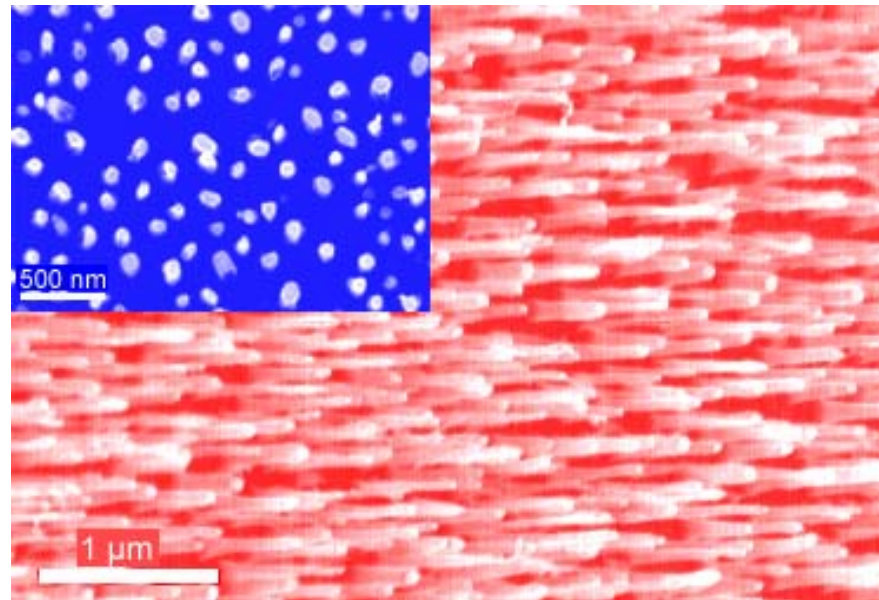
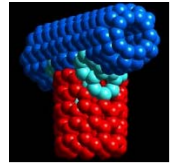


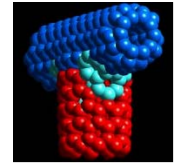


An Overview of Recent Developments in Nanotechnology



M. Meyyappan
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Why Nanotechnology at NASA?



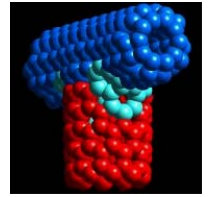
- Advanced miniaturization, a key thrust area to enable new science and exploration missions
 - Ultrasmall sensors, power sources, communication, navigation, and propulsion systems with very low mass, volume and power consumption are needed
- Revolutions in electronics and computing will allow reconfigurable, autonomous, “thinking” spacecraft
- Nanotechnology presents a whole new spectrum of opportunities to build device components and systems for entirely new space architectures
 - Networks of ultrasmall probes on planetary surfaces
 - Micro-rovers that drive, hop, fly, and burrow
 - Collection of microspacecraft making a variety of measurements

Europa Submarine





NASA Ames Nanotechnology Research Focus



* Carbon Nanotubes

- Growth (CVD, PECVD)
- Characterization
- AFM tips
 - Metrology
 - Imaging of Mars Analog
 - Imaging Bio samples
- Electrode development
- Biosensor (cancer diagnostics)
- Chemical sensor
- Logic Circuits
- Chemical functionalization
- Gas Absorption
- Device Fabrication

* Molecular Electronics

- Synthesis of organic molecules
- Characterization
- Device fabrication

* Inorganic Nanowires

* Protein Nanotubes

- Synthesis
- Purification
- Application Development

* Genomics

- Nanopores in gene sequencing
- Genechips development

* Computational Nanotechnology

- CNT - Mechanical, thermal properties
- CNT - Electronic properties
- CNT based devices: physics, design
- CNT based composites, BN nanotubes
- CNT based sensors
- DNA transport
- Transport in nanopores
- Nanowires: transport, thermoelectric effect
- Transport: molecular electronics
- Protein nanotube chemistry

* Quantum Computing

* Computational Quantum Electronics

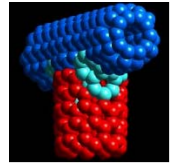
- Noneq. Green's Function based Device Simulator

* Computational Optoelectronics

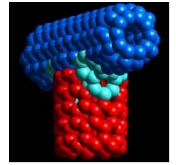
* Computational Process Modeling



Nanotechnology Research of Interest to IEEE Community

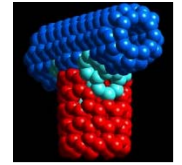


- Nanoelectronics (CNTs, molecular electronics)
- Non-CMOS circuits and architectures, reconfigurable systems
- Spintronics, quantum computing, nanomagnetism
- Nanophotonics, nano-optics, nanoscale lasers....
- Chemical and biological sensors
- Novel materials for all applications (CNTs, quantum dots, inorganic nanowires...)
- Integration of nano-micro-macro
- Bio-nano fusion
-
-
-



- Carbon Nanotubes
 - CNT - growth and characterization
 - CNT based nanoelectronics
 - CNT based microscopy
 - CNT interconnects
 - CNT based biosensors
 - CNT chemical sensors
- Some other Nano examples
 - Inorganic nanowires
 - Protein nanotubes
 - Nano in gene sequencing

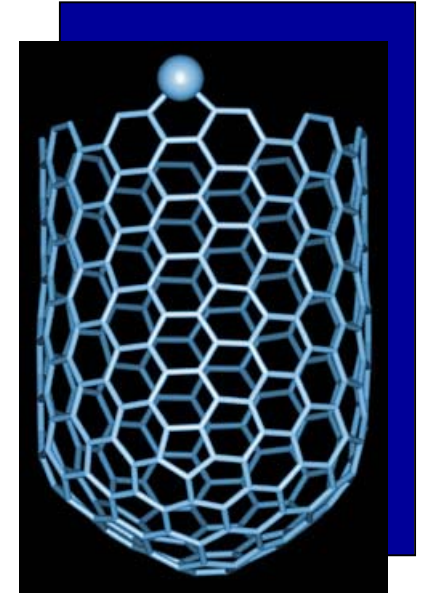
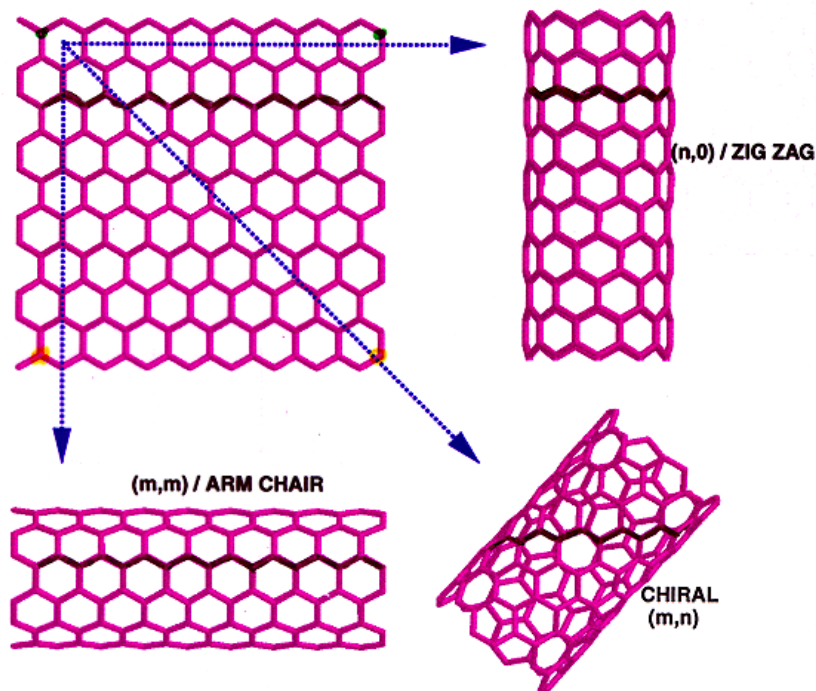
Carbon Nanotube



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.

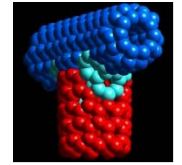
- STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE



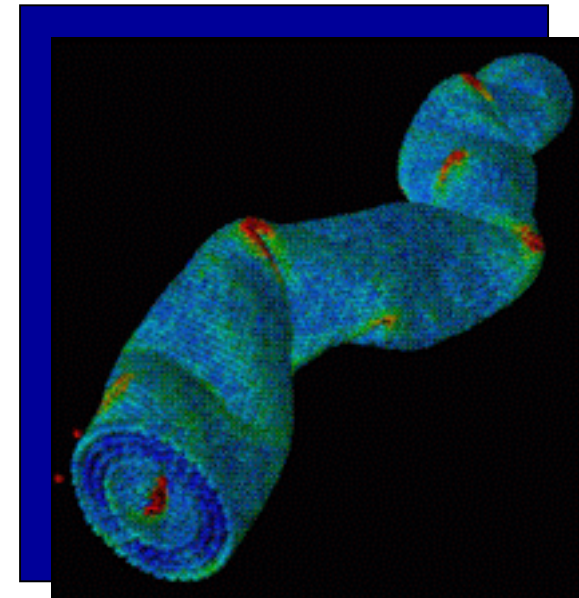
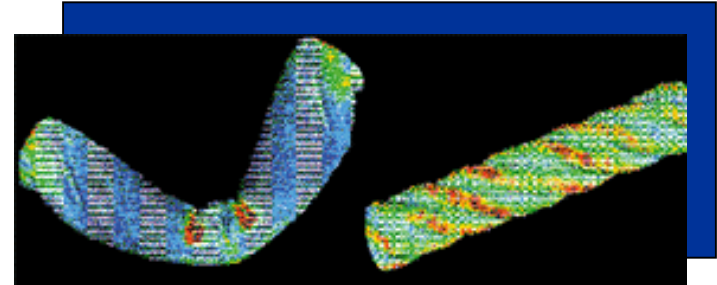
CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal, as stiff as diamond, and tensile strength ~ 200 GPa.

CNT can be metallic or semiconducting, depending on chirality.

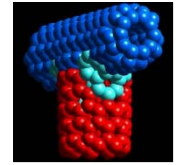
CNT Properties



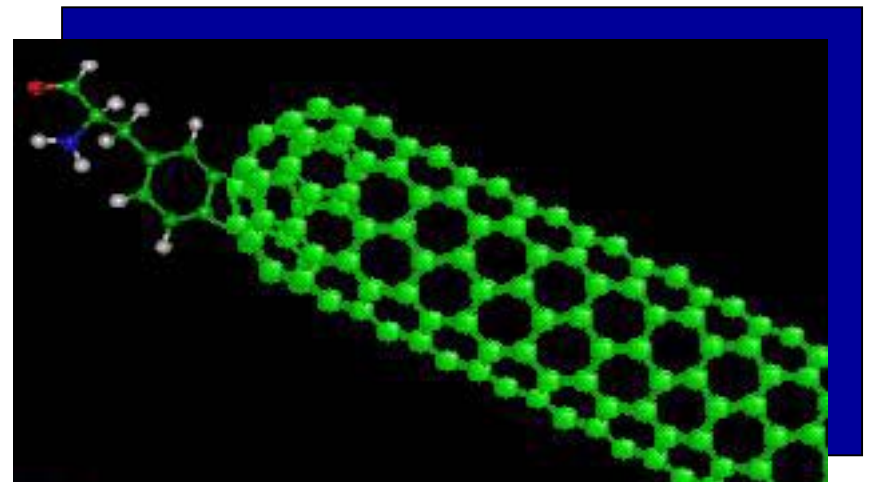
- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture
- Young's modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPa for C-fiber
 - strength to weight ratio 500 times > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy
- Maximum strain $\sim 10\%$ much higher than any material
- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction

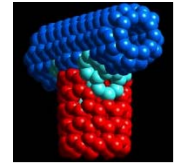


CNT Properties (cont.)

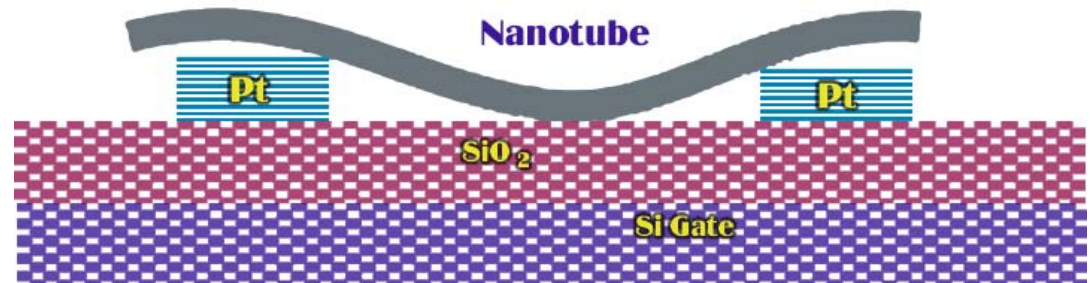


- Electrical conductivity six orders of magnitude higher than copper
- Can be metallic or semiconducting depending on chirality
 - ‘tunable’ bandgap
 - electronic properties can be tailored through application of external magnetic field, application of mechanical deformation...
- Very high current carrying capacity
- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission
- Can be functionalized





- CNT quantum wire interconnects
- Diodes and transistors for computing
- Capacitors
- Data Storage
- Field emitters for instrumentation
- Flat panel displays
- THz oscillators

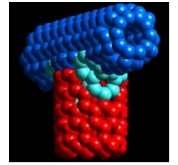


Challenges

- Control of diameter, chirality
- Doping, contacts
- Novel architectures (not CMOS based!)
- Development of inexpensive manufacturing processes



CNT Applications: Structural, Mechanical



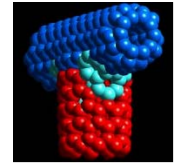
- High strength composites
- Cables, tethers, beams
- Multifunctional materials
- Functionalize and use as polymer back bone
 - plastics with enhanced properties like “blow molded steel”
- Heat exchangers, radiators, thermal barriers, cryotanks
- Radiation shielding
- Filter membranes, supports
- Body armor, space suits

Challenges

- Control of properties, characterization
- Dispersion of CNT homogeneously in host materials
- Large scale production
- Application development



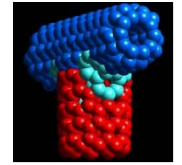
CNT Applications: Sensors, NEMS, Bio



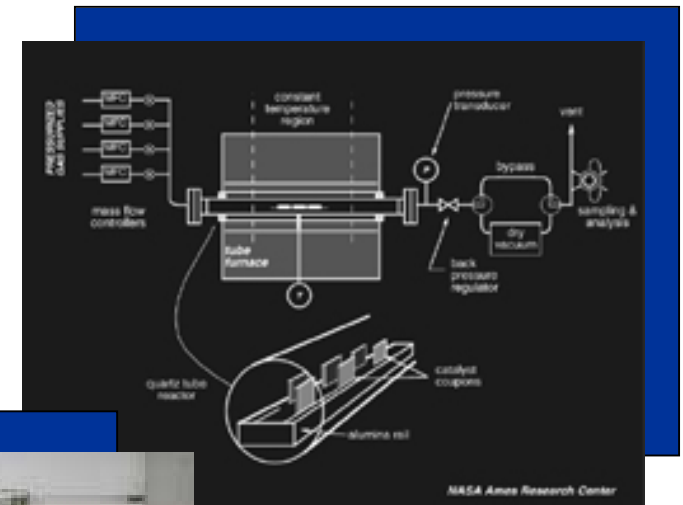
- CNT based microscopy: AFM, STM...
- Nanotube sensors: force, pressure, chemical...
- Biosensors
- Molecular gears, motors, actuators
- Batteries, Fuel Cells: H₂, Li storage
- Nanoscale reactors, ion channels
- Biomedical
 - in vivo real time crew health monitoring
 - Lab on a chip
 - Drug delivery
 - DNA sequencing
 - Artificial muscles, bone replacement, bionic eye, ear...

Challenges

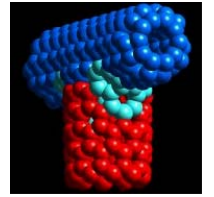
- Controlled growth
- Functionalization with probe molecules, robustness
- Integration, signal processing
- Fabrication techniques



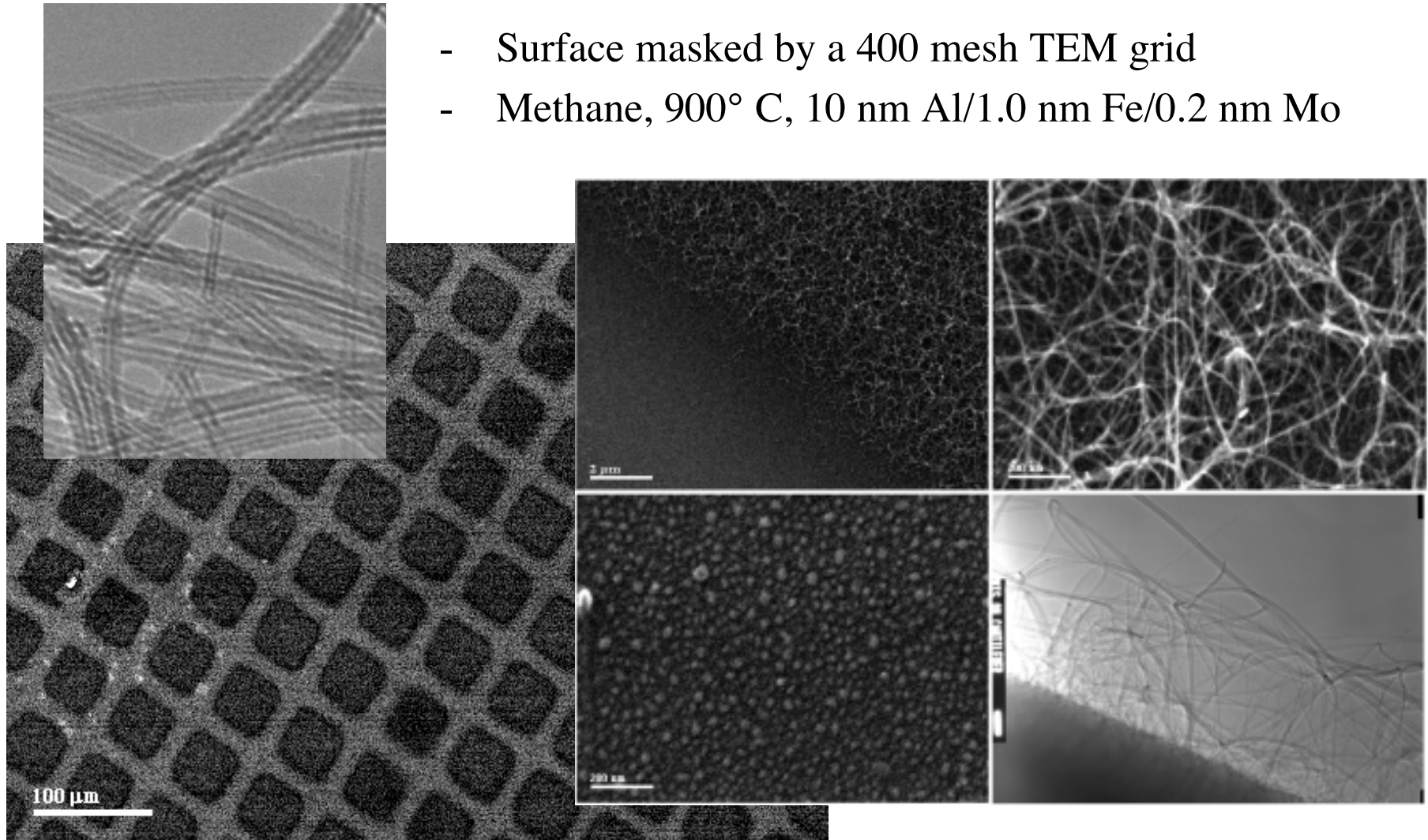
- CNT has been grown by laser ablation (pioneering at Rice) and carbon arc process (NEC, Japan) - early 90s.
 - SWNT, high purity, purification methods
- CVD is ideal for patterned growth (electronics, sensor applications)
 - Well known technique from microelectronics
 - Hydrocarbon feedstock
 - Growth needs catalyst (transition metal)
 - Multiwall tubes at 500-800° deg. C.
 - Numerous parameters influence CNT growth



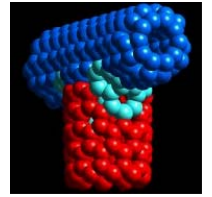
SWNTs on Patterned Substrates



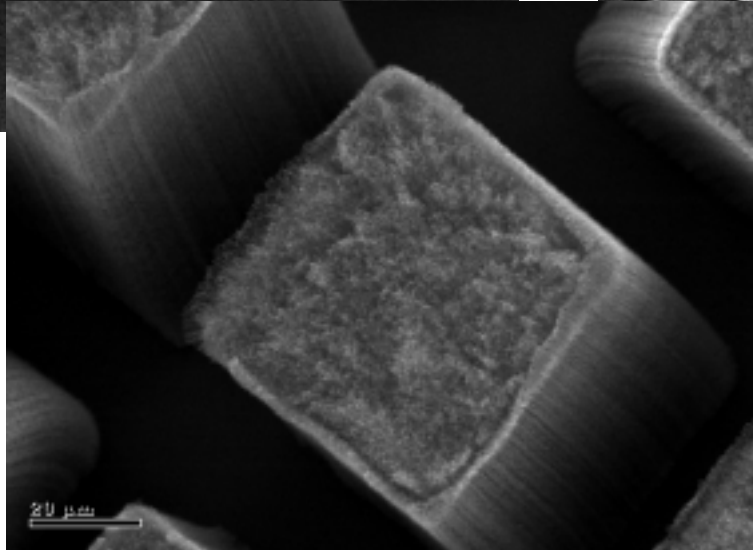
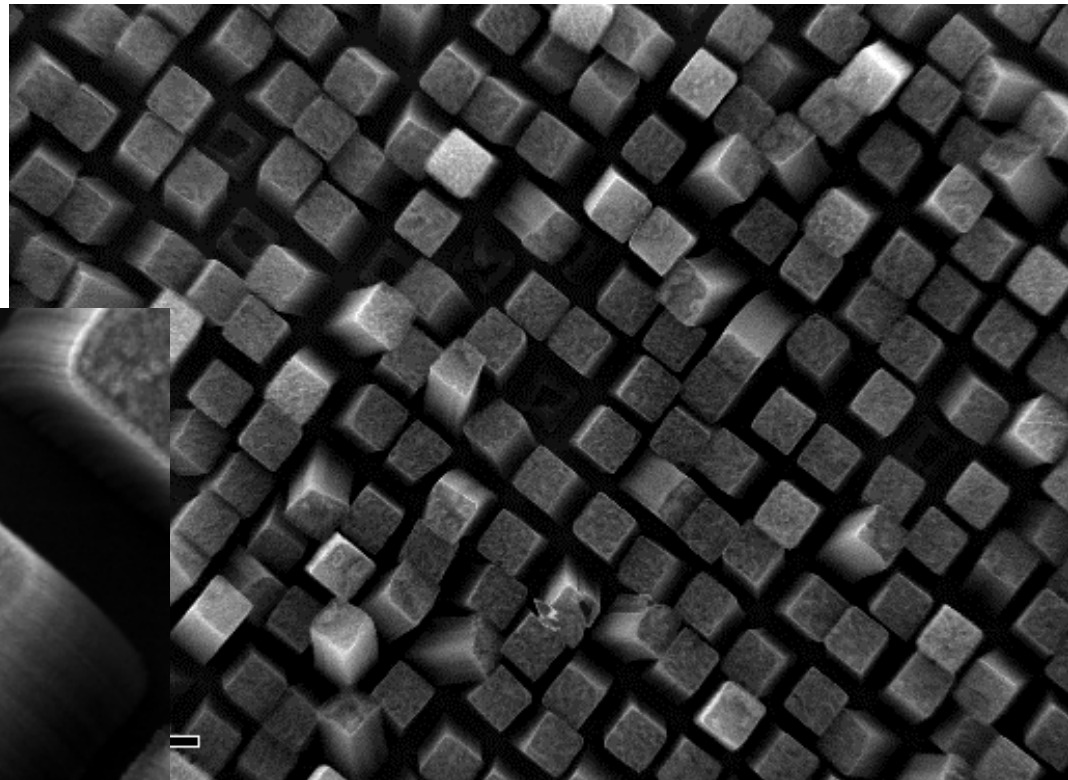
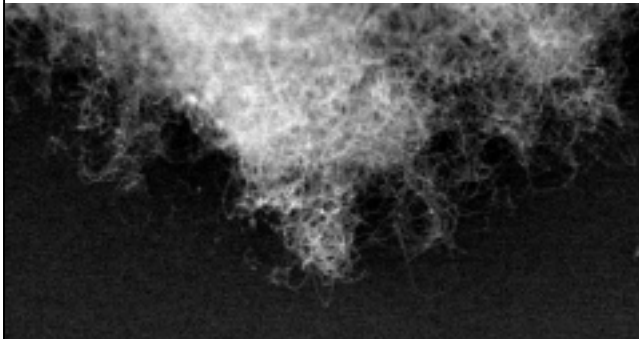
- Surface masked by a 400 mesh TEM grid
- Methane, 900° C, 10 nm Al/1.0 nm Fe/0.2 nm Mo



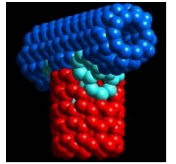
Multiwall Nanotube Towers



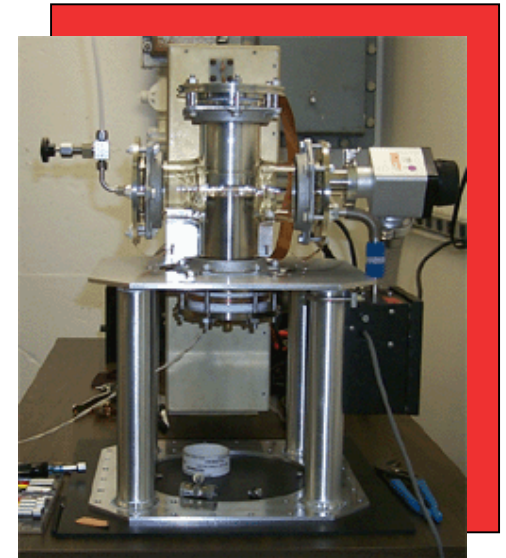
- Surface masked by a 400 mesh TEM grid; 20 nm Al/ 10 nm Fe; nanotubes grown for 10 minutes

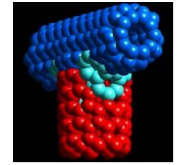


Grown using ethylene @ 75

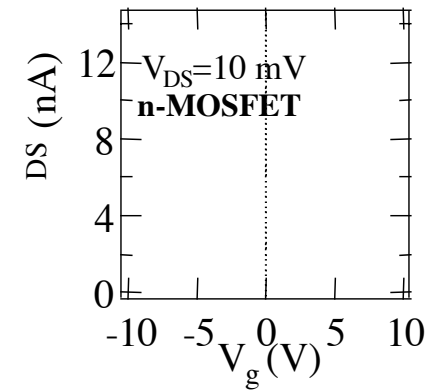
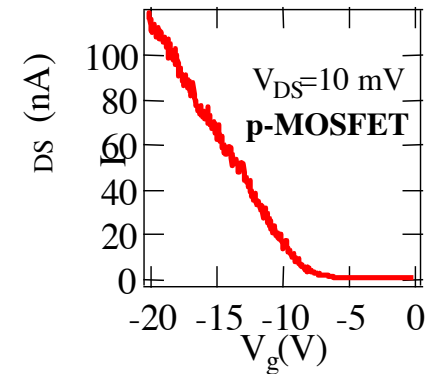
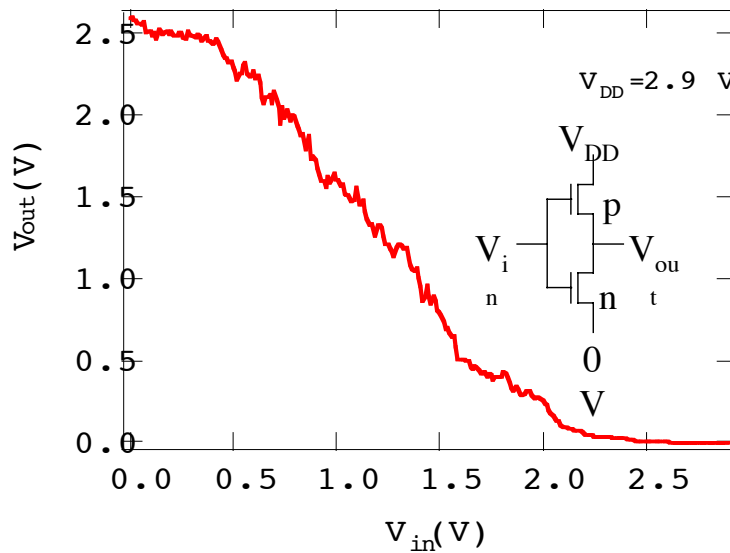
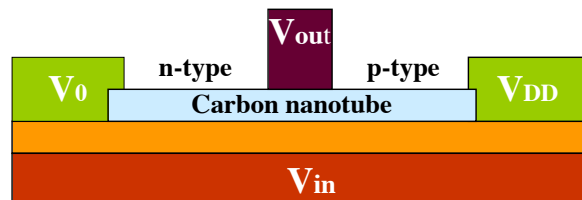


- Inductively coupled plasmas are the simplest type of plasmas; very efficient in sustaining the plasma; reactor easy to build and simple to operate
- Quartz chamber 10 cm in diameter with a window for sample introduction
- Inductive coil on the upper electrode
- 13.56 MHz independent capacitive power on the bottom electrode
- Heating stage for the bottom electrode
- Operating conditions
 - CH₄/H₂ : 5 - 20%
 - Total flow : 100 sccm
 - Pressure : 1 - 20 Torr
 - Inductive power : 100-200 W
 - Bottom electrode power : 0 - 100 W

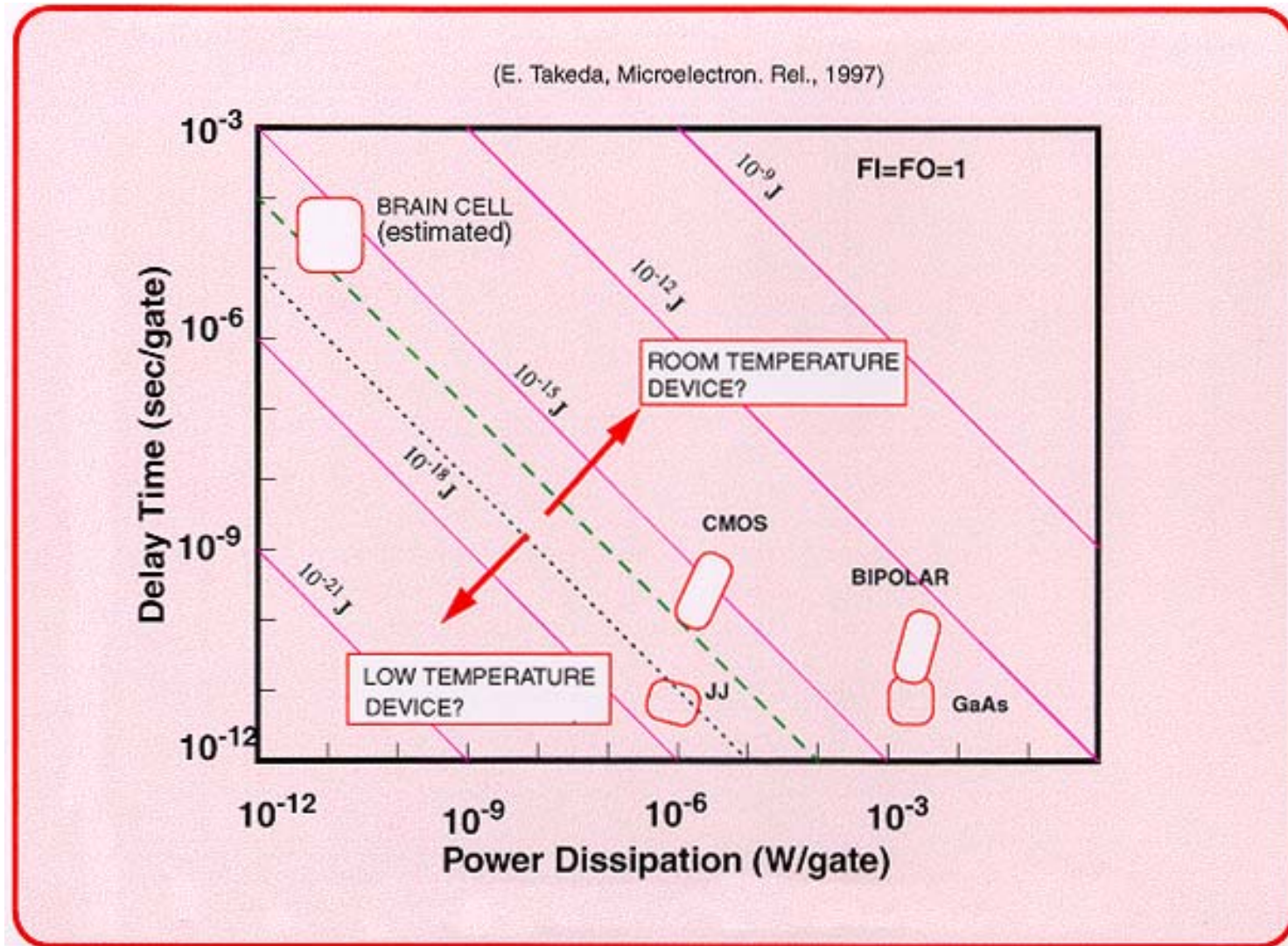
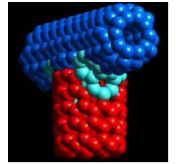




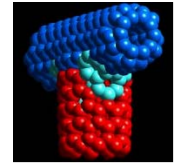
*First single nanotube logic device demonstration, *Appl. Phys. Lett.*, Nov. 2000
 by Chongwu Zhou (USC) and Li Gan (NASA Ames)



Switching Energy of Electron Devices and Brain Cells

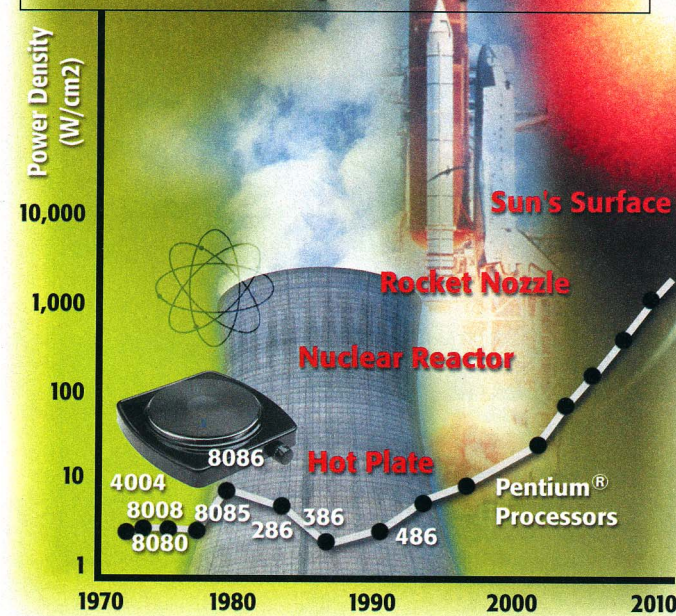


Too Hot to Handle



As device feature size continues to shrink (180 nm \longrightarrow 130 nm \longrightarrow 100 nm) and chip density continues to increase, heat dissipation from the chip is becoming a huge challenge.

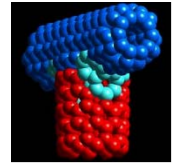
Power Density Extrapolation



SOURCE: INTEL

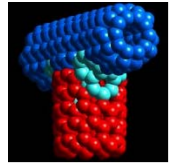


Nanoelectronics: What is Expected from Alternative Technologies? (Beyond the SIA Roadmap for Silicon)

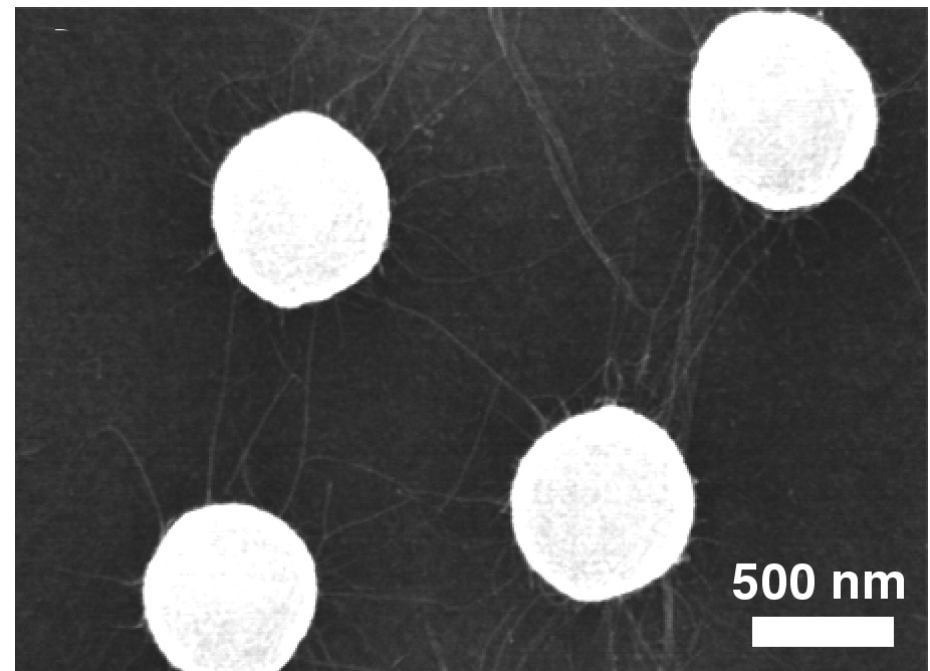
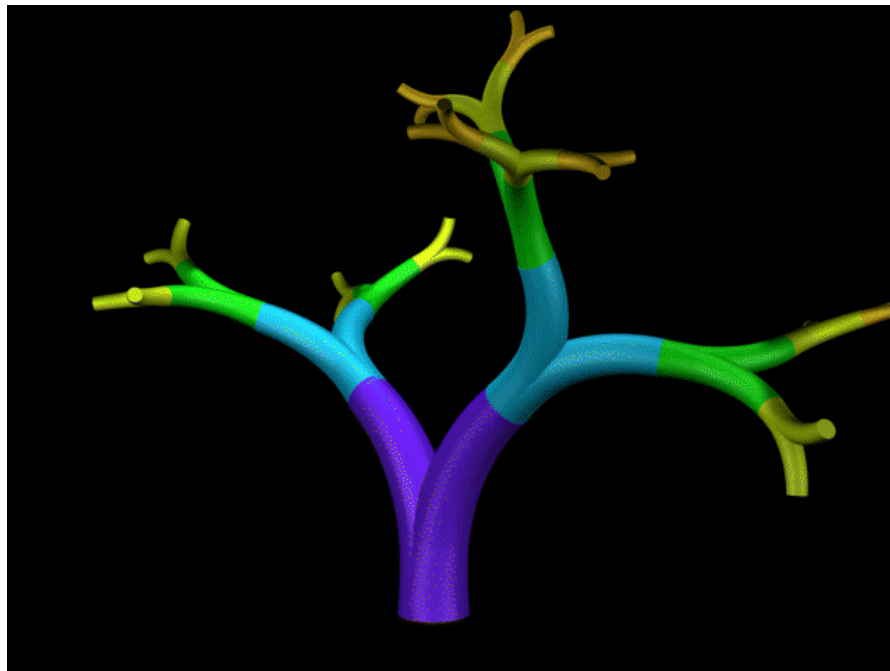


- Must be easier and cheaper to manufacture than CMOS
- Need high current drive; should be able to drive capacitances of interconnects of any length
- High level of integration ($>10^{10}$ transistors/circuit)
- High reproducibility (better than $\pm 5\%$)
- Reliability (operating time > 10 years)
- Very low cost ($< 1 \mu\text{cent/transistor}$)
- Better heat dissipation characteristics and amenable solutions
- Everything about the new technology must be compelling and simultaneously further CMOS scaling must become difficult and not cost-effective. Until these two happen together, the enormous infrastructure built around silicon will keep the silicon engine humming....

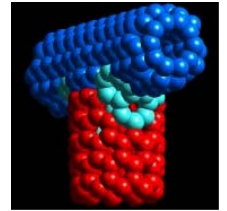
Four-level CNT Dendritic Neural Tree



- Neural tree with 14 symmetric Y-junctions
- Branching and switching of signals at each junction similar to what happens in biological neural network
- Neural tree can be trained to perform complex switching and computing functions
- Not restricted to only electronic signals; possible to use acoustic, chemical or thermal signals

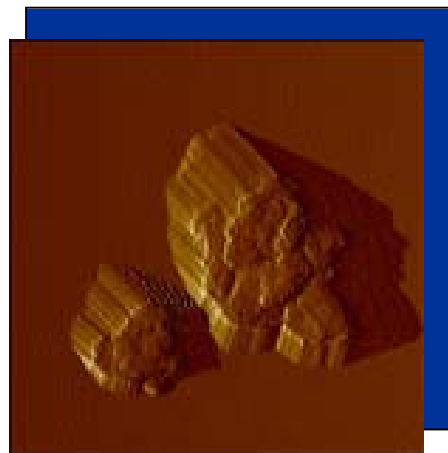
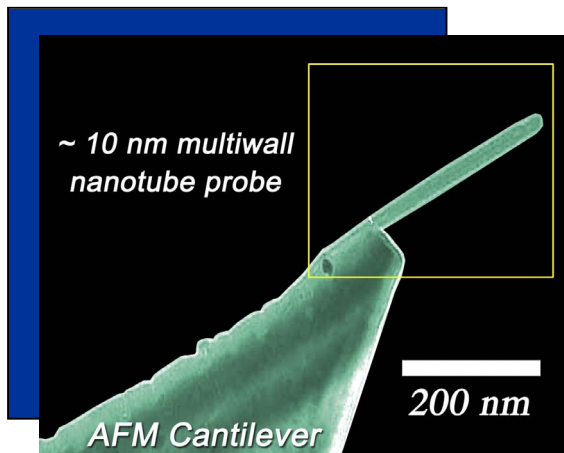


CNT in Microscopy

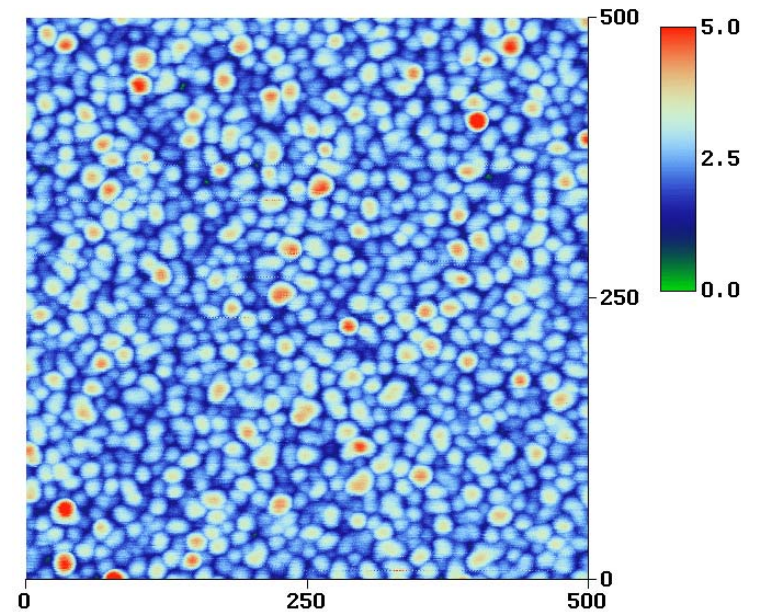


Atomic Force Microscopy is a powerful technique for imaging, nanomanipulation, as platform for sensor work, nanolithography...

Conventional silicon or tungsten tips wear out quickly.
CNT tip is robust, offers amazing resolution.



Simulated Mars dust

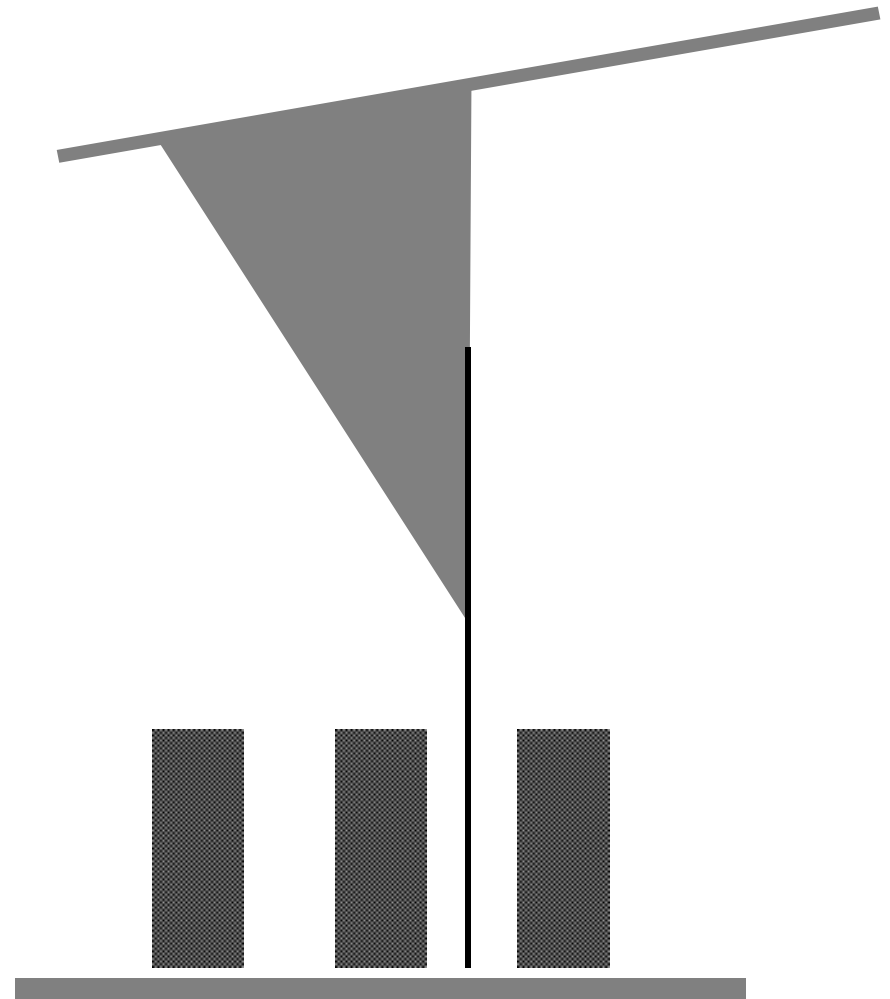
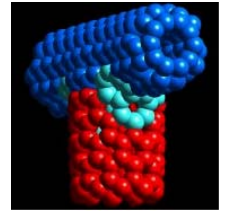


2 nm thick Au on Mica

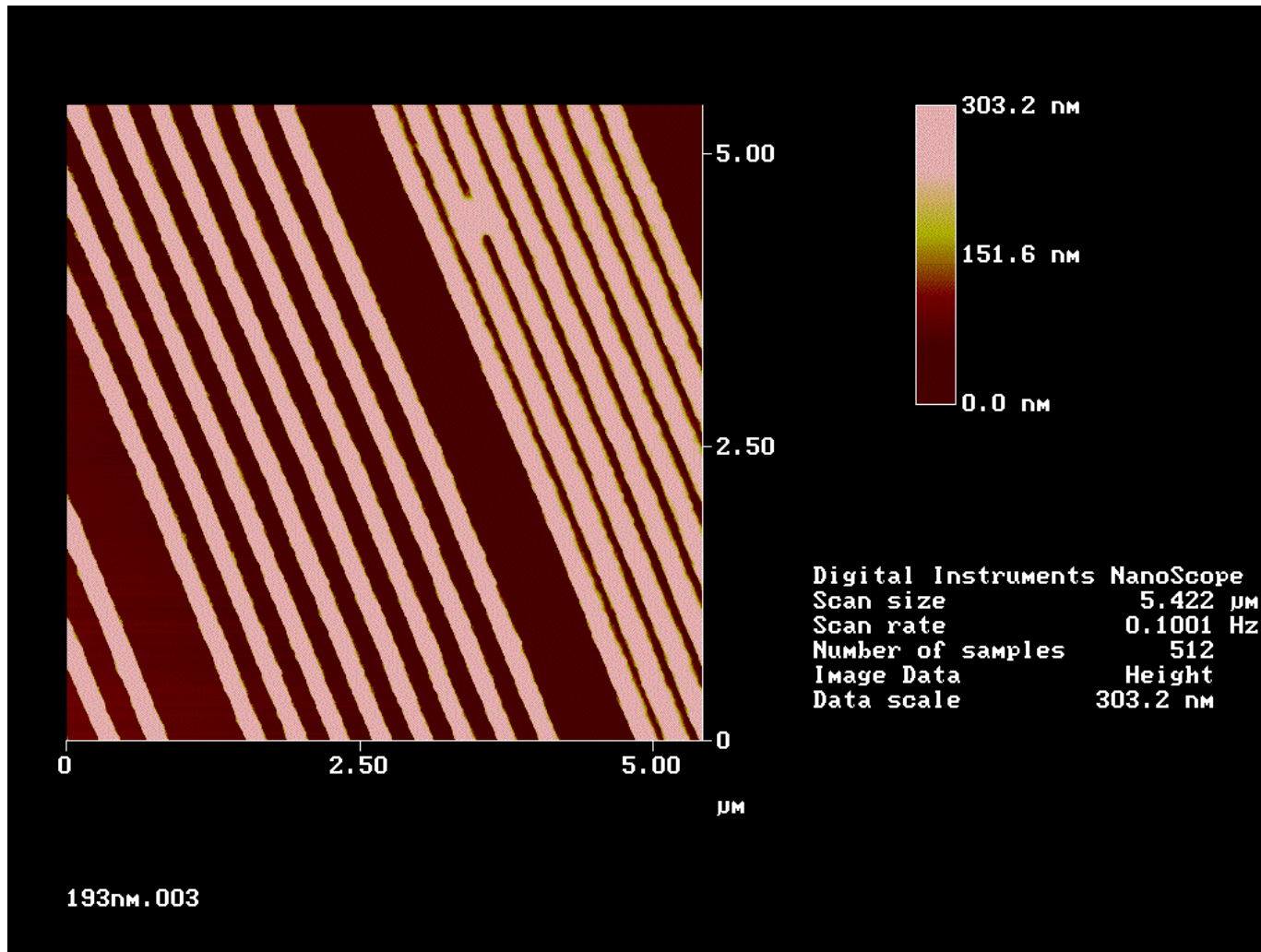
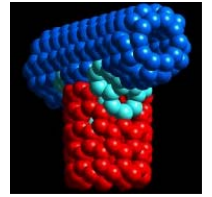


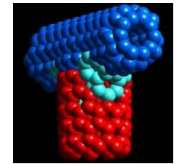
NASA Ames Research Center
Ramsey Stevens, Lance Delzeit, Cattien Nguyen

MWNT Scanning Probe

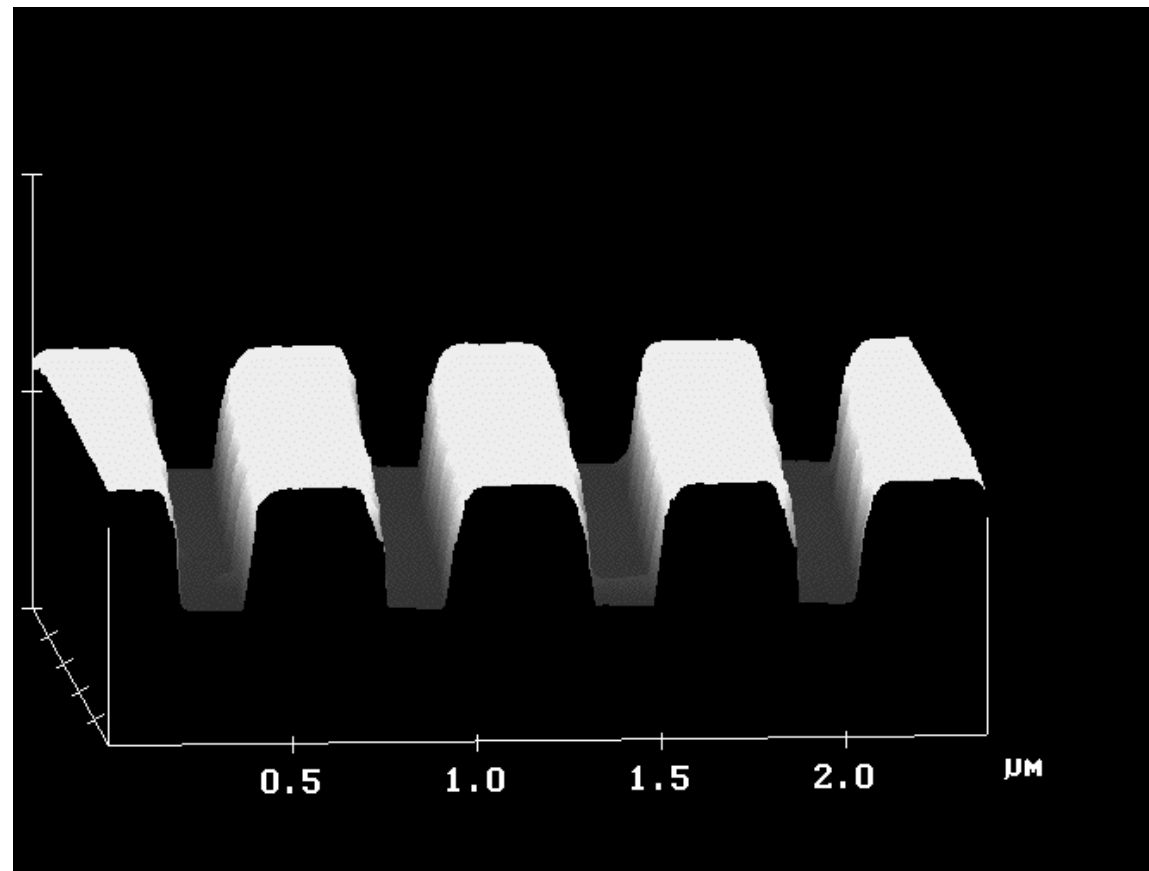


AFM Image with a MWNT Tip 193 nm IBM Version 2 Resist

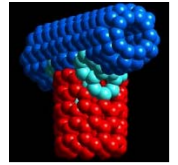




DUV Photoresist Patterns Generated by Interferometric Lithography



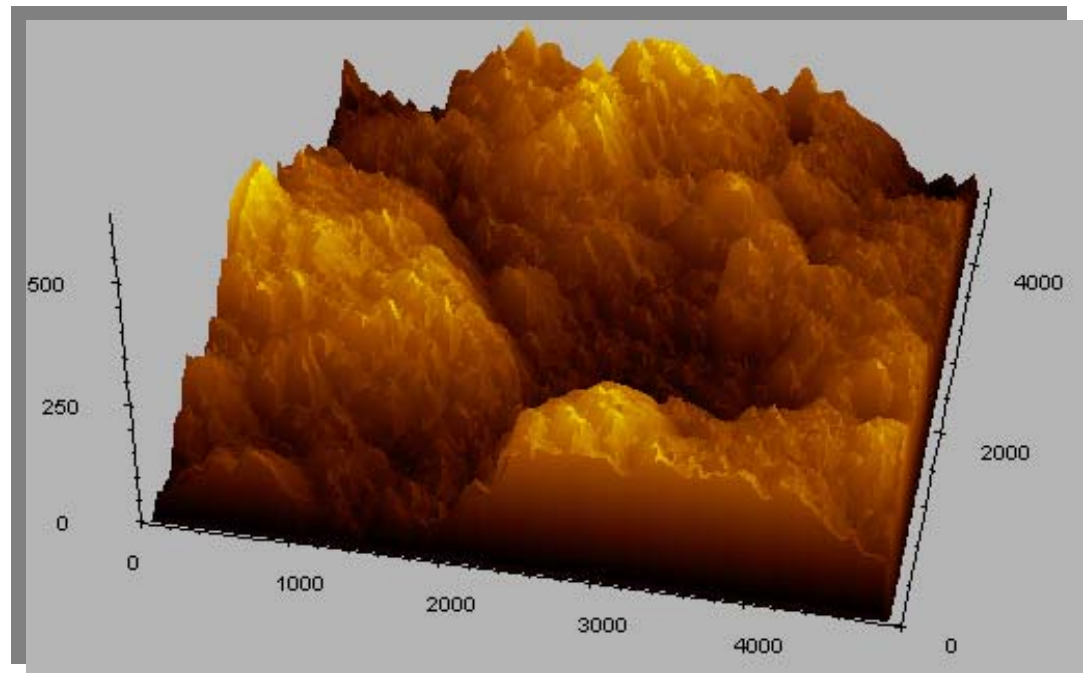
Nguyen et al., *App. Phys. Lett.*, 81, 5, p. 901 (2002).



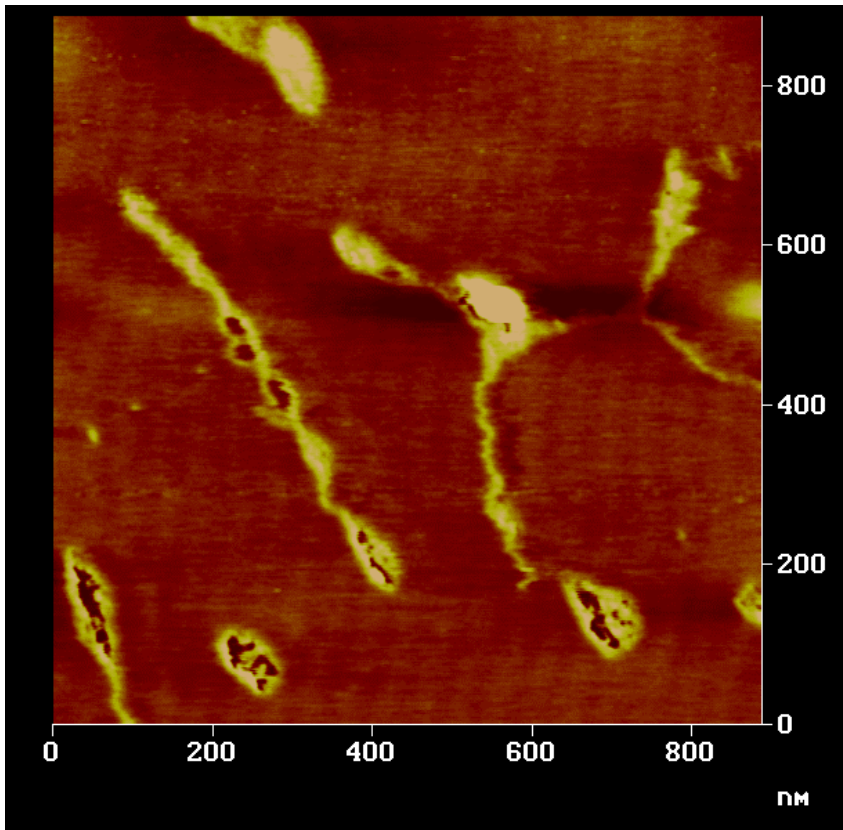
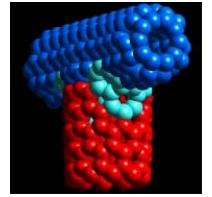
Optical image

Red Dune Sand (Mars Analog)

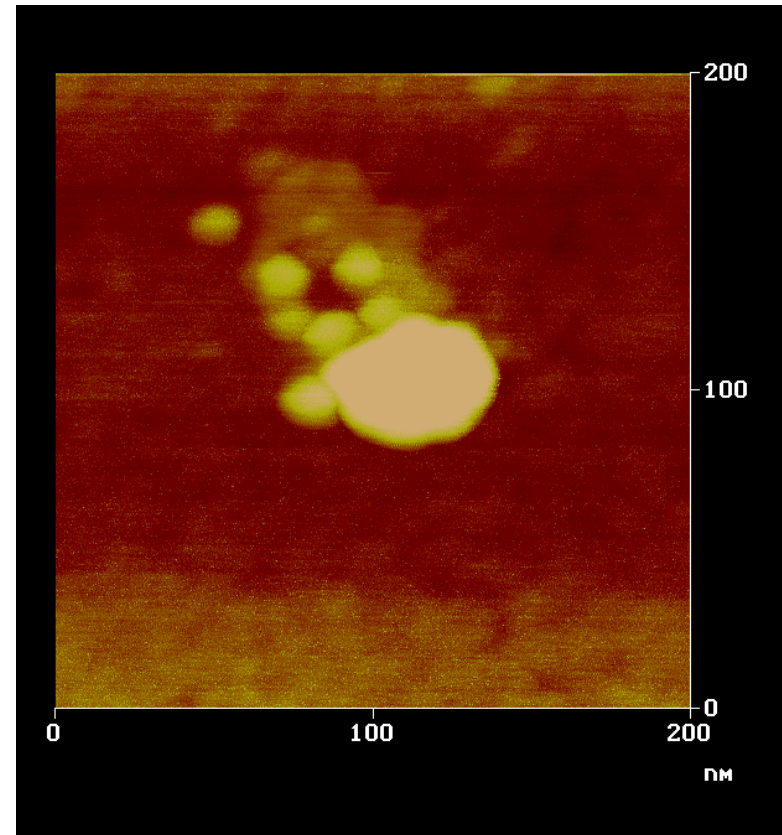
AFM image using
carbon nanotube tip



High Resolution Imaging of Biological Materials

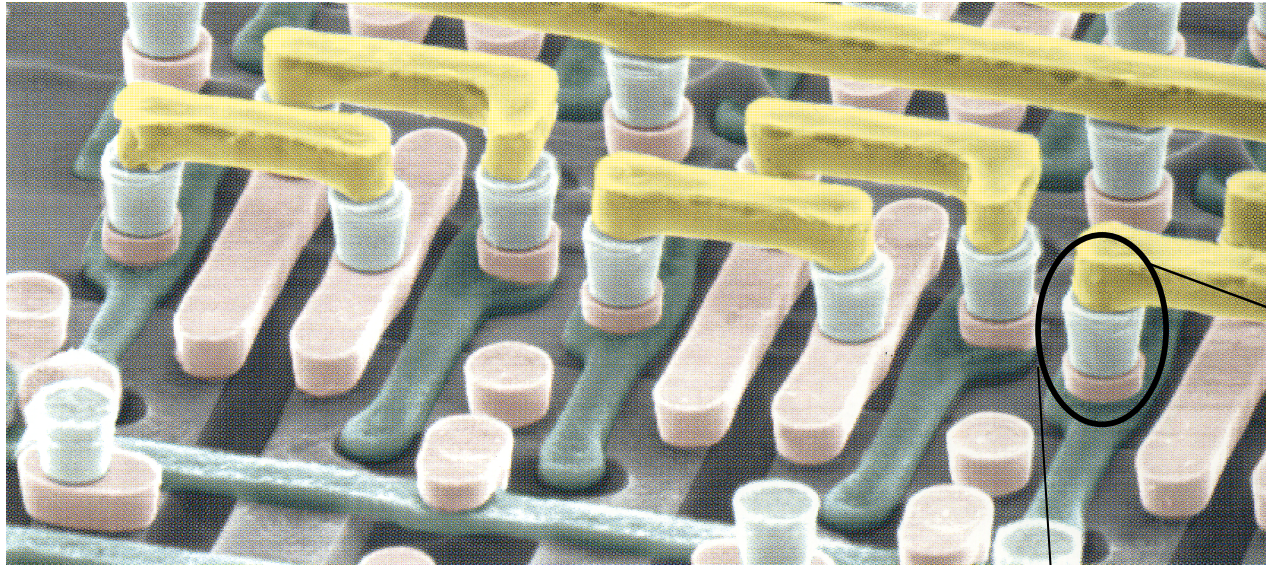


DNA



PROTEIN

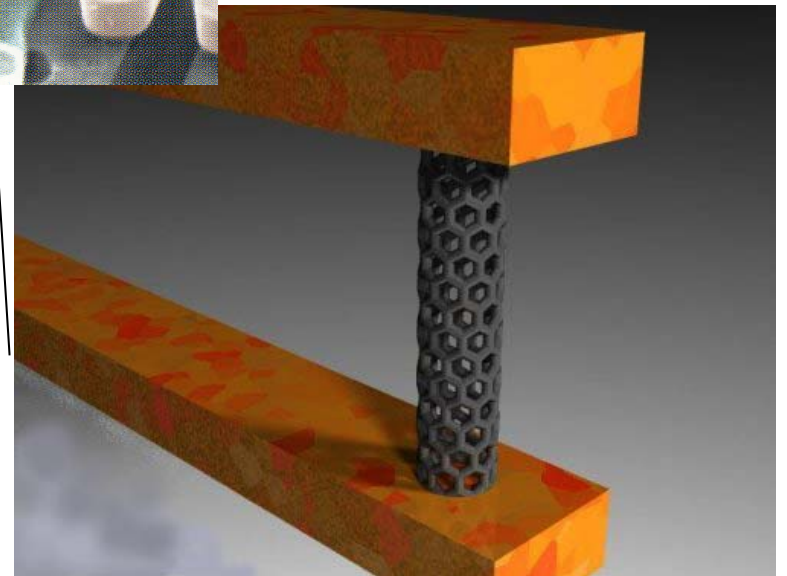
MWNT Interconnects ?



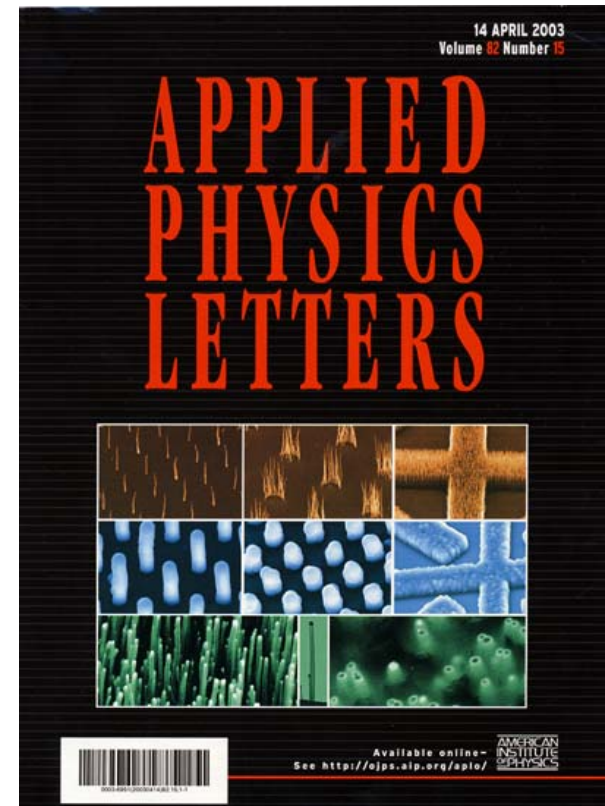
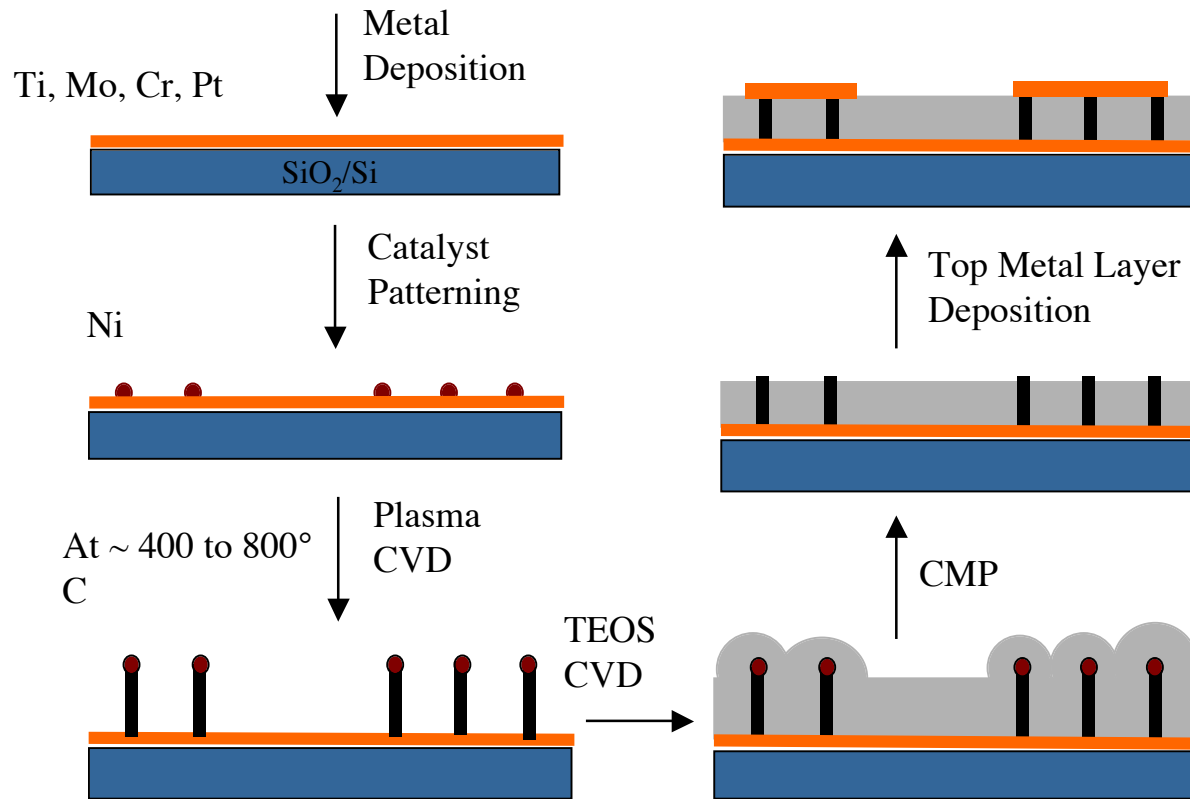
CNT advantages:

- (1) Small diameter
- (2) High aspect ratio
- (3) Highly conductive along the axis
- (4) High mechanical strength

Question: How to do this ?

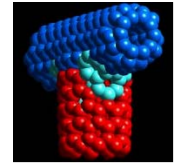


Bottom-up Approach for CNT Interconnects

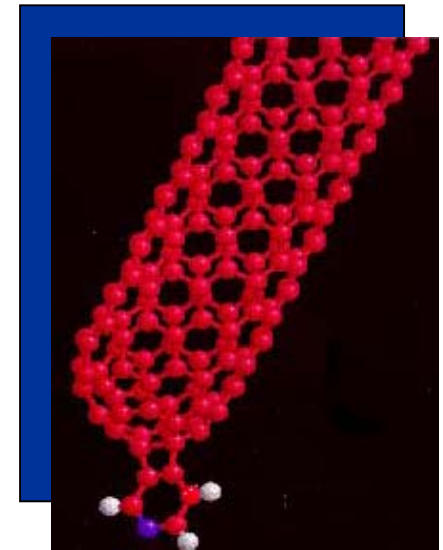


J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han, M. Meyyappan, *Appl. Phys. Lett.*, **82**(15), 2491 (2003)

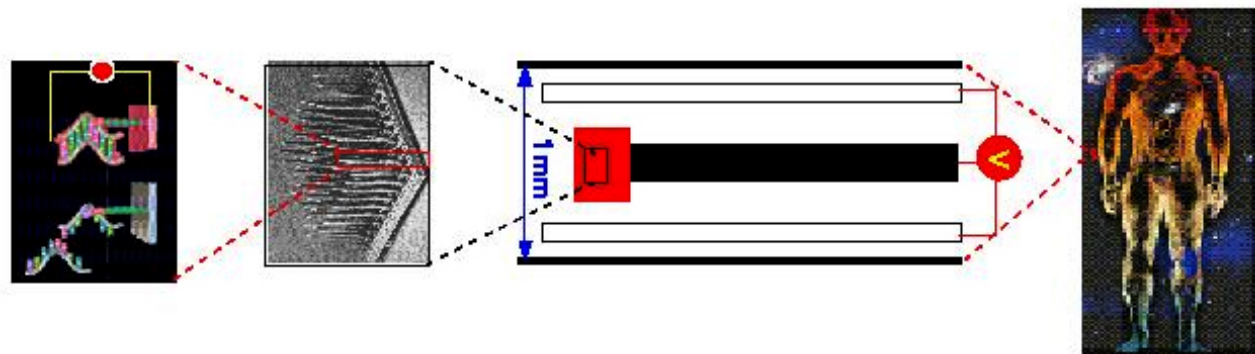
CNT Based Biosensors



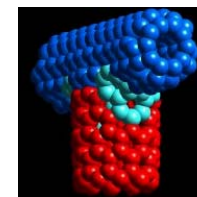
- Our interest is to develop sensors for astrobiology to study origins of life. CNT, though inert, can be functionalized at the tip with a probe molecule. Current study uses AFM as an experimental platform.
- The technology is also being used in collaboration with NCI to develop sensors for cancer diagnostics
 - Identified probe molecule that will serve as signature of leukemia cells, to be attached to CNT
 - Current flow due to hybridization will be through CNT electrode to an IC chip.
 - Prototype biosensors catheter development



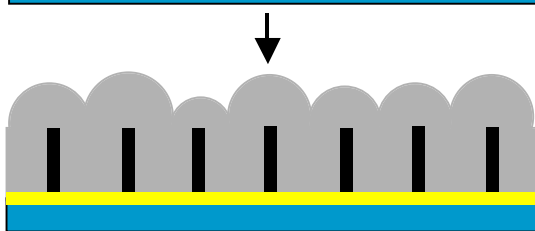
- **High specificity**
- **Direct, fast response**
- **High sensitivity**
- **Single molecule and cell signal capture and detection**



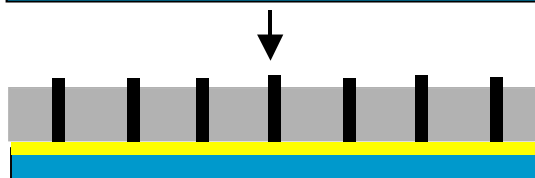
The Fabrication of CNT Nanoelectrode Array



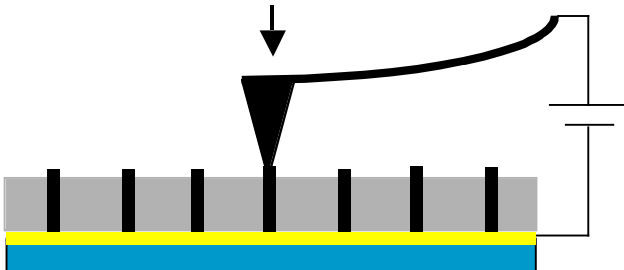
**(1) Growth of Vertically Aligned
CNT Array**



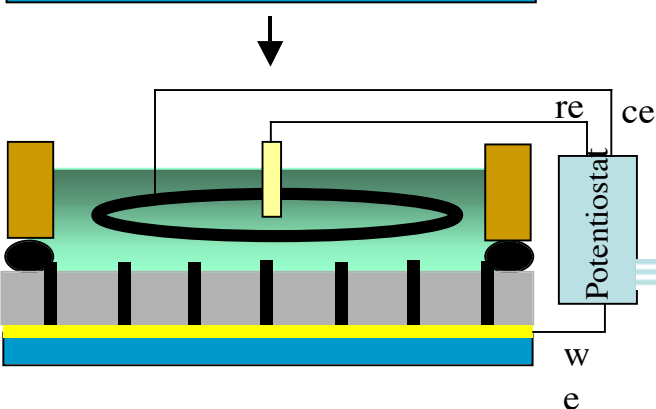
(2) Dielectric Encapsulation



(3) Planarization



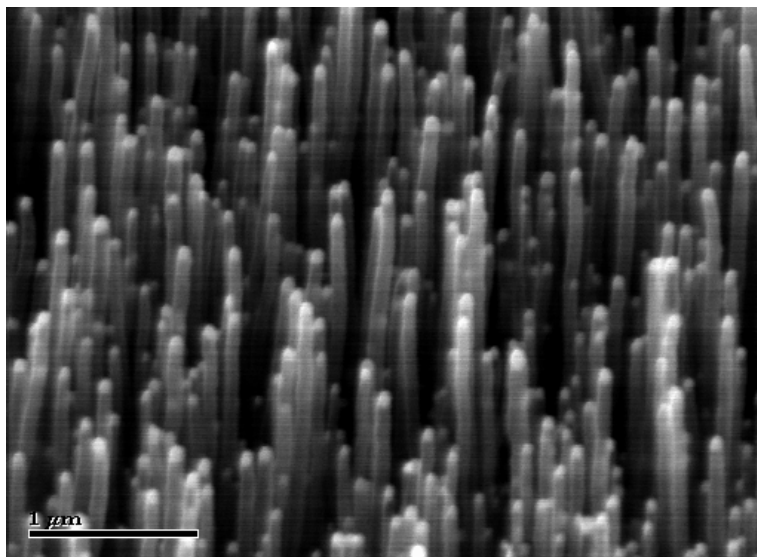
**(4) Electrical Property Characterization
By Current-sensing AFM**



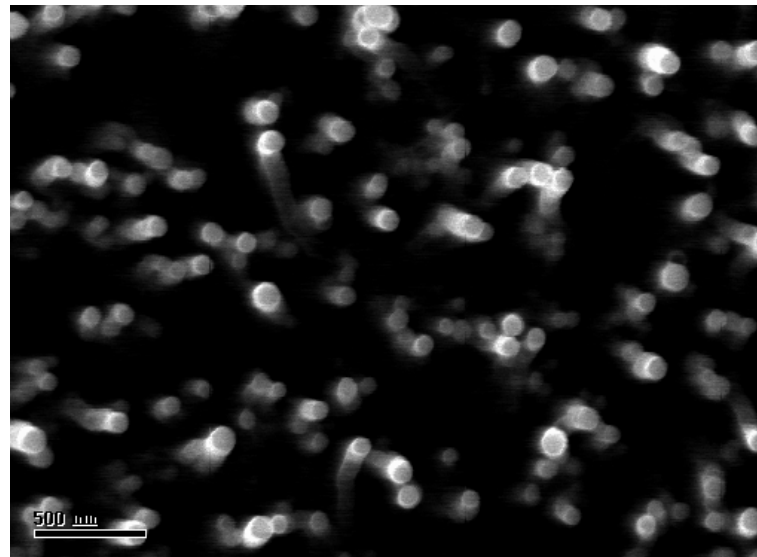
**(5) Electrochemical
Characterization**



Fabrication of CNT Nanoelectrodes

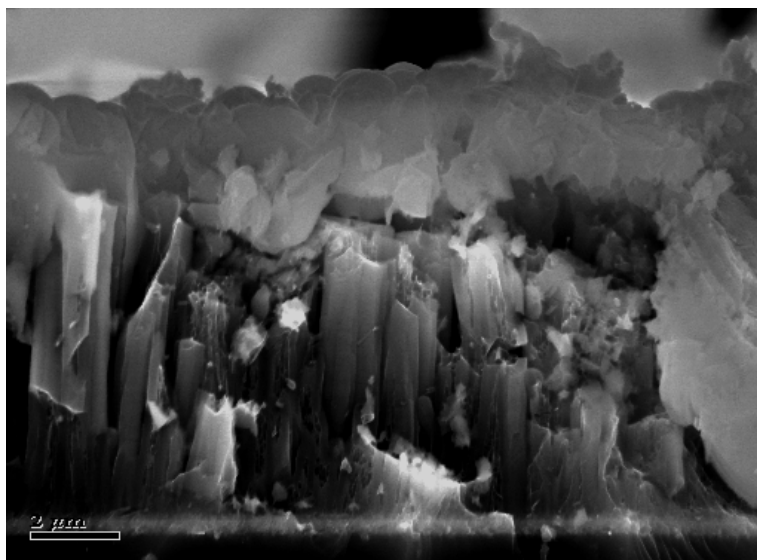


45 degree perspective view

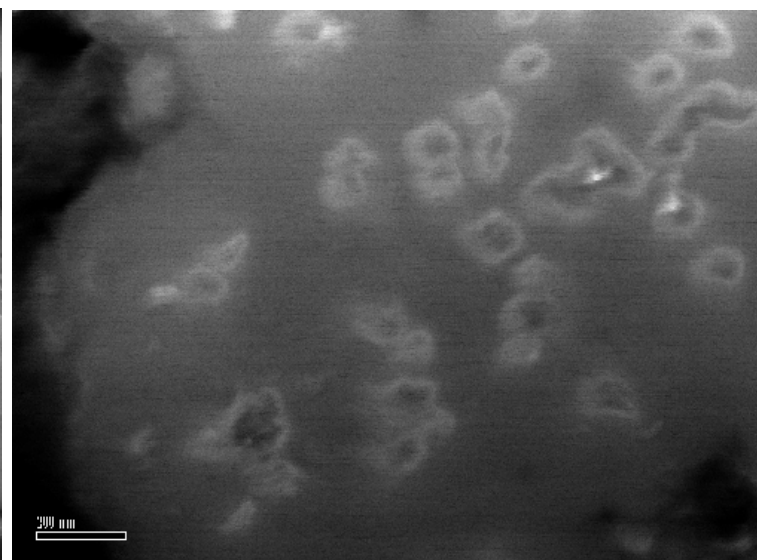


Top view

J. Li et al, *Appl. Phys. Lett.*, **81**(5), 910 (2002)

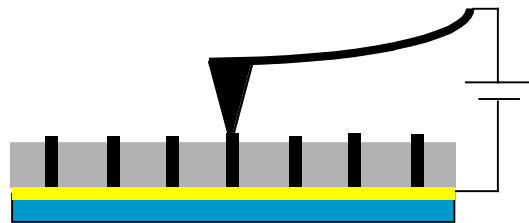
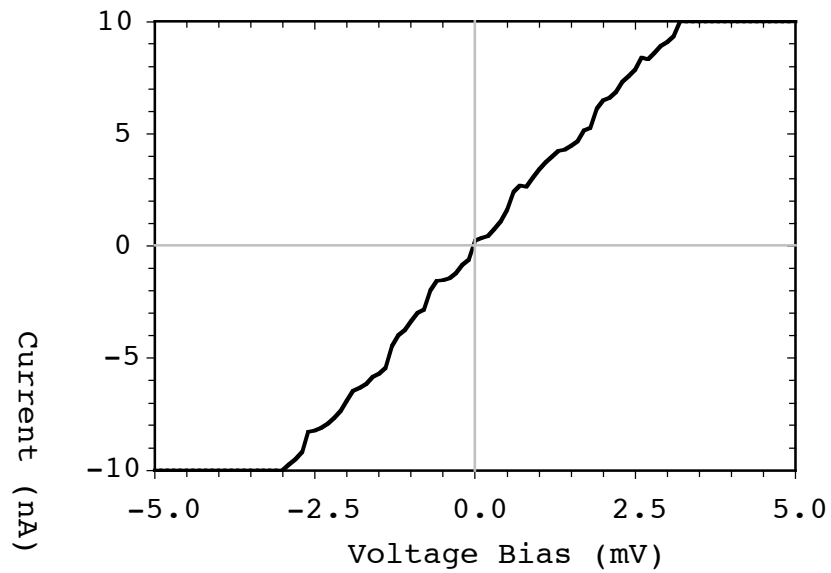
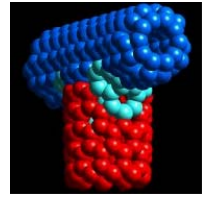


Side view after encapsulation

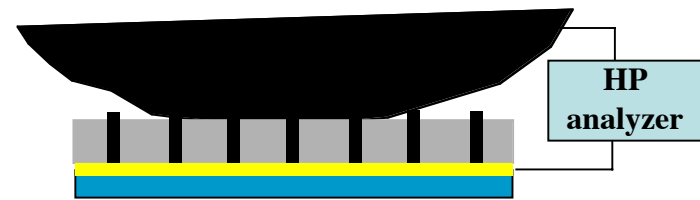
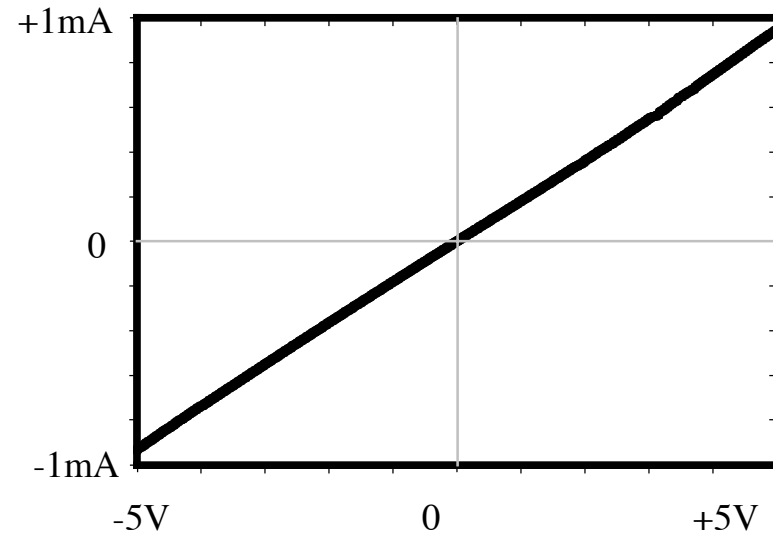


Top view after planarization

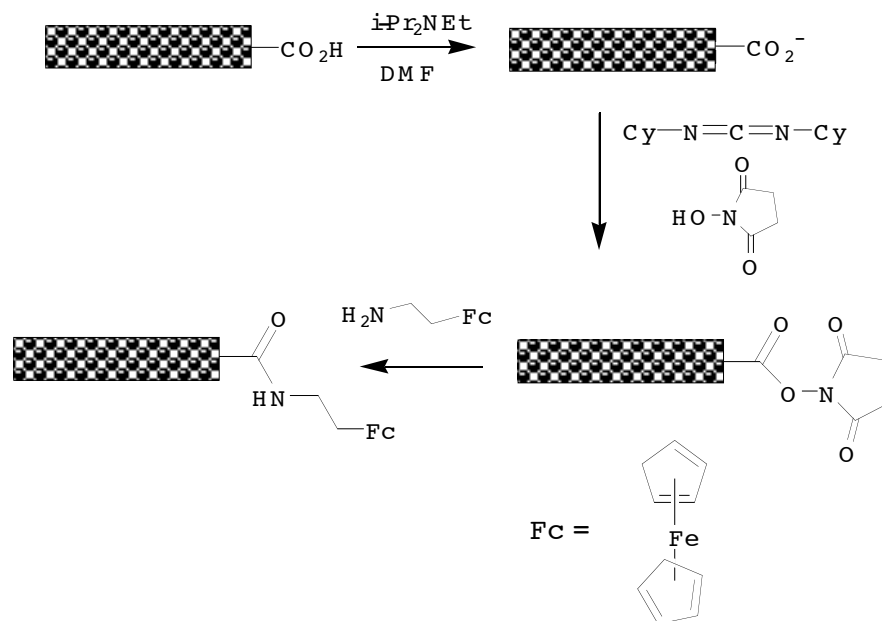
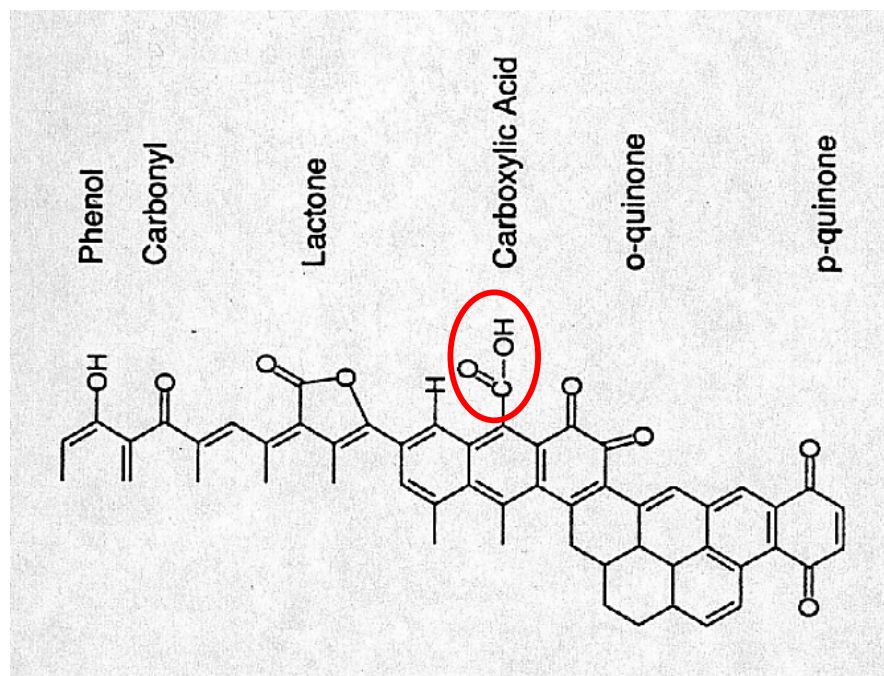
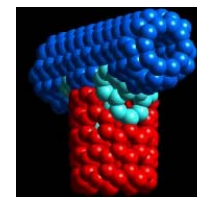
Electrical Properties of CNTs



Current Sensing AFM

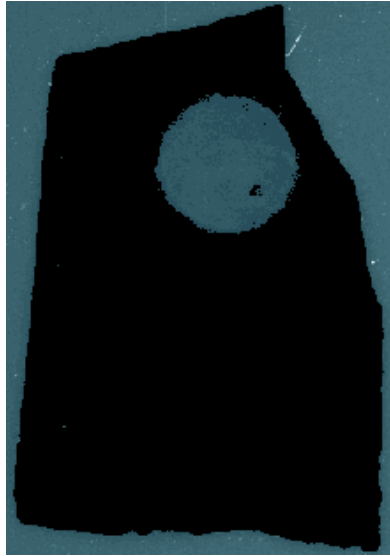
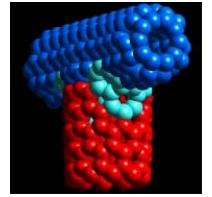


Four-probe station
And HP parameter analyzer

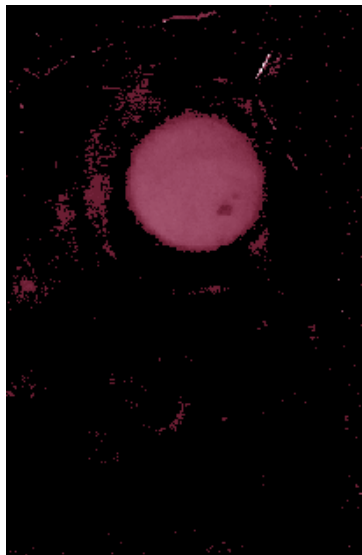


Highly selective reaction of primary amine with surface $-\text{COOH}$ group

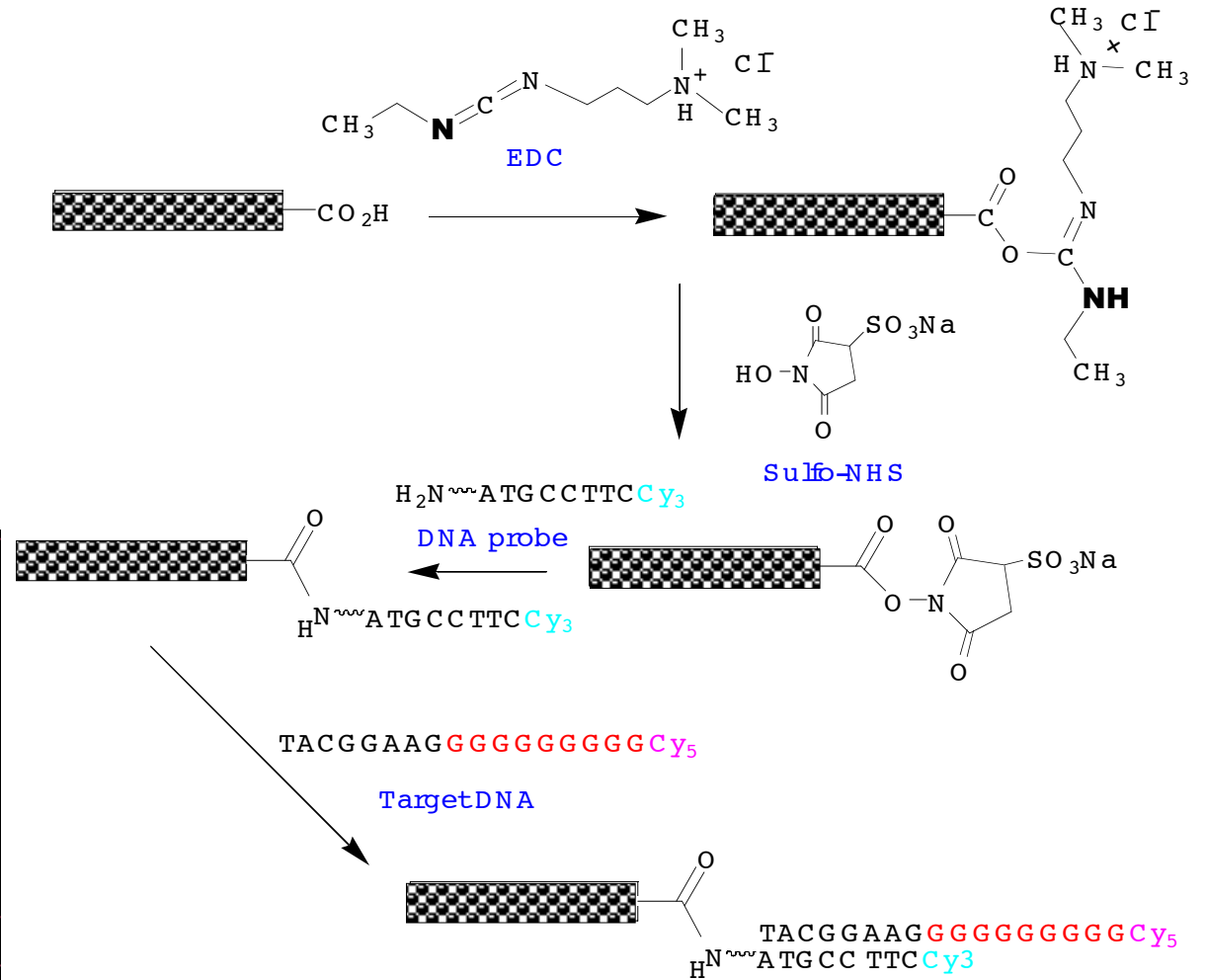
Functionalization of DNA



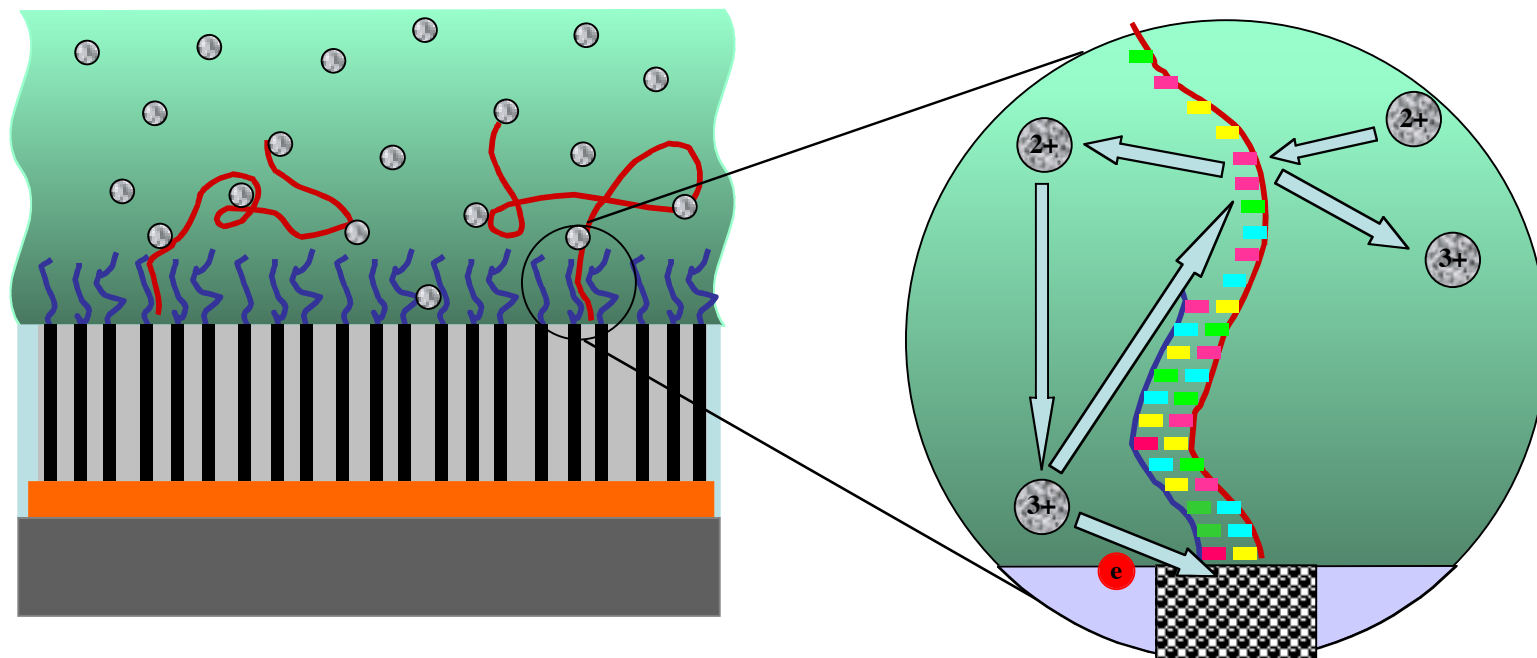
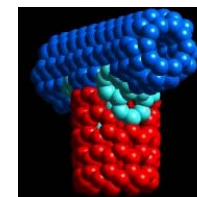
Cy3 image



Cy5 image



CNT DNA Sensor Using Electrochemical Detection

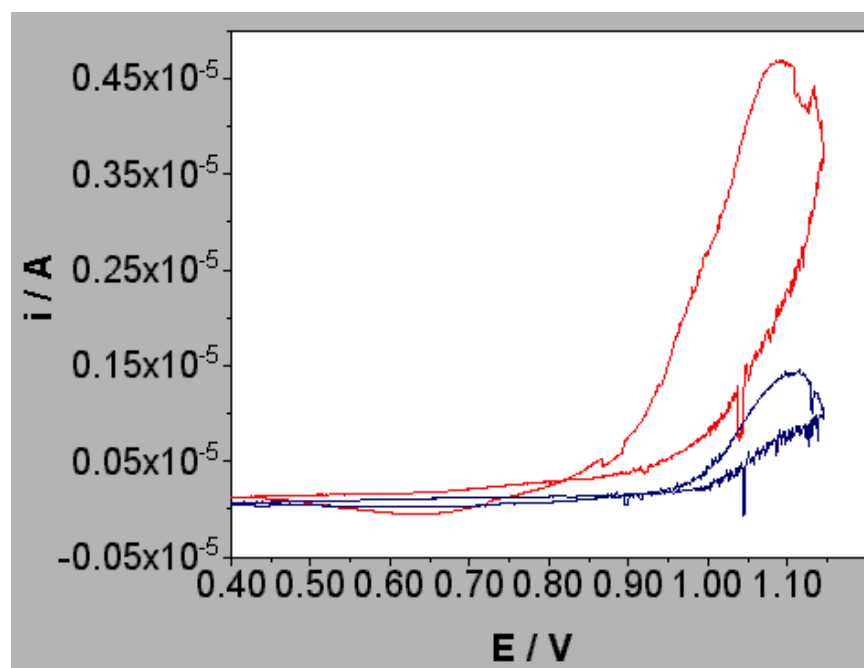
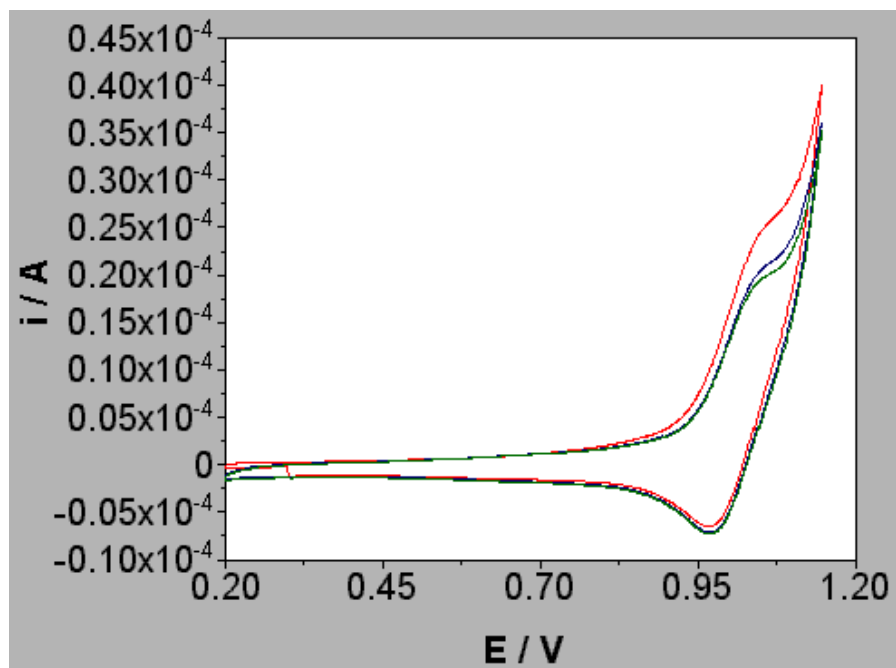
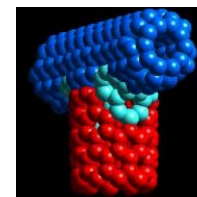


❑ MWNT array electrode functionalized with DNA/PNA probe as an ultrasensitive sensor for detecting the hybridization of target DNA/RNA from the sample.

- Signal from redox bases in the excess DNA single strands

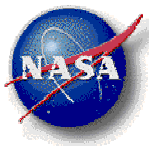
❑ The signal can be amplified with metal ion mediator $[Ru(bPy)_3]^{2+}$ oxidation catalyzed by Guanine.

Electrochemical Detection of DNA Hybridization

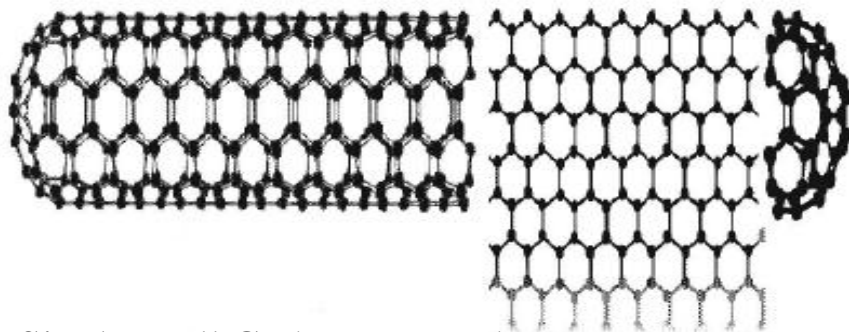


1st, 2nd, and 3rd cycle in cyclic voltammetry

1st – 2nd scan: mainly DNA signal
2nd – 3rd scan: Background

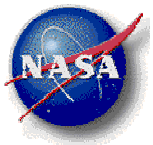


Single-Walled Carbon Nanotubes For Chemical Sensors



Single Wall Carbon Nanotube

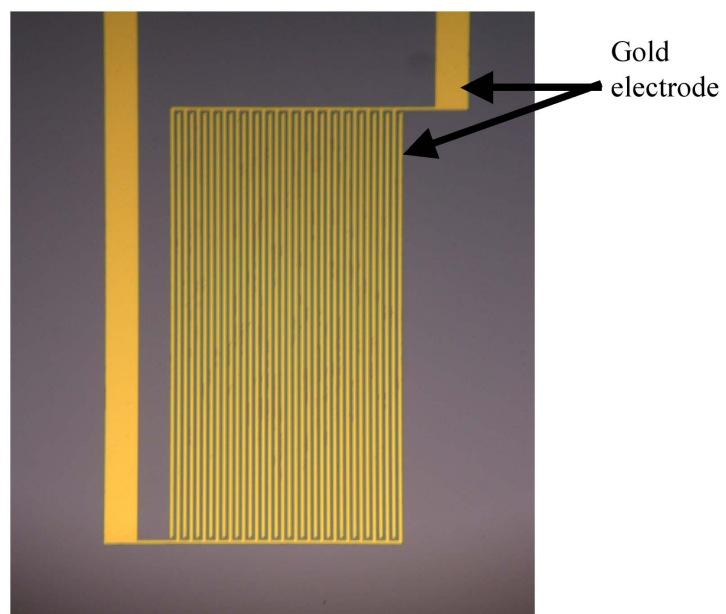
- Every atom in a single-walled nanotube (SWNT) is on the surface and exposed to environment
- Charge transfer or small changes in the charge-environment of a nanotube can cause drastic changes to its electrical properties



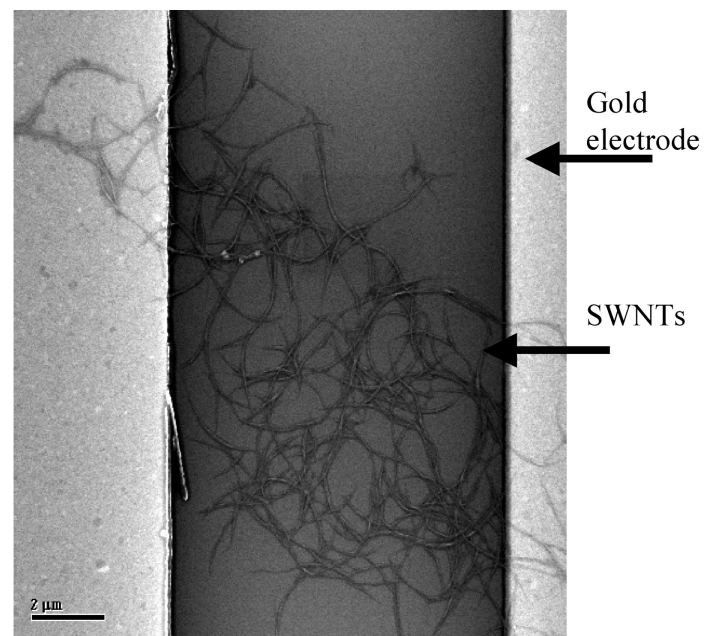
SWNT Sensor Assembly

- Purified SWNTs in DMF solution
- Cast the SWNT/DMF onto IDE

a

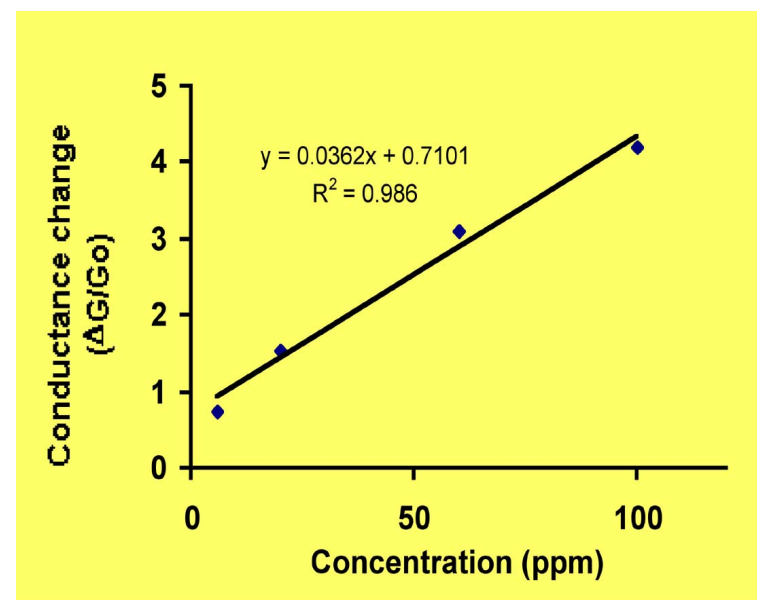
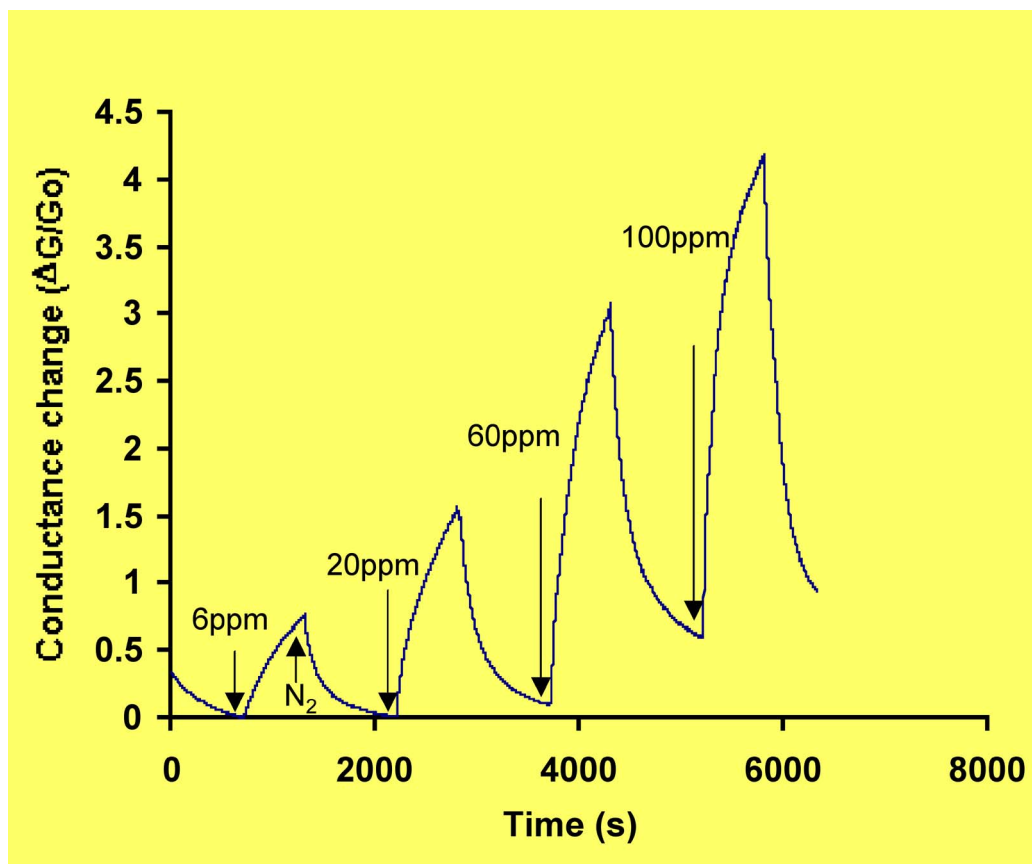


b





SWNT Sensor Response to NO₂ with UV Light Aiding Recovery



Detection limit to NO₂ is 44 ppb.



Motivations for selecting Single Crystalline Nanowires & Nanowalls (in Nano-scale Electronics)

- ❖ High single crystallinity ⇒ Low defect density, grain boundary free
- ⌘ Well-defined surface structural properties ⇒ Enhanced interfacial engineering
- ❖ Predictable electron transport properties ⇒ Predictable device performance
- ❖ Unique physical properties due to quantum confinement effects ⇒ Enhancement in device characteristics
- ❖ Tunable electronic properties by doping ⇒ Enhancement in device characteristics
- ❖ Truly bottom-up integration approach ⇒ Innovative fabrication schemes
- ❖ Potential to revolutionize nano-scale science and technology



Challenges in Nanowire Growth

- Uni-directional nanowire growth; vertical or horizontal
- Uniform nanowire diameter
- Acceptable uniform height ($\pm 10\%$)
- Localized single nanowire growth
- High structural integrity

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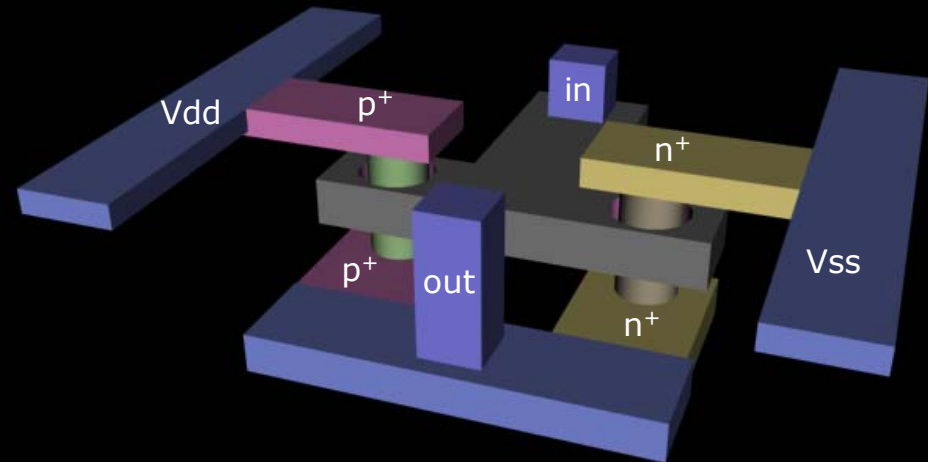
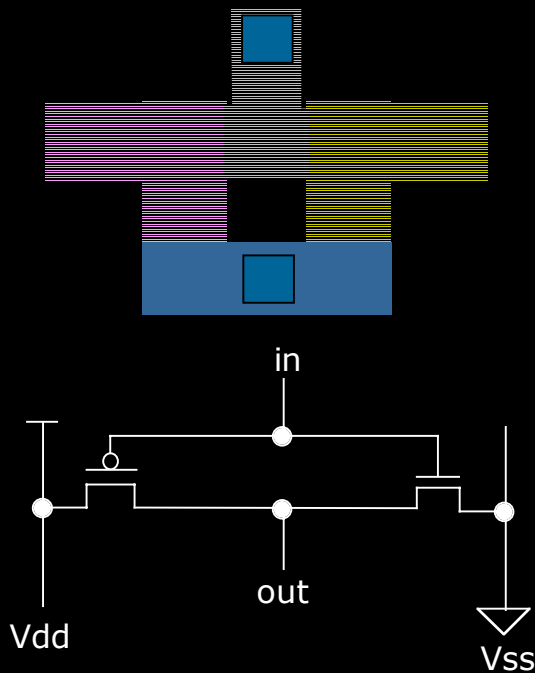
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substrate engineering
electric field directed
soft template control
reactor optimization
substrate patterning
materials characterization

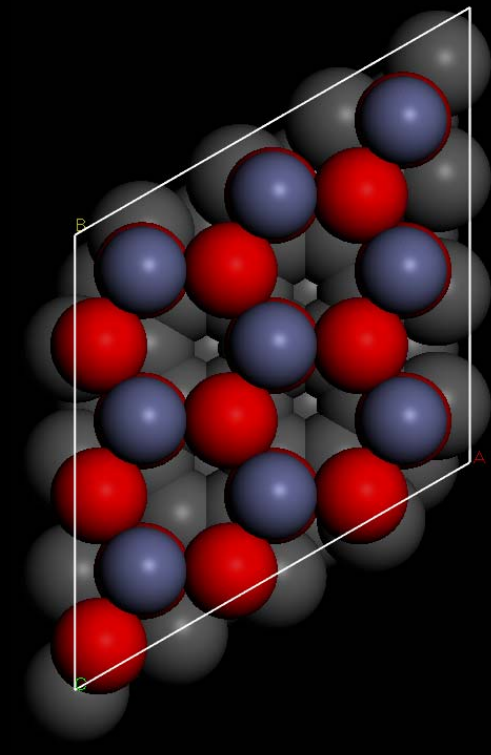
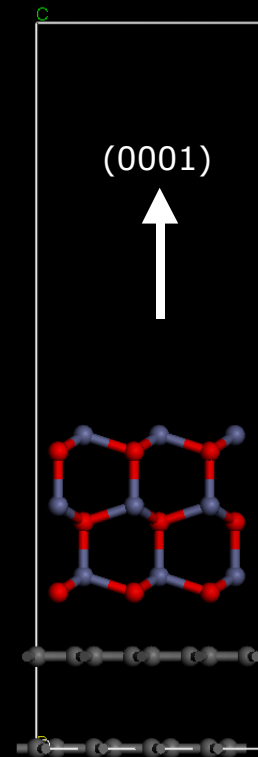
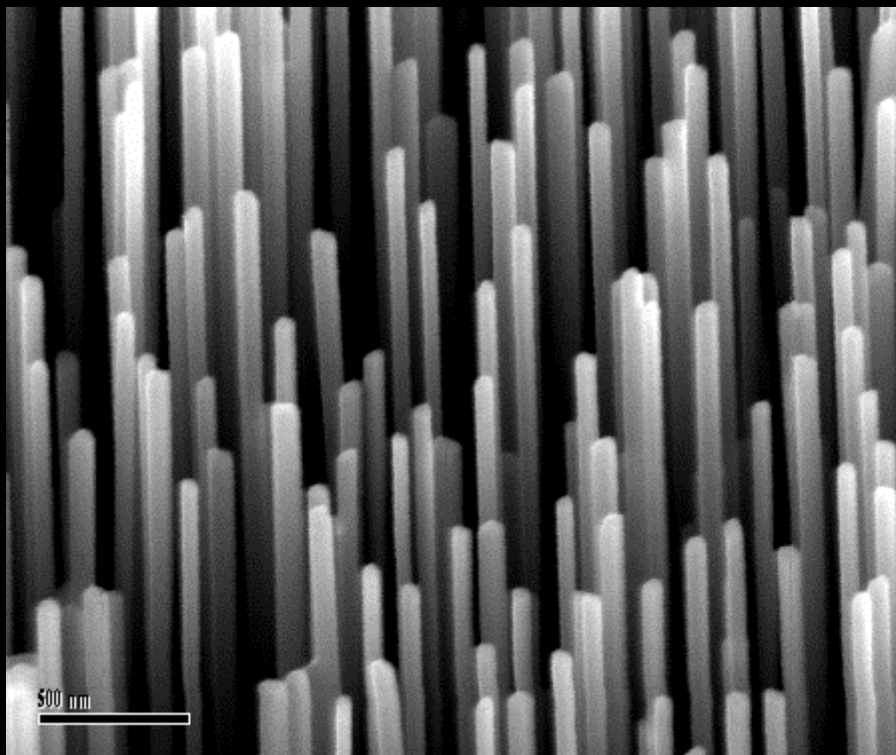


3D view of NW-based CMOS inverter

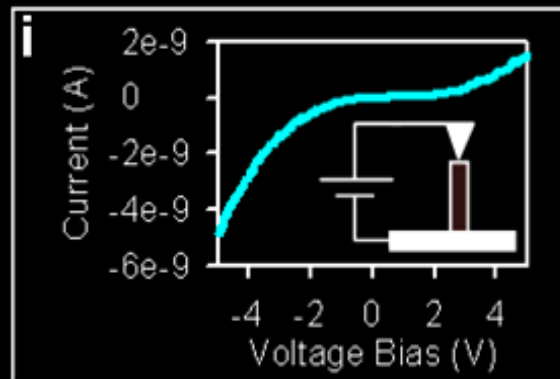
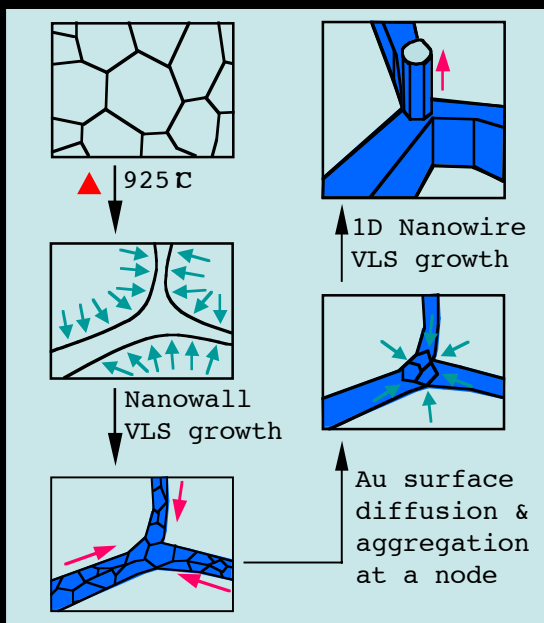
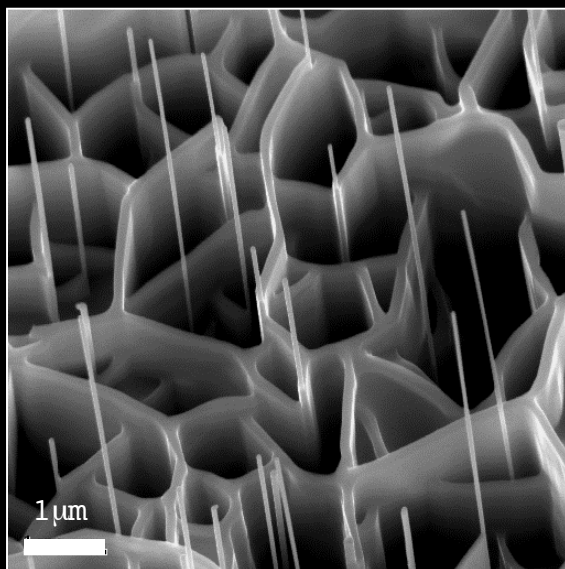
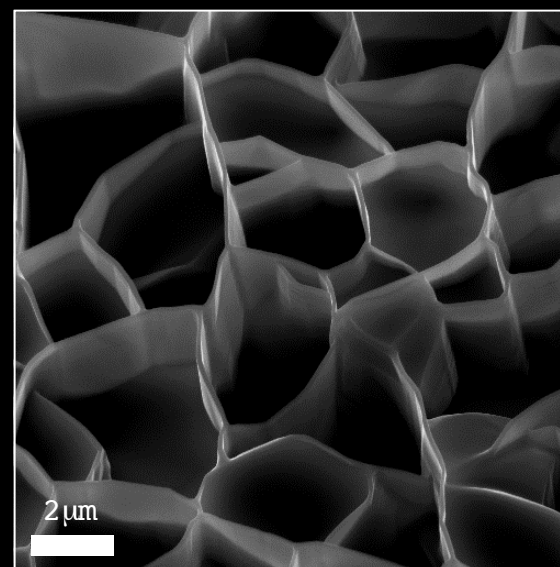
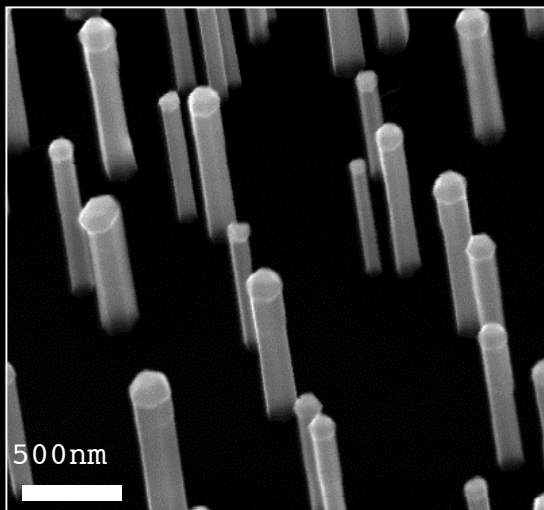
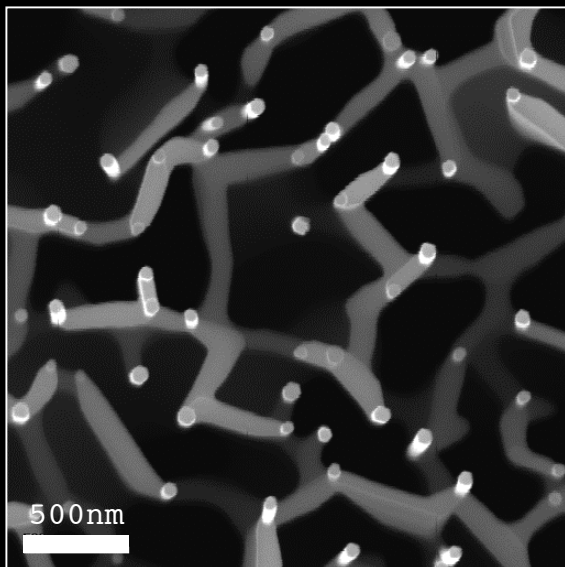
Challenges in Nanowire Growth

- Uni-directional nanowire growth; vertical or horizontal \Leftrightarrow substrate engineering \Leftrightarrow electric field directed

Understanding of the interfacial epitaxial relationship between potential substrates and nanowire structures \Leftrightarrow modeling and simulations \Leftrightarrow experiments \Leftrightarrow combinatorial approach

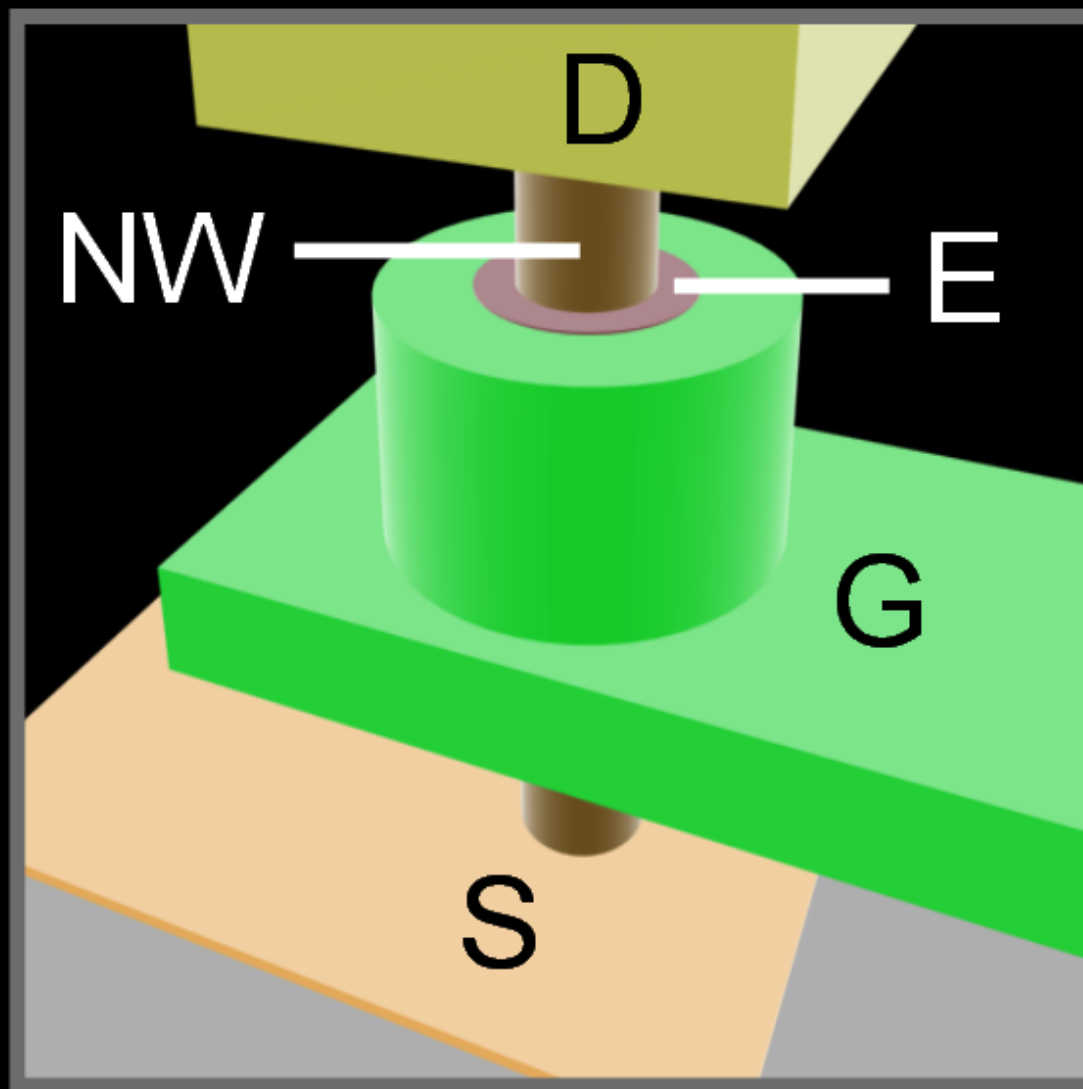


Directional Metal Oxide Nanowires & Nanowalls Growth (Cont')



Ng et al *Science* 300, 1249 (2003)

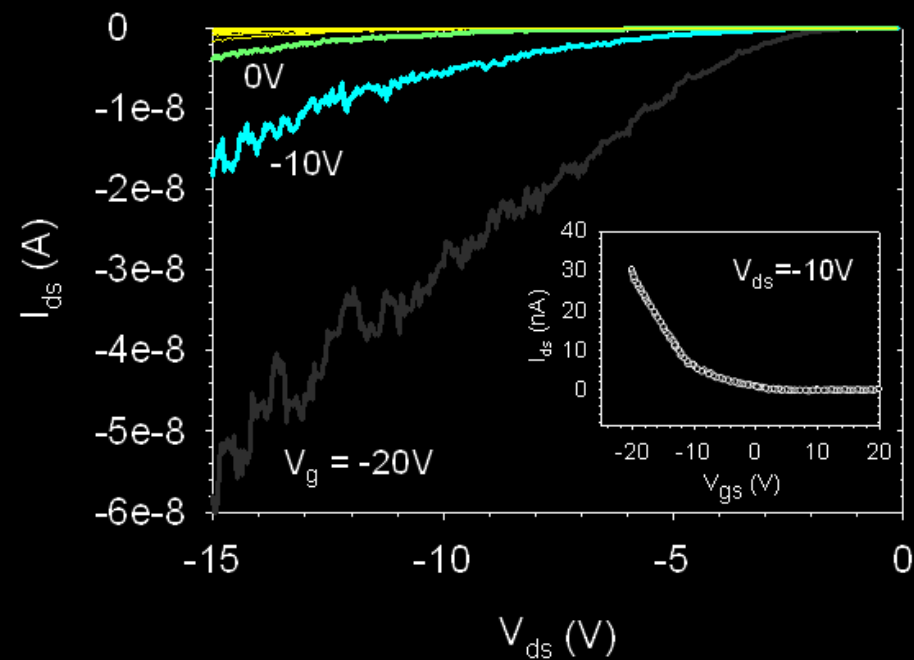
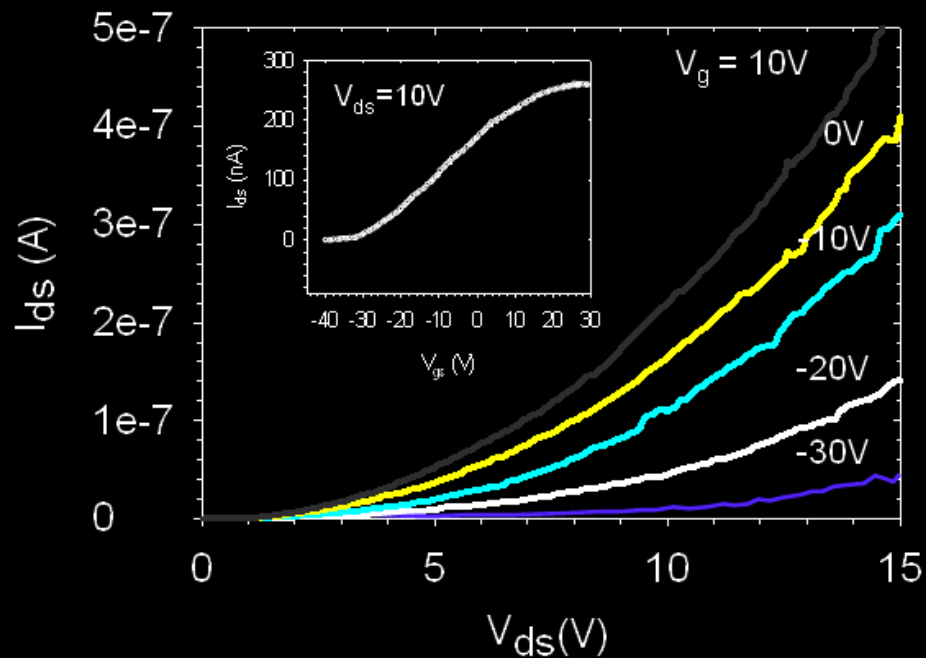
Nanowire-based Vertical Surround Gate FET



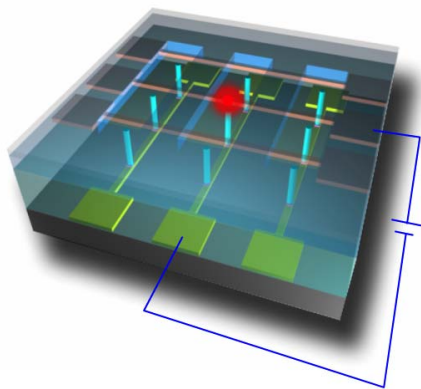
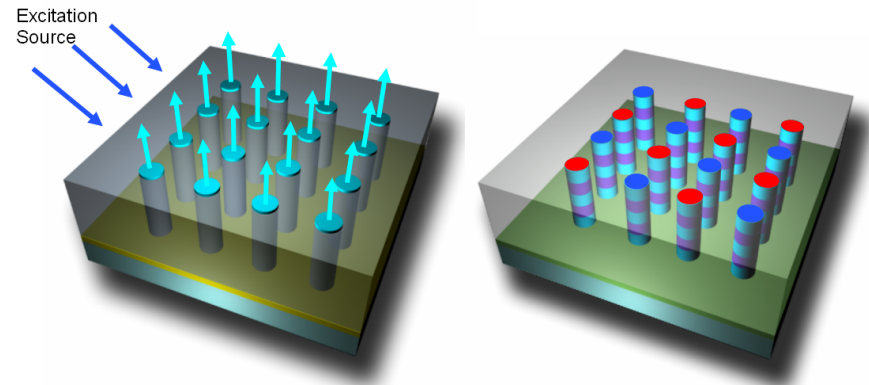
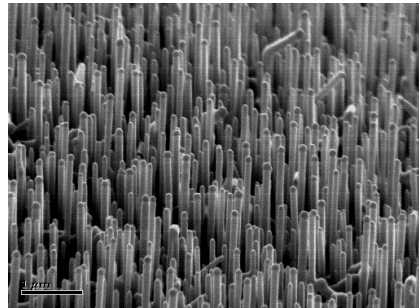
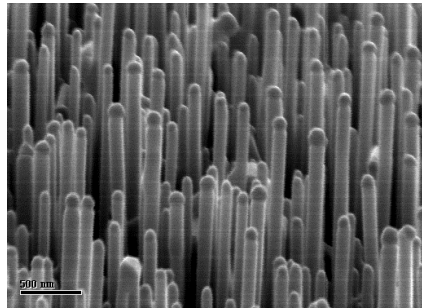
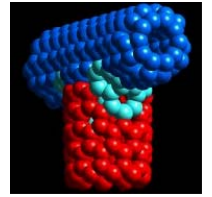
Nanowire-based Vertical Surround Gate FET

n-NWVFET

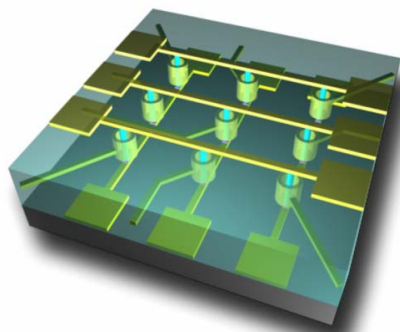
p-NWVFET



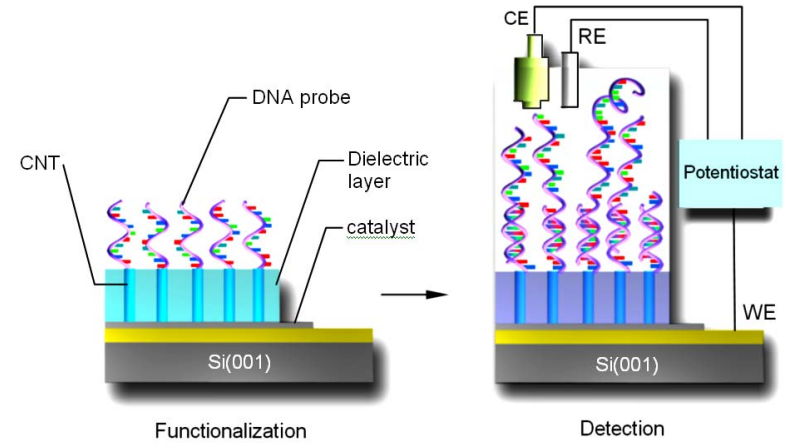
Zinc Oxide Nanowires



Field-Emitter Display



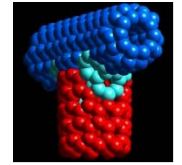
Vertical Transistor Arrays



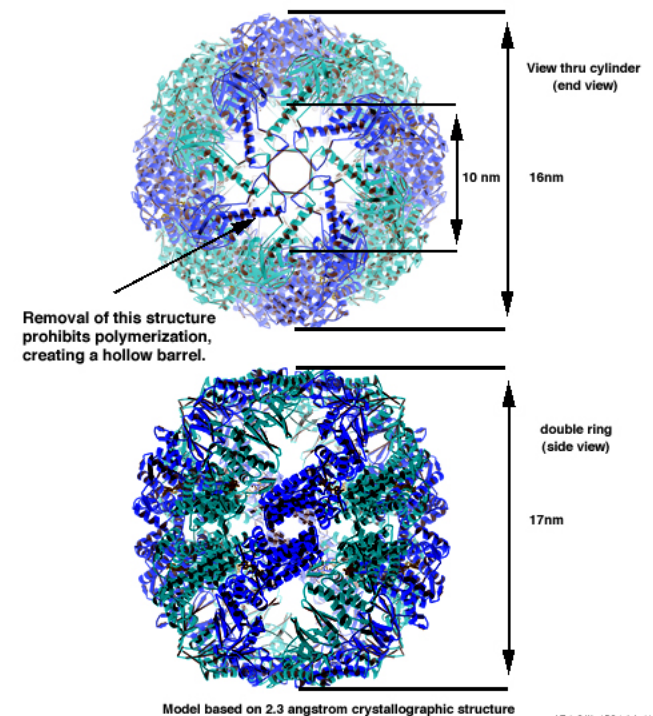
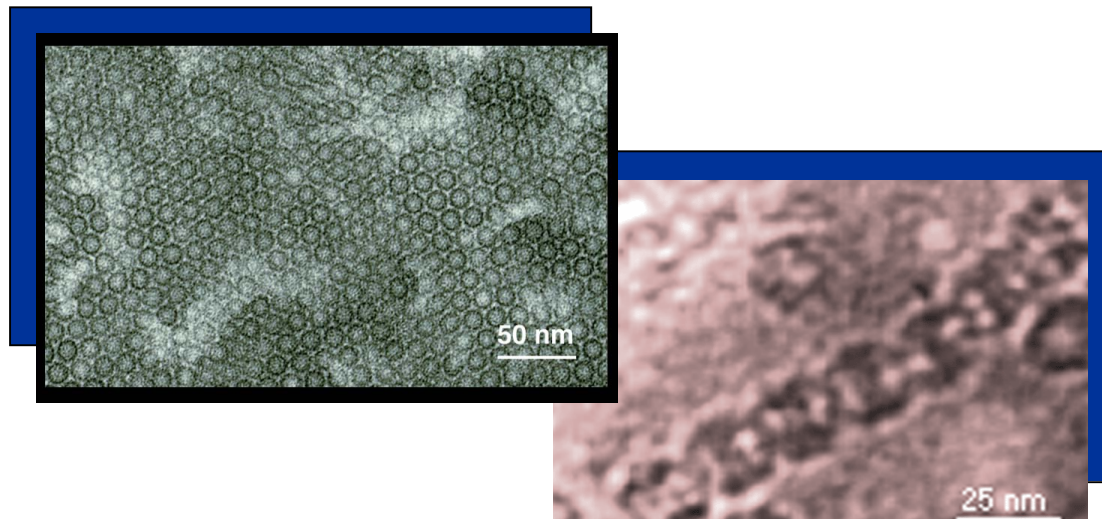
Functionalization

Detection

Protein Nanotubes



- Heat shock protein (HSP 60) in organisms living at high temperatures (“extremophiles”) is of interest in astrobiology
- HSP 60 can be purified from cells as a double-ring structure consisting of 16-18 subunits. The double rings can be induced to self-assemble into nanotubes.

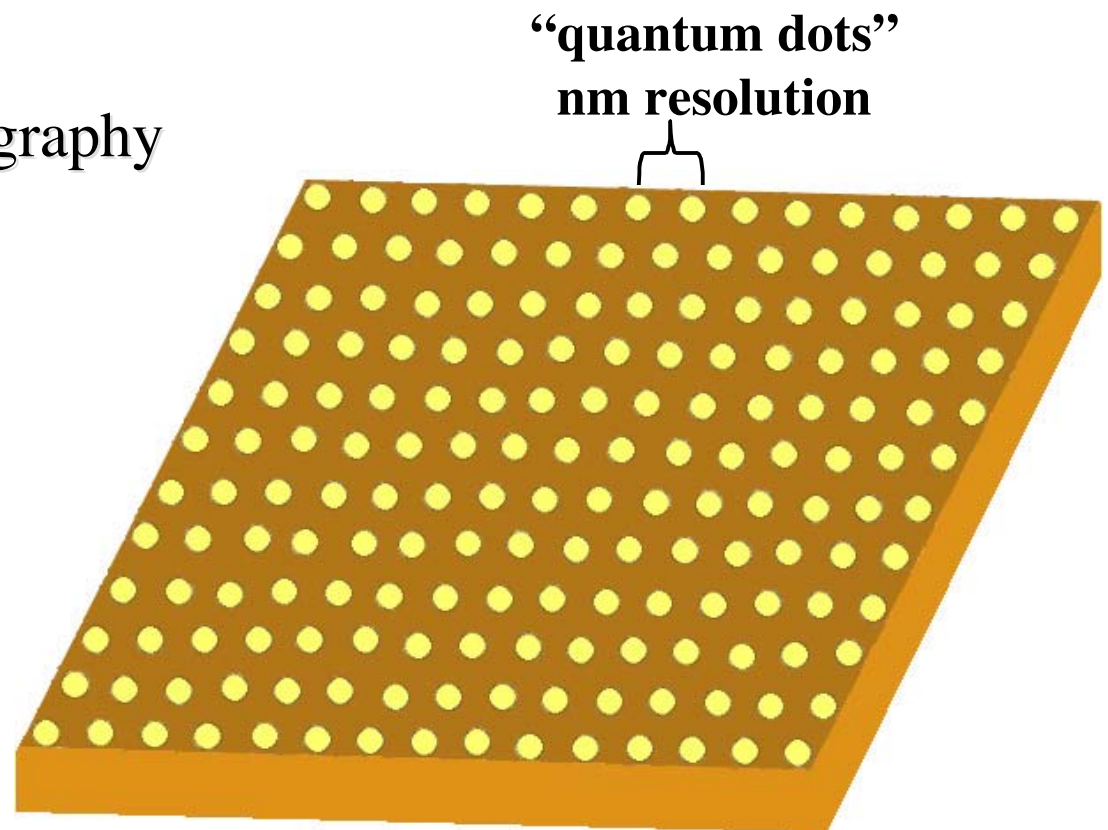


Extremophile Proteins for Nano-scale Substrate Patterning

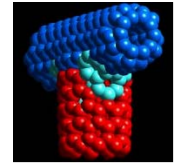
Nano-scale engineering for high resolution lithography

Future: Bio-based lithography

- Batch self-assembly
- Evolving
- Inexpensive

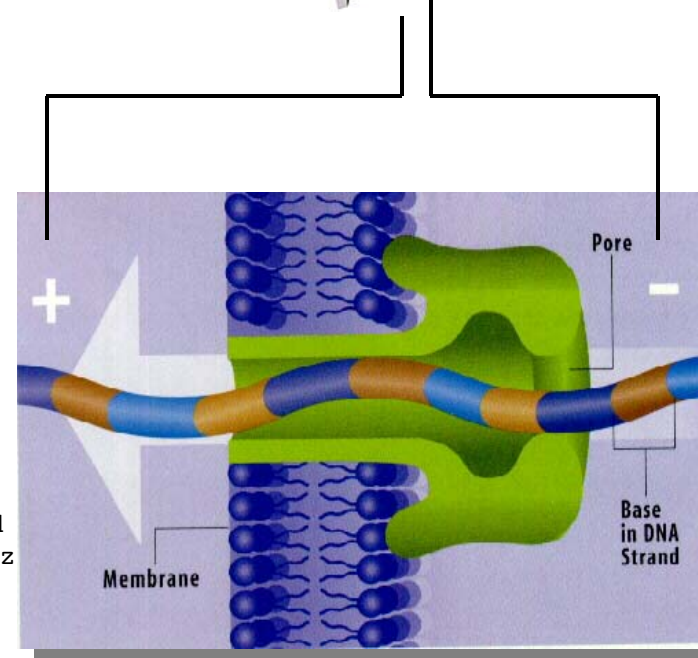


DNA Sequencing with Nanopores



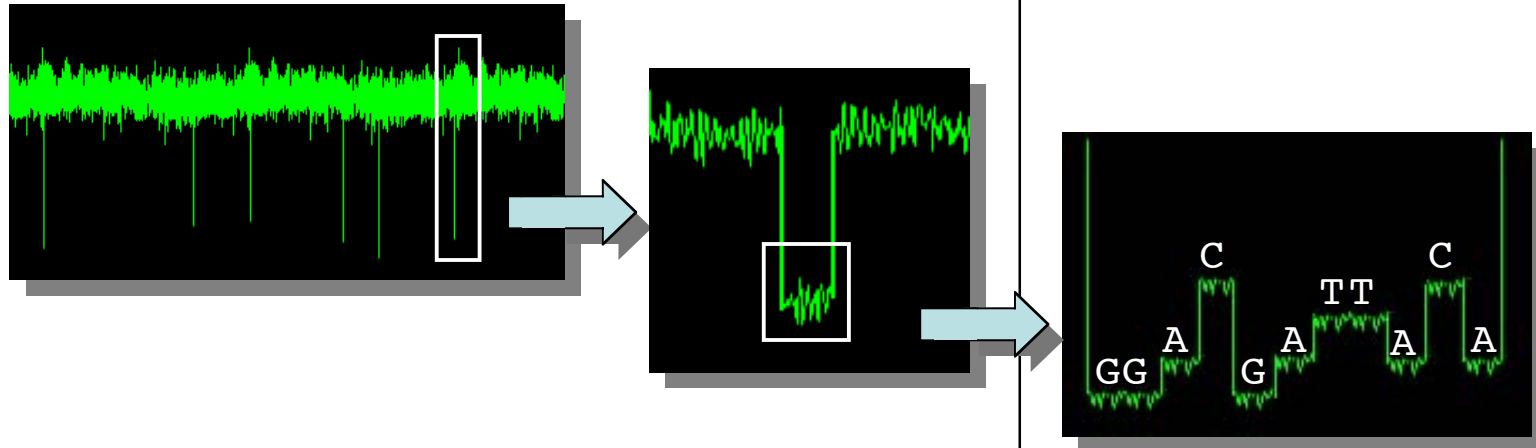
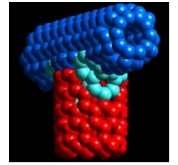
The Concept

- Nanopore in membrane ($\sim 2\text{nm}$ diameter)
- DNA in buffer
- Voltage clamp
- Measure current



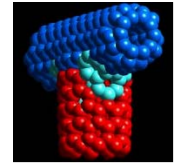
G. Church, Ed. Cantor, J. Golovchenko, Harvard
D. Deamer, UC Santa Cruz

The Sequencing Concept



Present

Future



- Nanotechnology is an enabling technology that will impact electronics and computing, materials and manufacturing, energy, transportation....
- The field is interdisciplinary but everything starts with material science. Challenges include:
 - Novel synthesis techniques
 - Characterization of nanoscale properties
 - Large scale production of materials
 - Application development
- Opportunities and rewards are great and hence, tremendous worldwide interest
- Integration of this emerging field into engineering and science curriculum is important to prepare the future generation of scientists and engineers