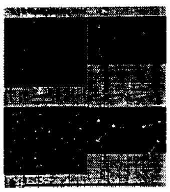
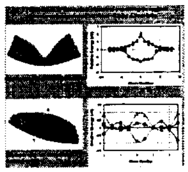
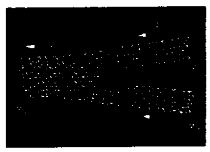
Computational Nanotechnology: Carbon Nanotubes and Fullerenes

Deepak Srivastava
Computational Nanotechnology at CSC/NAS
NASA Ames Research Center
Moffett Field, CA 95014







Carbon Nanotube

CNT is a tubular form of carbon with diameter as small as 1 nm.
Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.

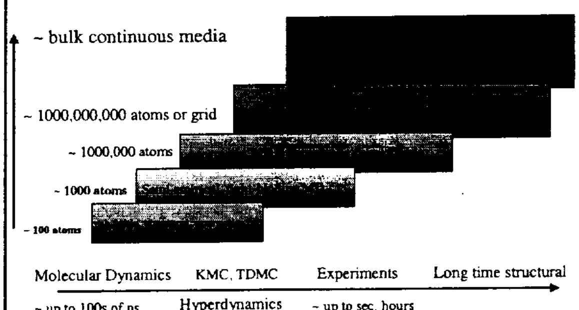
CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.

CNT can be metallic or semiconducting, depending on chirality.

Computational Nanotechnology Projects Collaborators (Acknowledgement)

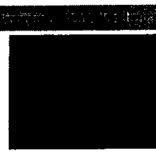
- **Nanomechanics of Nanotubes and Nanotube+Polymer Composites**
  →Dr. Chengyu Wei (Postdoc), Prof. K. Cho (Stanford University)
- **Chemical Functionalization, Thermal Conductivity, Gas Storage**
  →Prof. Don Brenner (NC State), Prof. M. Osman (Washington State)
- **Molecular Electronics with Nanotube Hetero-junctions**
  →Dr. Madhu Menon (U. Ky) and Dr. Antonis Andriotis (U. Crete)
- **Quantum Computing with Doped Bucky Onions and Fullerenes**
  →Seongjun Park (Student), Prof. K. Cho (Stanford)
- **Genetic Algorithm based Searches for New Molecular Force Field**
  →Al Globus (NASA Ames)

Spatio-Temporal Resolution



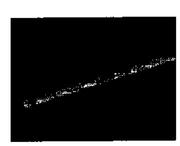
Nanomechanics of Nanomaterials

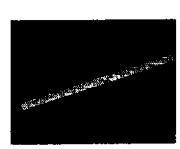
- **High value of Young's Modulus (1.2 -1.3 T Pa for SWNTs)**
- **Elastic limit upto 10-15% strain**

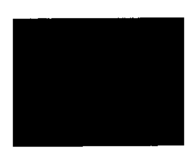


- *redistribution of strain*
- *sharp buckling leading to bond rupture*
- *SWNT is stiffer than MWNT*

Mechanics of Nanotubes: Classical MD





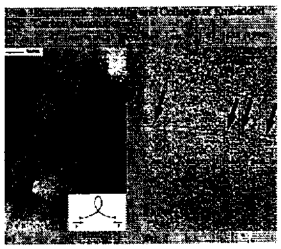


D. Srivastava and S. Barnard, SuperComputing 97 (1997)
D. Srivastava et. al., *Handbook of Nanotechnology, 665 (Academic Press: 1999)*

Nanotubes in Composites

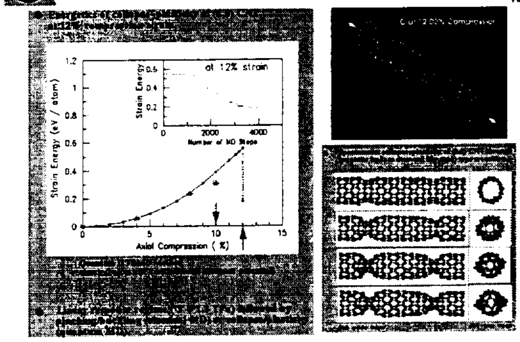
- Experiment: buckling and collapse of nanotubes embedded in polymer composites.

Buckle, bend and loops of thick tubes..



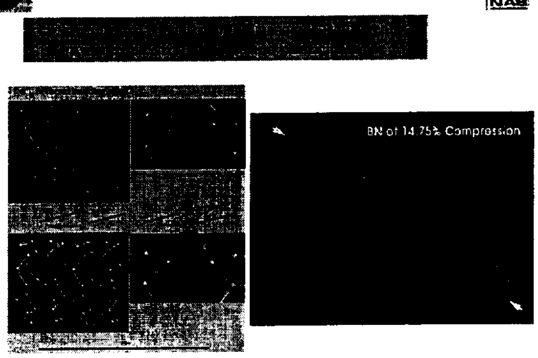
Local collapse or fracture of thin tubes.

Stiffness and Plasticity of Carbon Nanotubes



D. Srivastava, M. Menon and K. Cho, Phys. Rev. Lett. Vol. 83, 2973 (1999)

Inclusion of Physics and Chemistry: BN Nanotubes



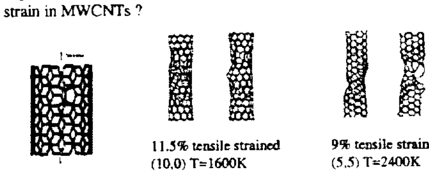
D. Srivastava, M. Menon and K. Cho, Phys. Rev. B., 2001

Bridging the Spatio-Temporal Scales

Example: Yielding of Nanotube under Tension

Simulation: 30% yielding strain from fast strain rate (1/ps) molecular dynamics simulations

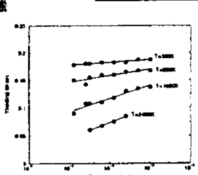
Experiments: 6% maximum strain in SWCNT ropes; 12% maximum strain in MWCNTs ?



11.5% tensile strained (10,0) T=1600K

9% tensile strained (5,5) T=2400K

Spatio-temporal dependence



- yielding: strongly dependent on the strain rate and temperature !

- Linear dependence on the temperature of the of the yielding strain vs strain rate ~ activated process

Transition State Theory Derived Formula

$$\varepsilon_Y = \frac{B}{[illegible]} + \frac{k_B T}{[illegible]} \ln\left(\frac{N [illegible]}{[illegible]}\right)$$

-Experimental feasible conditions: length ~ 1μm; strain rate ~ 1/hour; T ~ 300K

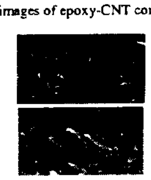
⟹ **Yield strain:** 9 ± 1 %, Experiments: 6-12% strain for SWNT ropes

C. Wei, K. Cho and D. Srivastava, submitted Phys. Rev. Lett.

Polymer-CNT composite

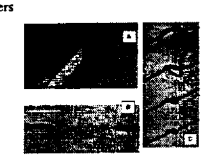
- Structural and thermal properties
- Load transfer and mechanical properties

SEM images of epoxy-CNT composite



(L.S.Schadler et.al., Appl. Phys. Lett. V73 P3842, 1998)

SEM images of polymer (polyvinylacohol) ribbon contained CNT fibers & knotted CNT fibers



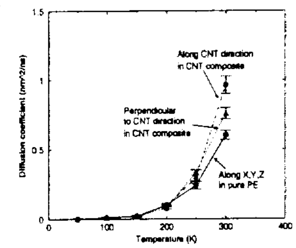
(B. Vigolo et.al., Science, V290 P1331, 2000)

Thermal Characterization of Nanotubes and Polymer-Nanotube Composites

- Thermal conductivity of single-wall nanotubes
- Nanotube/polymer composites as high thermal expansion coefficient materials
- Thermal conductivity of nanotube/polymer composite

Thermal Diffusion coefficients

Small system: L/D~2, Np=10



Diffusion coefficients of polymer with CNTs embedded

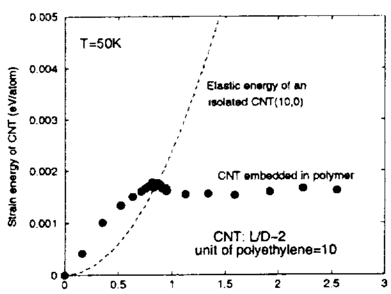
Diffusion coefficient increased, especially along CNT axis direction, indicating enhancement of thermal conductivity

* Experiments on diffusivity in ABS/CNT & RTV/ CNT show larger increase (Rick Berrera's group at Rice University)

* C. Wei, D. Srivastava, and K. Cho (submitted 2001)

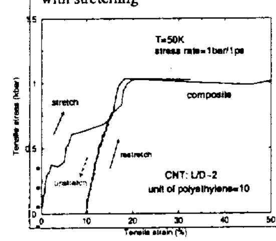
Nanomechanics of Composite under Tensile Stress

Strain energy of CNT



Loading sequence

Work hardening of composite with stretching



TEM images of alignment of CNTs in a polymer matrix by stretching

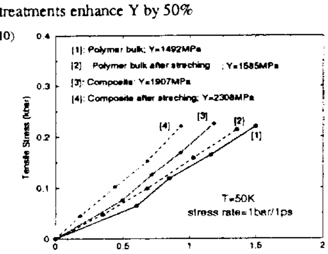
(L. Jin et al. Appl.Phys. Lett. V73 P1197, 1998)

Young's Modulus

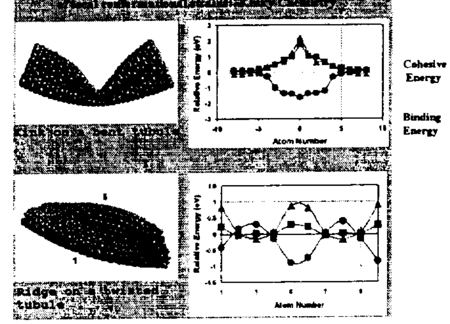
-Young's modulus of CNT composites 30% higher than polymer matrix

-Stretching treatments enhance Y by 50%

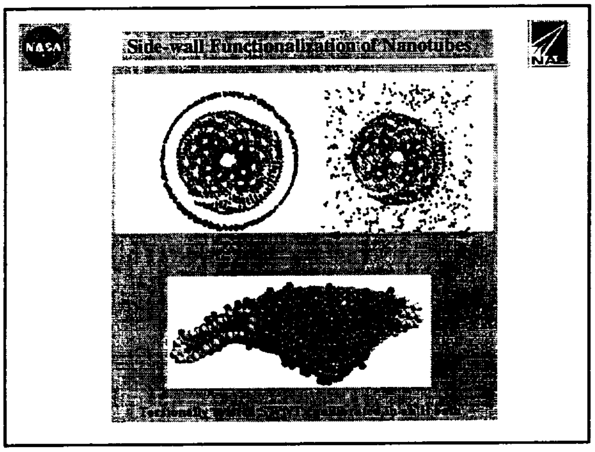
(L/D~2, Np=10)

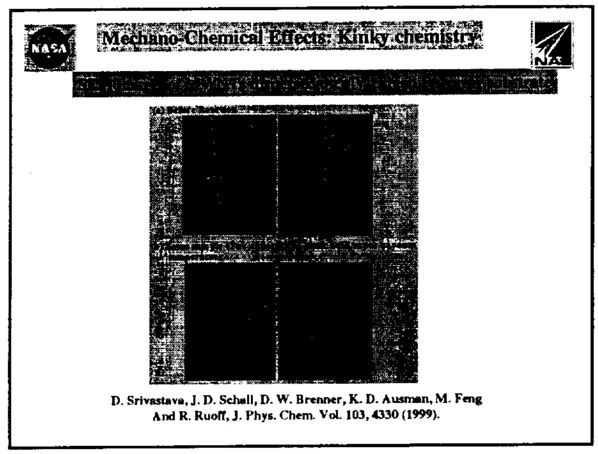


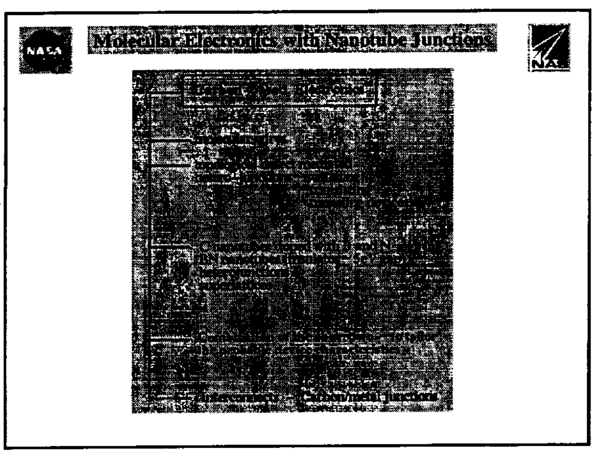
Side-Wall Functionalization of Nanotubes: Kinky Chemistry

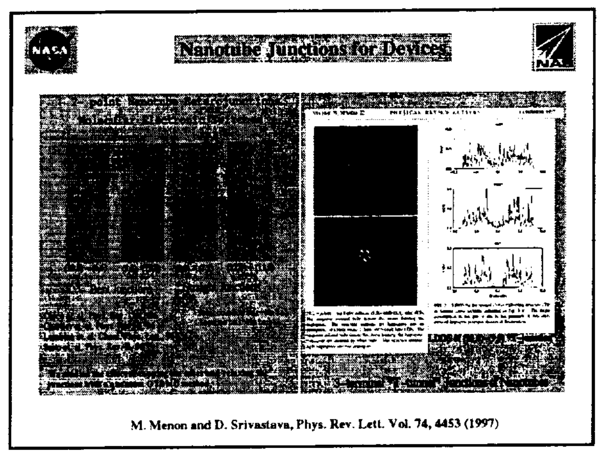


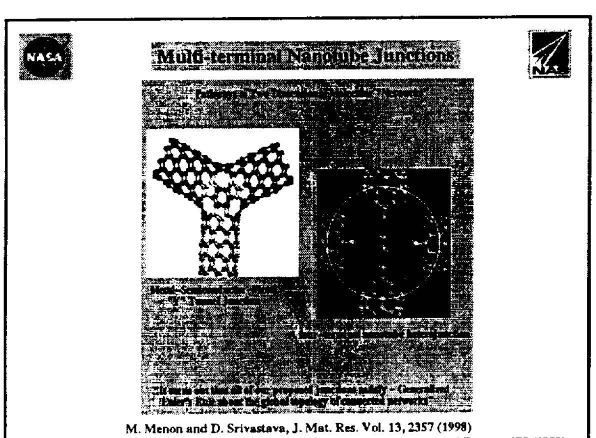
D. Srivastava, J. D. Schall, D. W. Brenner, K. D. Ausman, M. Feng And R. Ruoff, J. Phys. Chem. Vol. 103, 4330 (1999).

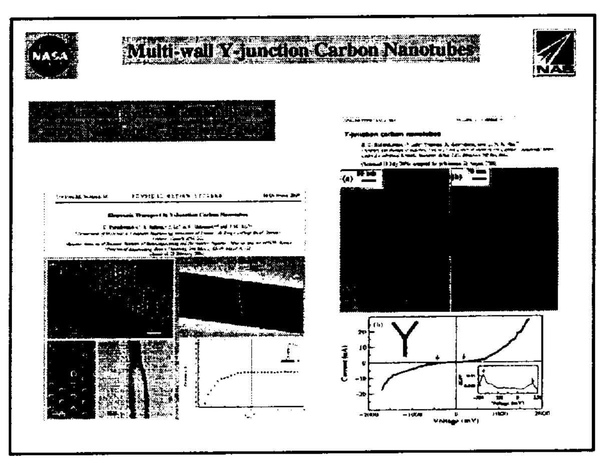

NASA
Side-wall Functionalization of Nanotubes


NASA
Mechano-Chemical Effects: Kinky chemistry
D. Srivastava, J. D. Schall, D. W. Brenner, K. D. Ausman, M. Feng
And R. Ruoff, J. Phys. Chem. Vol. 103, 4330 (1999).

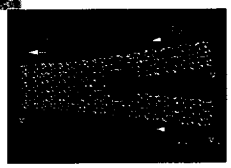

NASA
Molecular Electronics with Nanotube Junctions

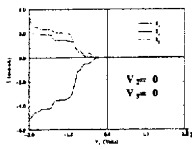

NASA
Nanotube Junctions for Devices
M. Menon and D. Srivastava, Phys. Rev. Lett. Vol. 74, 4453 (1997)

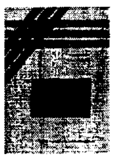

NASA
Multi-terminal Nanotube Junctions
M. Menon and D. Srivastava, J. Mat. Res. Vol. 13, 2357 (1998)
D. Srivastava, S. Saini and M. Menon, Molecular Electronics, Ed. Aviram and Ratner, 178 (1998)


NASA
Multi-wall Y-junction Carbon Nanotubes
Y

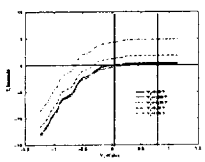
Rectification and Analog Logic Devices







V2	V3	OR	XOR
0	0	0	0
0	1	1	1
1	0	1	1
1	1	1	0

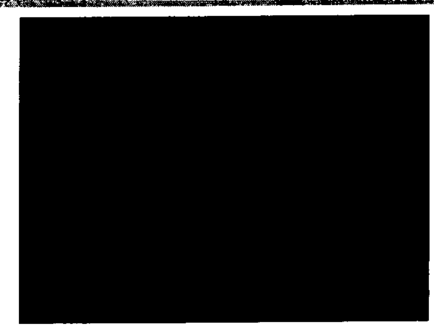


Andriotis, Menon, Srivastava, Chernozatonskii, Phys. Rev. Lett. (2001)

Our Proposed Model: Neural Signal Processing/Sensing in Biological Systems

Ceral Sensory System (inter-neuron) of a cricket

Bio-mimetic Dendritic Neurons: Carbon Nanotube



A 4-level dentritic neural tree: 14 branched carbon nanotube junctions

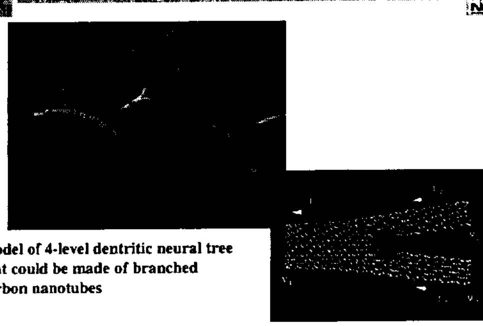
D. Srivastava et. al., Comp. in Science and Engineering, IEEE, APS (2001)

Bio-mimetic Dendritic Neurons: Carbon Nanotube

Biological Dendritic Neural Tree	Carbon Nanotube: Dendritic Tree
• One dimensional cable theory + Hodgkin-Huxley model for action-potential based information flow • Information processing is coded in (a) branching at the junctions, and (b) time-series sequencing of the signal spikes • Input – output – control: is based on (a) structural details of the branches and junctions, and (b) via chemical environment • Short and long term memory is part of the structure: evolutionary in nature	• Electronic, acoustic, thermal, and chemical signal transmission and information processing • Information processing can be based on (a) branching + switching at the junctions, and (b) time series sequencing of signal-spikes • Input – output – control: can be based on (a) structural details, (b) chemical environment, and (c) physical contacts at the ends? • Short and long term memory can be part of structure by defect and chemical adsorbate placements: design for specific purpose/functionality

D. Srivastava et. al., Comp. in Science and Engineering, IEEE, APS (2001)

Bio-mimetic Dendritic Neurons: Carbon Nanotube

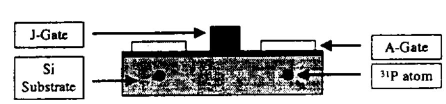


Model of 4-level dentritic neural tree that could be made of branched carbon nanotubes

D. Srivastava et. al., Comp. in Science and Engineering, IEEE, APS (2001)

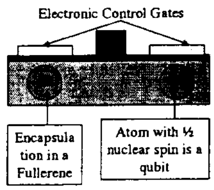
Nanotechnology for Solid-State Quantum Computers Using Fullerenes

- **Kane' Model: Solid state quantum bits: Nuclear spins of ^{31}P dopant atoms in bulk Si, controlled by external electronic gates using hyperfine interactions, serve as solid-state qubits. [1]**
- **Problem: Uniform arrays of individual ^{31}P dopant atoms in bulk Si are experimentally difficult to fabricate !**



1. Kane, B.E., *Nature*, 393, p.133 (1998)

Solution: Use Encapsulated Atoms as Qubits !



Proposal: Arrays of "encapsulated" atoms (with ½ nuclear spin – qubits) will be easy to fabricate as compared to the arrays of the similar bare atoms.

Example: ^{1}H encapsulated in C_{36}

Electronic charge density shows a weak meta-stable state of ^{1}H at the center of C_{36}

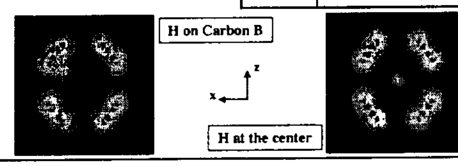
Suitable Solid-state Qubits Identified:

- ^{1}H encapsulated in a $C_{20}D_{20}$ fullerene
- ^{31}P encapsulated in a diamond nanocrystallite

Example 1: ^{1}H Encapsulated in C_{36}

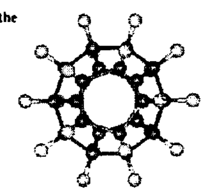
- Center is a meta-stable site.
- ^{1}H strongly prefers to make a bond with a carbon atom, then it is not suitable as a qubit

	Formation Energy (eV)
Carbon A	-1.28
Carbon B	-1.54
Carbon C	-1.40
Center	-0.46



Reactivity Control to Encapsulate ^{1}H: $C_{20}D_{20}$

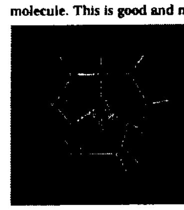
- ^{1}H prefers to make a bond with C atom within fullerene.
  → Reduce the chemical reactivity of the interior surface
- sp^3 hybrid on C atom will reduce the electron density at the interior surface.
  → Hydrogenation on exterior
- Hexagon has lower escape barrier than a pentagon.
  → Non-hexagon smaller fullerene structure is preferred
- As a conclusion, we examined $C_{20}D_{20}$

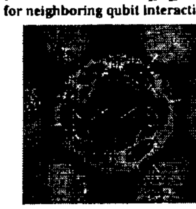


$C_{20}D_{20}$

Charge Density of ^{1}H Encapsulated in $C_{20}D_{20}$

- The valance electron charge density of ^{1}H leakes out of $C_{20}D_{20}$ cage molecule. This is good and needed for neighboring qubit interactions.

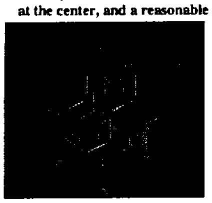




S. Park, D. Srivastava and K. Cho, J. NanoSc. NanoTech. (2001)

Model 2: ^{31}P doped in Diamond or Silicon

- Weakly bound donor electron has strong S-like electronic charge density at the center, and a reasonable spread of the decay for off center positions

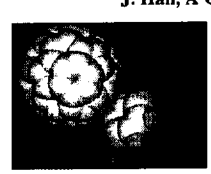


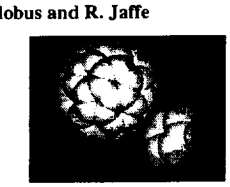
^{31}P in Diamond

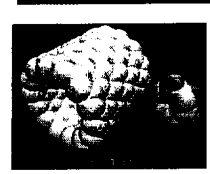
^{31}P in Si

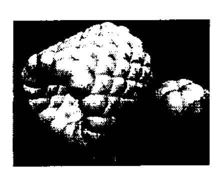
S. Park, D. Srivastava and K. Cho, J. NanoSc. and NanoTech. (2001)

J. Han, A Globus and R. Jaffe

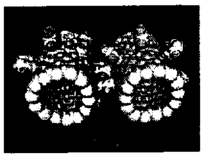


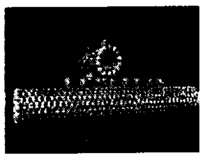






Molecular Machines and [illegible]





Computational Nanotechnology: CSE

Nanomanipulation in Virtual World

Next Generation of Technology and Products

Summary and Future

- **Nanomechanics of Individual Nanotubes and Comparison with Experiments: (Nanotube + Polymer Composite)**
- **Kinky Chemistry and Functionalization of Nanotubes: (Generalized to a universal theory of reaction)**
- **Temperature Dependence of Thermal Conductivity (Generalized to Multi-wall nanotubes and nanotube junctions)**
- **Rectification and Switches with Nanotube Y-Junctions (Generalized a variety of logic gates and devices)**
- **Solid State Quantum Bits: (Initiate Experimental Efforts)**

D. Srivastava, M. Menon and K. Cho, invited review article, *Computing In Engineering and Sciences*, submitted (2001)