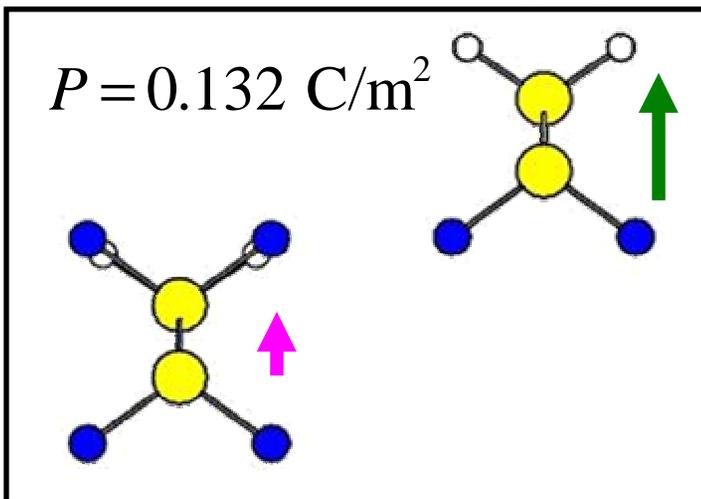
$$P = 0.120 - 0.160 \text{ C/m}^2$$

(Furukawa, IEEE Trans. 1989)

β -PVDF:

$$P = 0.178 \text{ C/m}^2$$

P(VDF/TeFE) 75/25 copolymer

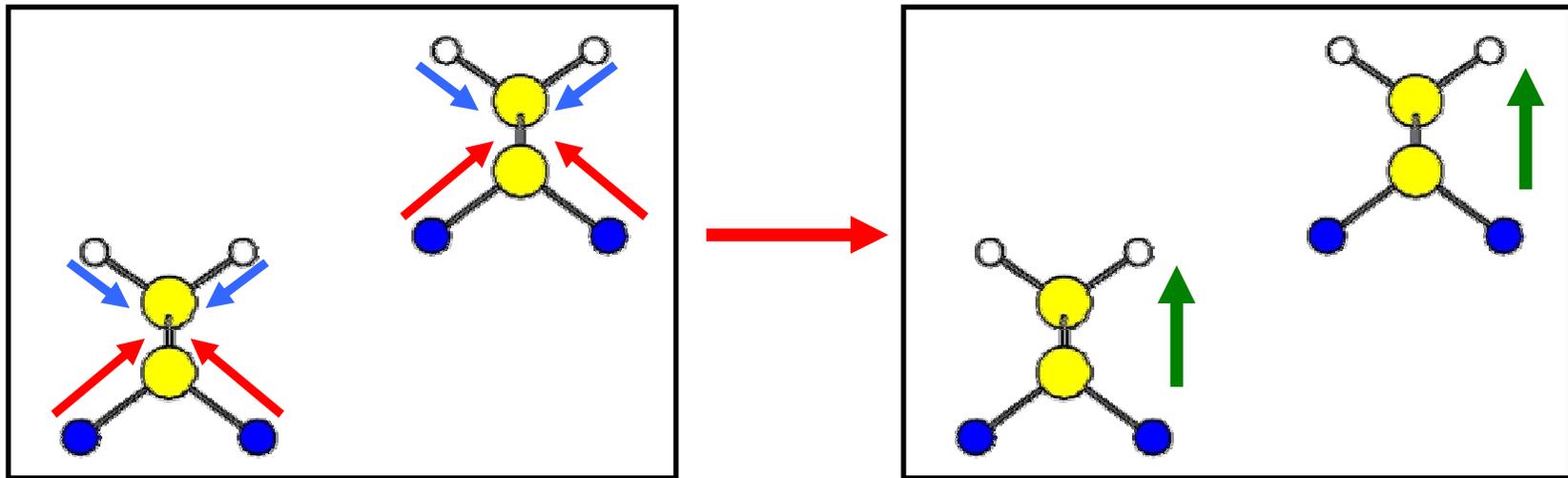


Comparison with experiment:
in 80/20 P(VDF/TeFE) copolymer
projected to 100% crystallinity

$$P = 0.126 - 0.140 \text{ C/m}^2$$

(Tasaka and Miyata, JAP 1985)

“Dipole summation” models for polarization in PVDF



Experimental polarization for approx. 50% crystalline samples: 0.05-0.076 C/m²

Empirical models (100% crystalline)

Polarization (C/m²)

Dipole summation with no interaction:

0.131

Mopsik and Broadhurst, JAP, 1975; Kakutani, J Polym Sci, 1970:

0.22

Purvis and Taylor, PRB 1982, JAP 1983:

0.086

Al-Jishi and Taylor, JAP 1985:

0.127

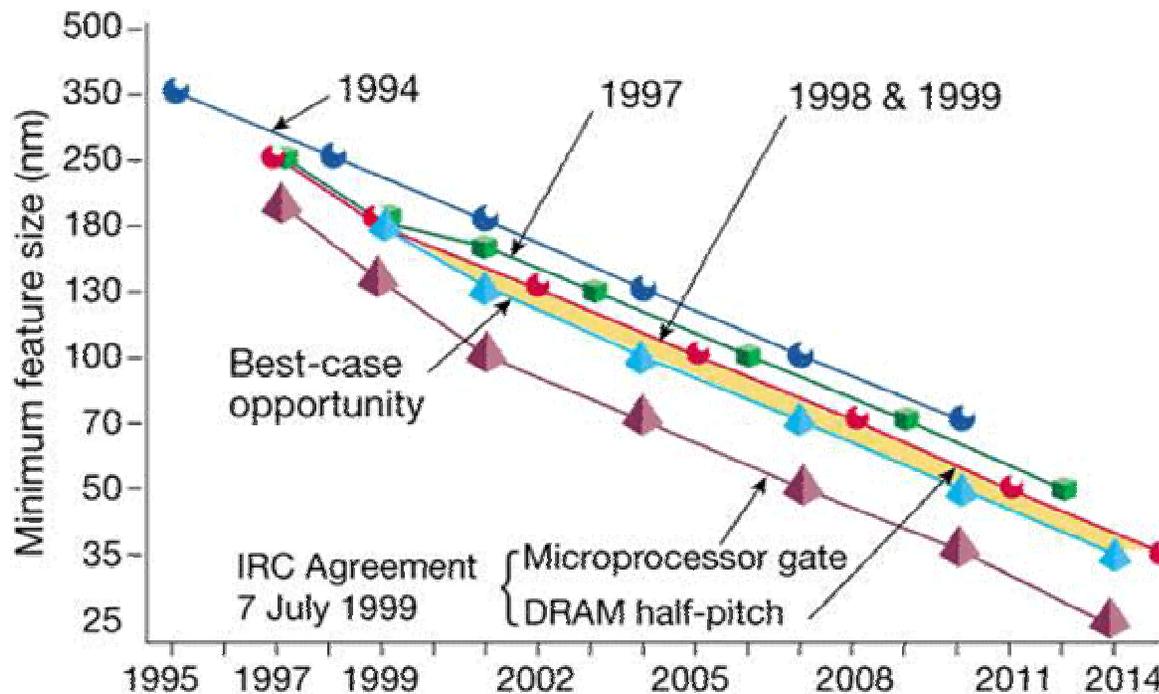
Carbeck, Lacks and Rutledge, J Chem Phys, 1995:

0.182

Moore's Law

The integration density of silicon-based integrated circuitry doubles every 12 to 18 months

[Moore, Electronics 38, 114 (1965)]



International Technology Roadmap for Semiconductors (ITRS)

[Percy, Nature 406, 1023 (2000)]

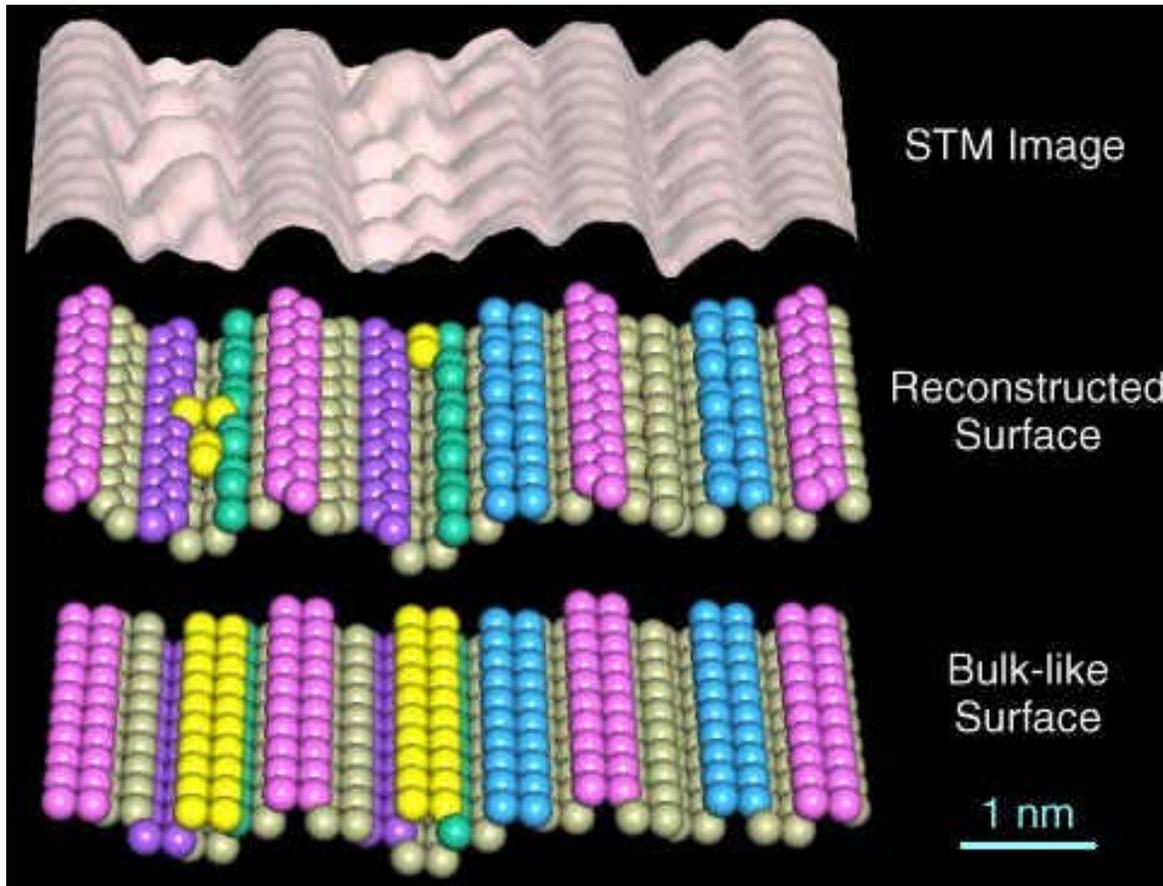
→ minimum feature sizes: nanometers

→ device function strongly influenced by surface and interface effects!

→ need to monitor and control microscopic structure of surfaces!

Semiconductor surfaces can be very complex...

example: Si(5 5 12), 68 atoms in unit cell
[Baski, Erwin, Whitman, Science 269, 1556 (1995)]



→ complicated structural rearrangement (relaxation & reconstruction)

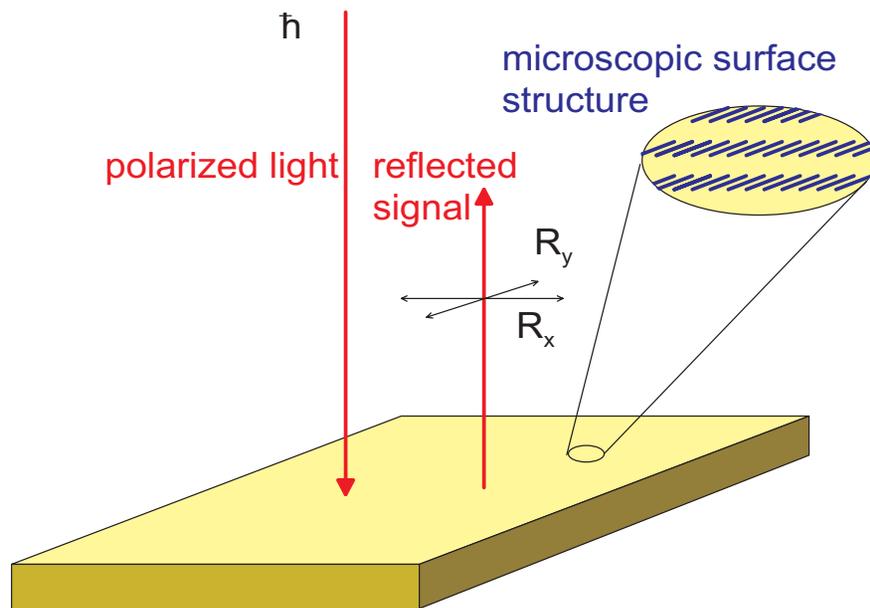
→ structure determination difficult

→ Scanning Tunnelling Microscopy (STM) or electron diffraction often not sufficient or not applicable

Surface information from optical spectroscopy??

Reflectance Difference Spectroscopy (RDS/RAS)

- Miniaturization of electronic devices requires *in situ* monitoring and feedback control of crystal growth
- “Standard” techniques to monitor surfaces use electron scattering and are restricted to ultrahigh vacuum

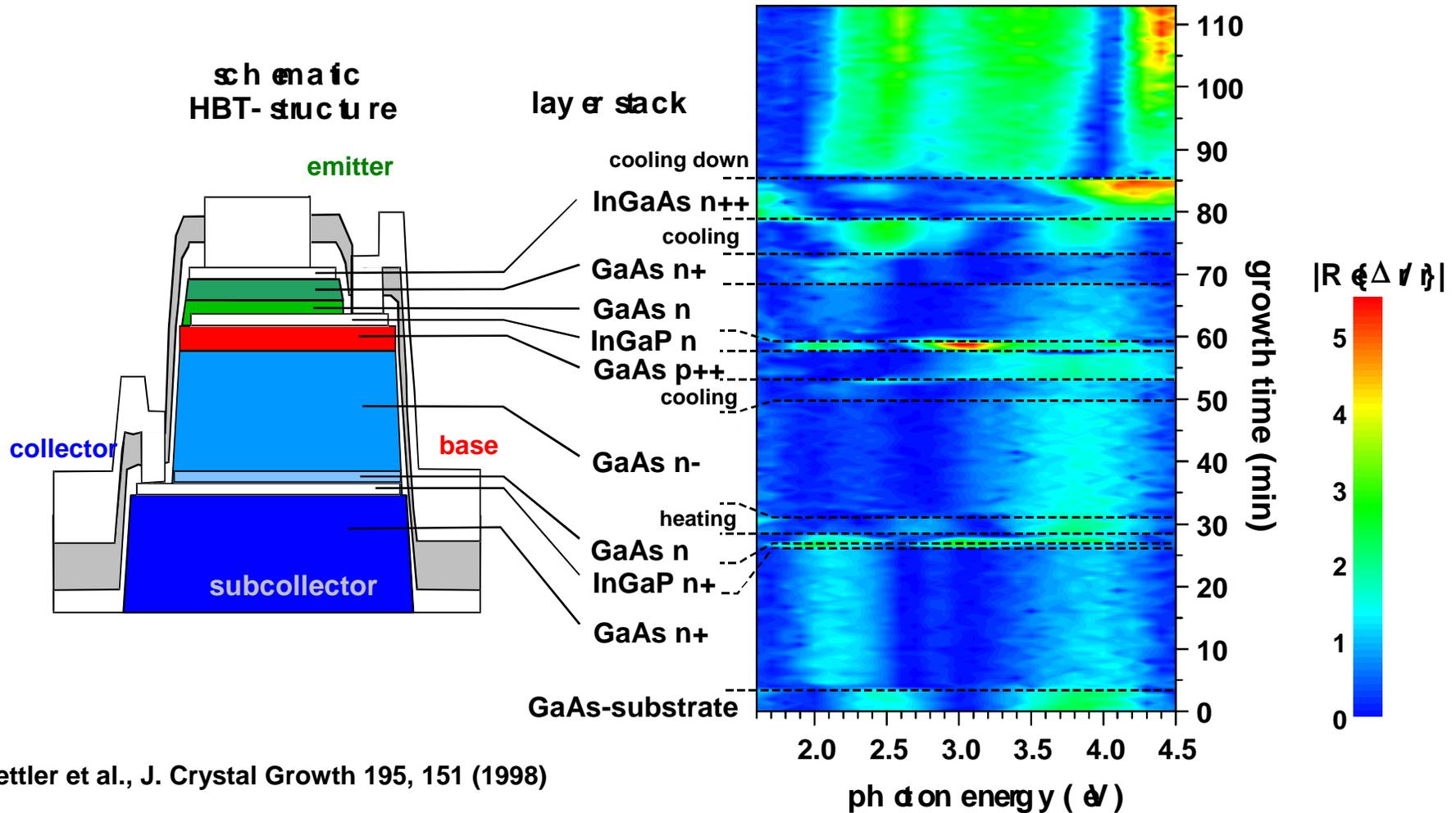


- Difference in reflectance between two polarizations
bulk contribution cancels out
- Very sensitive to atomic structure at the surface
- Can **unambiguously** determine surface structure, even when other techniques fail
- Optical probe: can be used for feedback control during growth in gaseous environments

Interpretation of spectra requires *accurate* calculations.

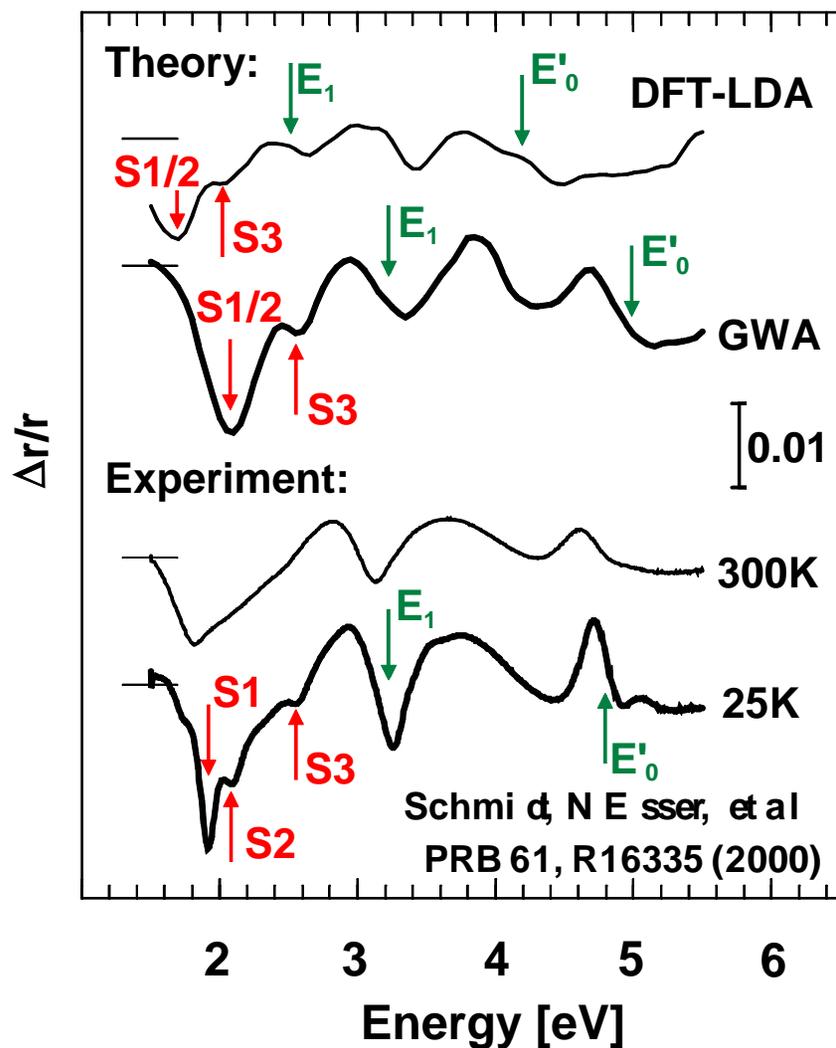
Reflectance anisotropy for industrial applications

Example: real-time monitoring of GaAs/InGaP HBT epitaxial growth



Zettler et al., J. Crystal Growth 195, 151 (1998)

In-rich InP(001)(2x4): self-energy effects on optical anisotropy

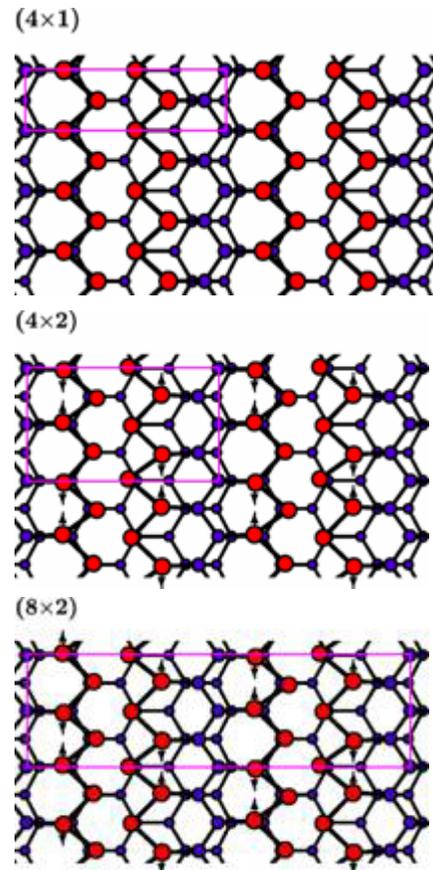


- non-uniform shift of **bulk** and **surface** related peaks with **GW** corrections
- line shape changes
- k-space resolution insufficient to resolve **S1/S2**

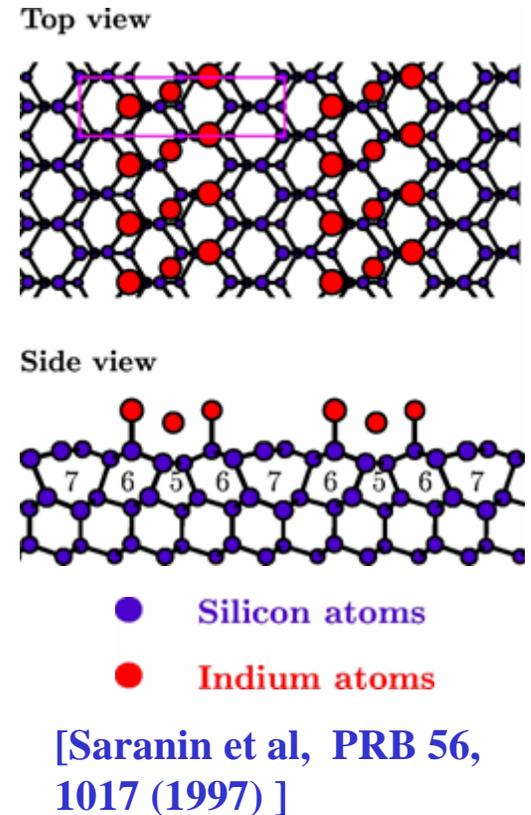
Si(111)-In nanowires

- ❖ In atoms on Si(111) self-organize into nanowires.
- ❖ Undergo a phase transition from (4x1) to (8x2) as temperature is lowered.
- ❖ Several models of (4x1) and (8x2) structures exist
- ❖ strongly anisotropic conductivity observed in experiments

Zigzag model



π -bonded-chain-stacking-fault (7656) model

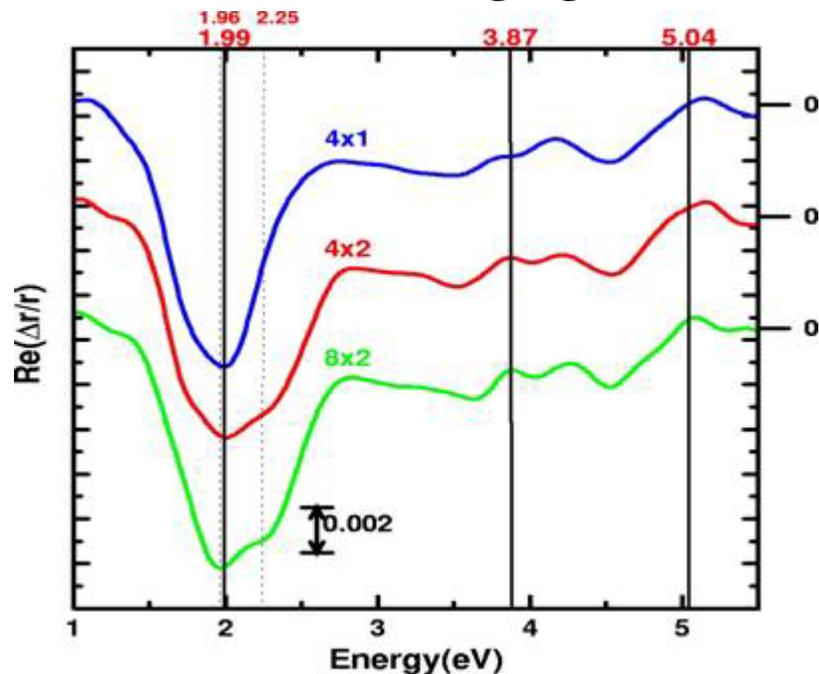


[Bunk et al, PRB 59, 12228 (1999).]

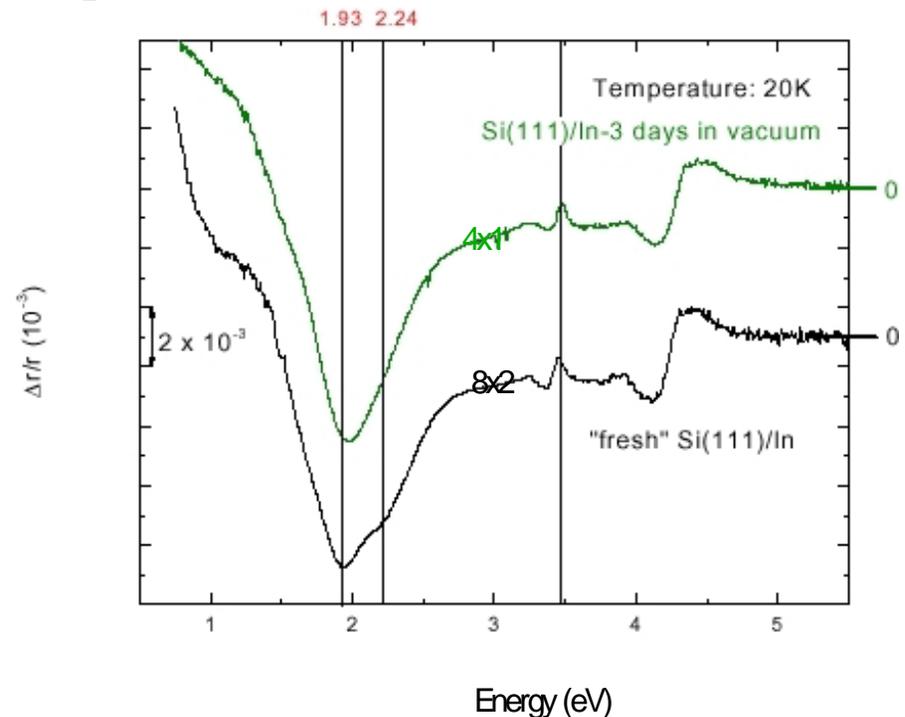
[Cho et al, PRB 64, 235302 (2001).]

Reflectance Difference Spectra (RDS/RAS) for zigzag model

Calculated RAS for zigzag model



Exp [Fleischer, Chandola et al, TU Berlin]

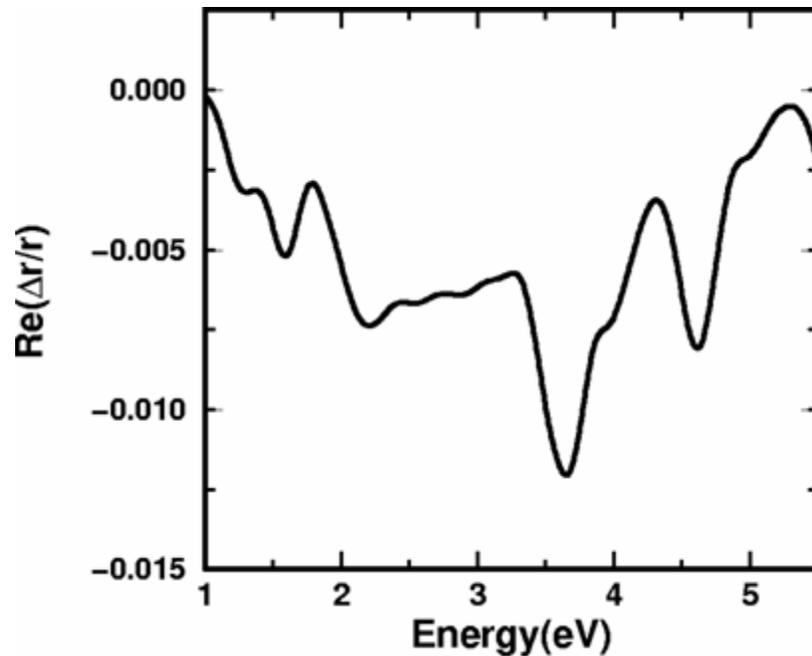


- Large anisotropy at 2.00 eV.
- Splitting of the dip at 1.99V for phase transition from (4x1) to (8x2).
- Excellent agreement between our calculations and experiments.

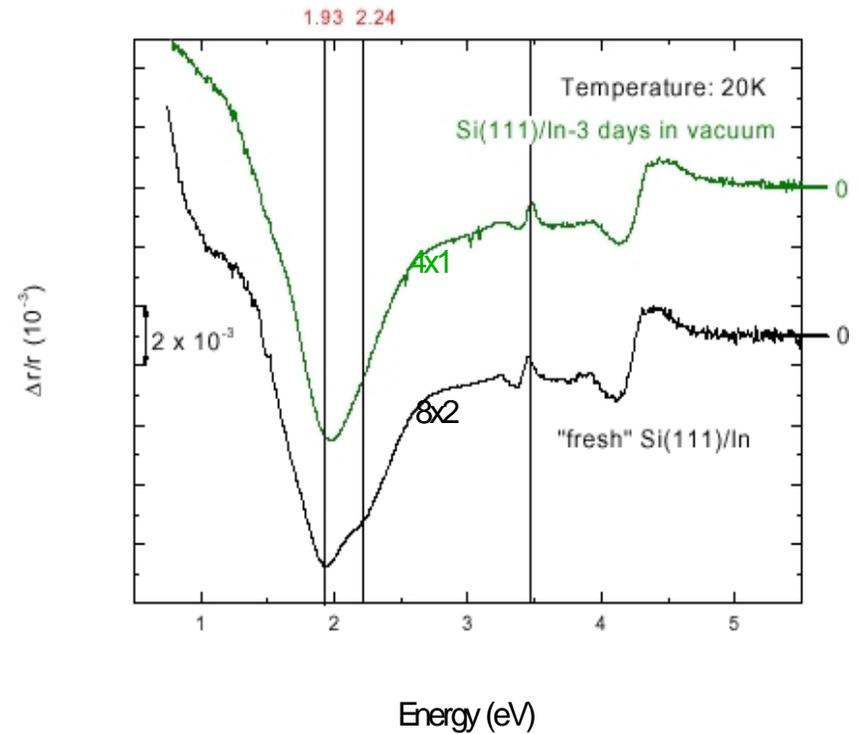
Our geometry agrees well with those of Bunk et al (PRB 1999) and Cho et al (PRB 2001)

Reflectance Difference Spectra (RDS/RAS) for 7656 model

Calculated RAS for 7656 model



Exp [Fleischer,Chandola et al, TU Berlin]

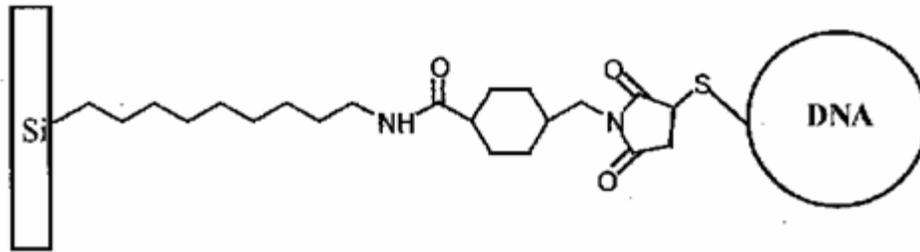


❌ No agreement with experiments.

❌ This model is can be discarded.

Si/organics surface structures

- Organics on Si can lead to novel sensors and detectors
- Cyclopentene monolayer can be used to **passivate** the Si surface
- It is a starting point for **DNA attachment**

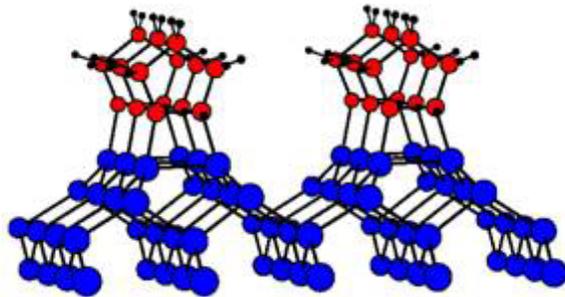


T.Strother, R. J. Hamers and
L.M. Smith,
Nucleic Acids Research, 28, 3535
(2000)

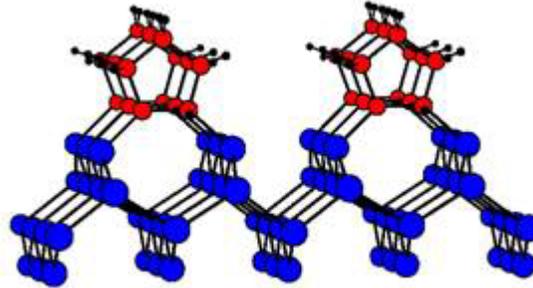
- DNA electrophoresis on a Si surface.
N. Pernodet et al, PRL85, 5651(2000).
- A new opportunity for **silicon-based microelectronics**
J. T. Yates Jr., Science 279, 335 (1998).
- Ordered array of organic molecules (cyclopentene) shows a strong optical anisotropy

Organic molecule adsorption: C5H8 on Si(001)

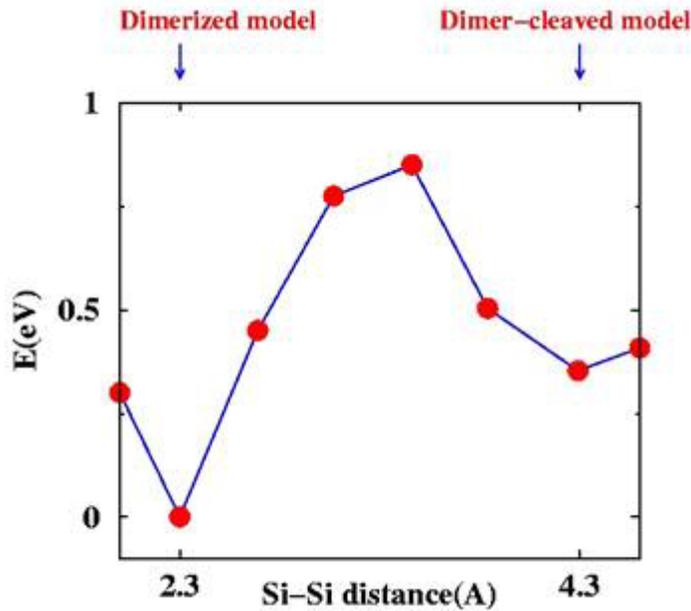
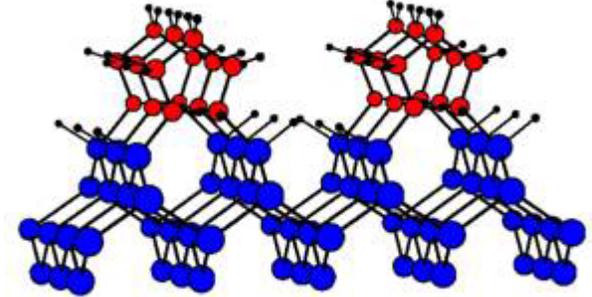
Dimerized model



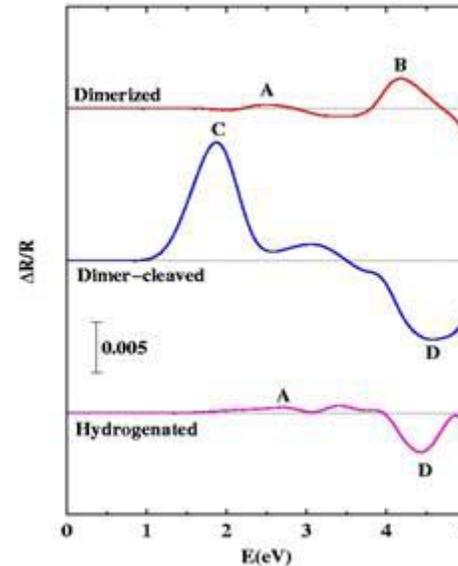
Dimer-cleaved model



Hydrogen co-adsorption



Energy barrier



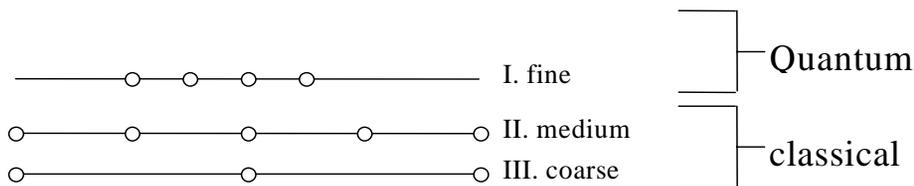
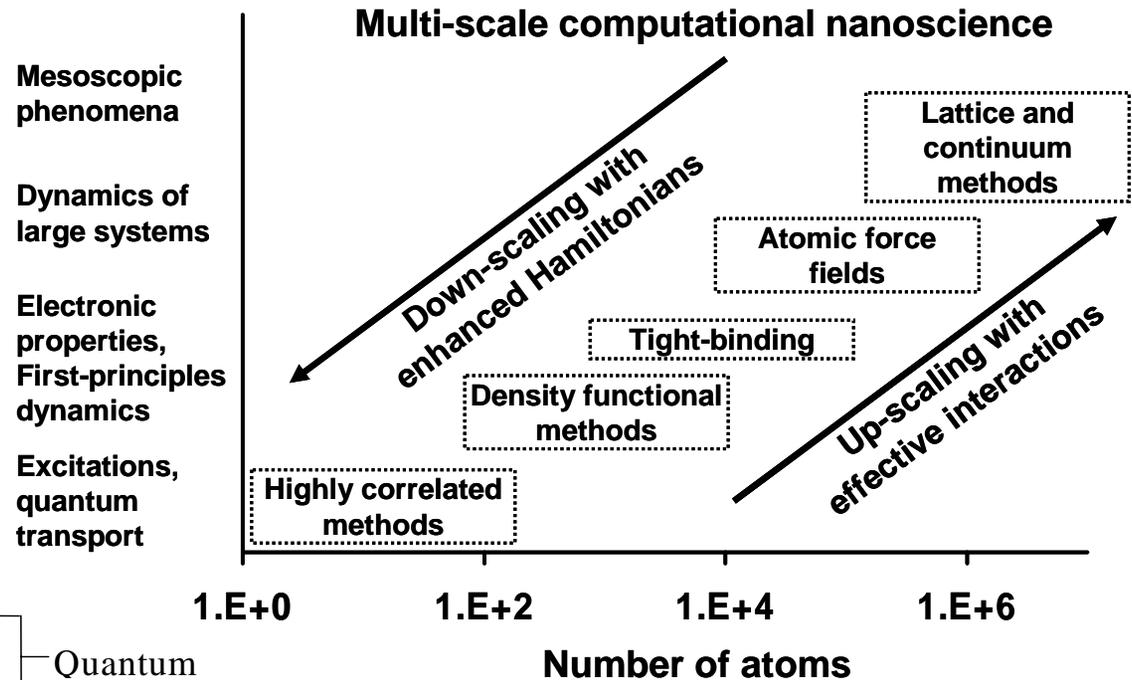
Calculated RAS

- A: molecular C5H8
- B: dimer-related
- C: dangling bond
- D: bulk-related

The Multiscale Challenge in Nanomaterials

“Real” nanomaterials and bio-problems encompass many length and time scales

- Methods for each “scale” exist
- Methods for “seamless” coupling between scales usually DO NOT



- A conceptual approach to multiscale exists, based on the multigrid analogy, but major problems remain
- Long term goal: Virtual Design of advanced materials and drugs
 - Principles-based design -- not a combinatorial approach
 - Evaluate only final candidates experimentally

Need for $O(N)$ quantum simulations

- **Estimated time for DFT calculations at 100 MFLOPS/CPU**
10,000 atoms, simple relaxation (100 ionic steps)
 $O(N)$ 12,000 CPU hr, $O(N)$ memory 77 GB
 $O(N^2)$ 842,000 CPU hr, $O(N^2)$ memory 6 TB
 $O(N^3)$ 60,000,000 CPU hr, $O(N^2)$ memory 6 TB

Large systems will require **many** simple relaxations

Efficient and reliable $O(N)$ methods are a must!

- **Time-dependent $O(N)$ simulations for 10,000 atoms**
1 ps ~ 168,000 CPU hr
1 ns ~ 168,000,000 CPU hr

Multiscale time-acceleration methods are a must!

Multidisciplinary Teams Needed

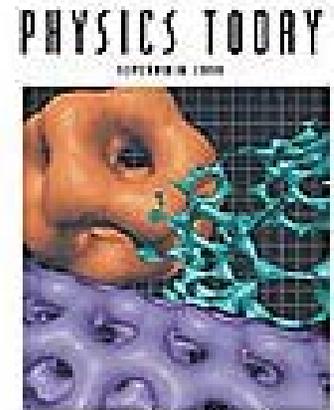
- **Nanoscale, algorithmic and petascale computing requires substantial teams!**
 - materials theorists and experimentalists, applied mathematicians, computer scientists
 - few mathematicians or computer scientists work on “quantum” problems
 - Close coupling to experiments, emerging computer hardware designs, etc
 - Goal-oriented: **focus on specific scientific accomplishments**
- **Methods, algorithms and software development is a long-term activity**

Summary and status of computational nanoscience

Reliable predictions can be made in many cases

- ❑ Nanotubes – many spectacular properties
- ❑ Carbon-based molecular electronics possible and exciting
- ❑ Understanding and predicting the properties of new materials
 - ❖ Ferroelectric polymers from first principles
- ❑ Building novel materials one layer at a time
 - ❖ Real-time monitoring and feedback control of growth
 - ❖ Precise electronic components
- ❑ Future: Novel tailor-made materials for specific applications
 - ❖ Nanoscale materials, sensors and devices
 - ❖ Multifunctional materials
 - ❖ Virtual synthesis of materials and drug design
 - ❖ principles of structure-property relationships:
e.g., proteins

Major impact on industry, medicine and defense



Computational
Materials Science