Introduction to Carbon Nanotubes: Near-term Applications and Future Promises

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Outline

1. Carbon Nanotubes: synthesis, structures and nanometer dimension
2. Properties
   a. Electrical Property
   b. Thermal conductivity
   c. Mechanical Property
3. Applications
   a. Great Future Potentials
      i. Nanoelectronics
      ii. Biointerface and Biosensors
   b. Near-Term Applications
      i. Field Emission: Flat Panel Display
      ii. Polymer composites
      iii. Chemical sensors
      iii. Tips for Scanning Probe Microscopy
4. Carbon nanotube scanning probe tips for nanocharacterization and nanofabrication
5. Summary and Perspective

Nanotechnology

How small is a nanometer?

1 nanometer = 10^{-9} meter

10,000X smaller than the diameter of human hair.

Nanotechnology = development of ***functional devices*** at the length scale of approximately 1 - 100 nm range (100's atoms)

(A hypothetical technology of the future in which objects can be designed and built on the atomic or molecular level)

Latest generation computer logic devices (Intel, AMD) are ~ 90 nm and therefore they are in the realm of nanotechnology.

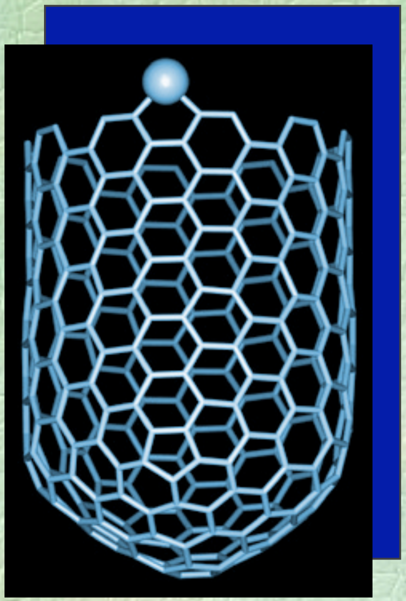
Breaking down of traditional and artificial barriers between scientific disciplines.

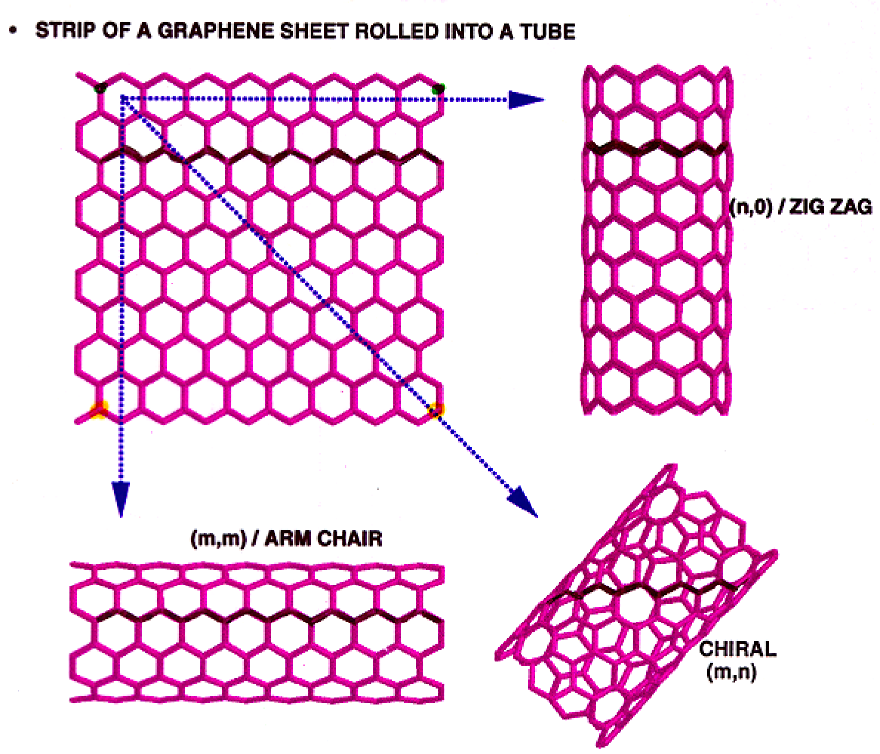
Use Knowledge of Biology, Chemistry, Physics, Engineering to develop useful technologies.

Sensors - combination of CMOS and Bio-Chemistry.

1. Carbon Nanotube

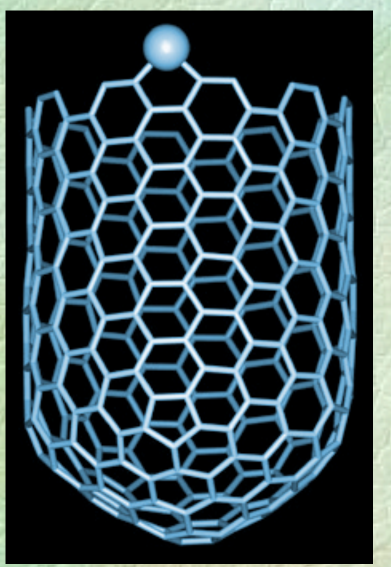
• CNT is a tubular form of carbon with diameter as small as nm.
• Length: few nm to microns.
• CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.



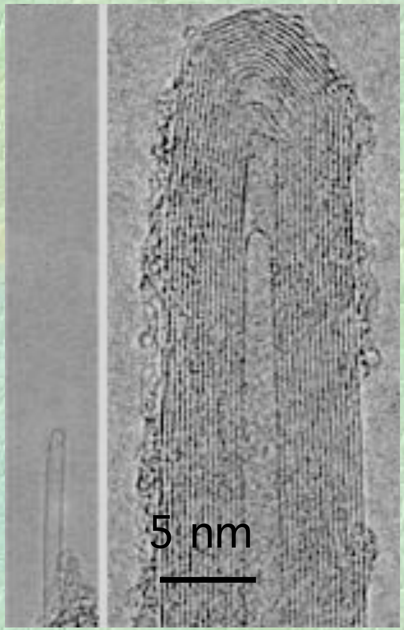


• CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal.
• CNT can be metallic or semiconducting, depending on chirality.

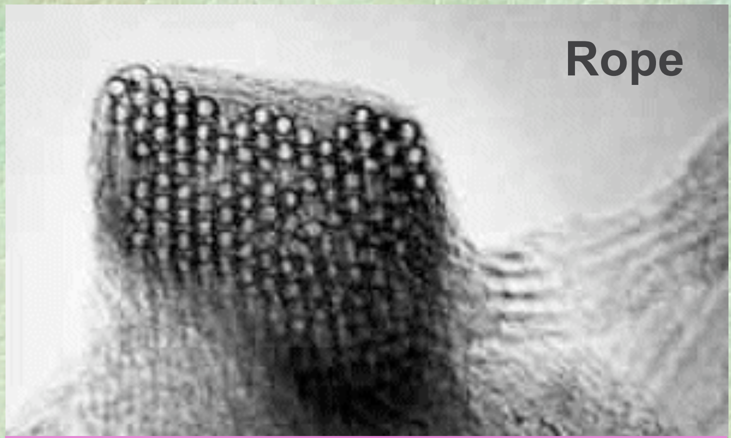
Nanotube Images



Single-Walled Tube
(SWNT)
Diameter ~ 0.5-2 nm



Multi-Walled Tube
(MWNT)
Diameter ~ 10 - 50 nm

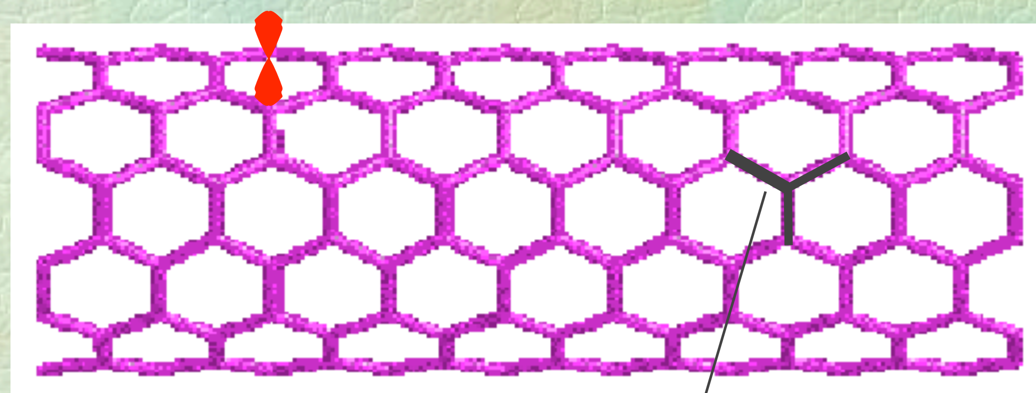


Thess et. al, Science (1996)

Bonding

Electrical properties

p orbital



Graphitic sp^2 C-C Bonds
sp^2 C=C 152 Kcal/mole
sp^3 C-C 88 Kcal/mole

sp^2 bonds with three nearest carbon atoms

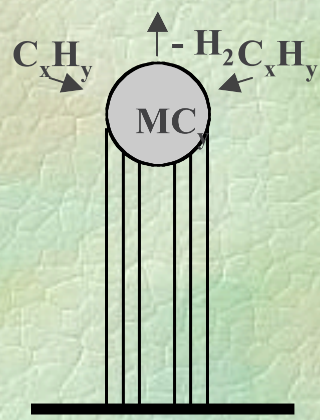
Mechanical Strength

CNT Synthesis

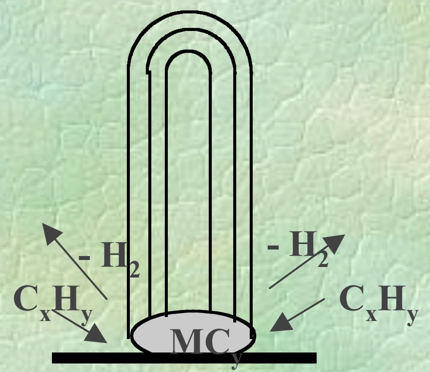
- CNT has been grown by laser ablation (pioneered at Rice) and carbon arc process (NEC, Japan) - early 90s.
  - SWNT, high purity, purification methods
- CVD is ideal for patterned growth (electronics, sensor applications)
  - Well known technique from microelectronics
  - Hydrocarbon feedstock
  - Growth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

CVD Growth Mechanisms For Carbon Nanotubes

- Adsorption and decomposition of feedstock on the surface of the catalyst particle
- Diffusion of carbon atoms into the particle from the supersaturated surface
- Carbon precipitates into a crystalline tubular form
- Particle remains on the surface and nanotube continues to lengthen - “base growth” mechanism
- Growth stops when graphitic overcoat occurs on the growth front - “catalyst poisoning”



M = Fe, Ni, Co, Pt, Rh, Pd and others



Tip Growth

Typically occurs when there are very weak metal-surface interactions

Base Growth

Occurs when the metal-surface interactions are strong

MWNTs vs. MWNFs

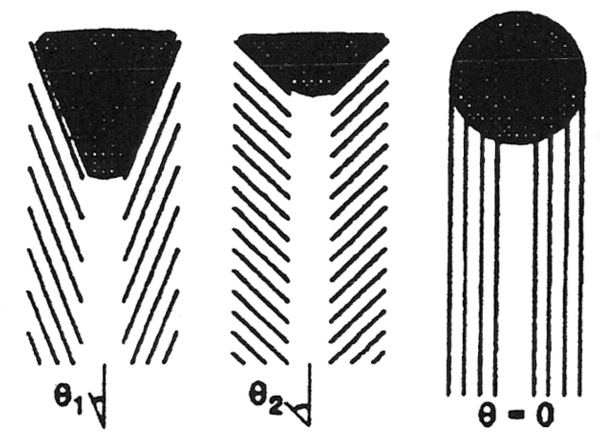
- Filaments consist of stacked-cone arrangement of graphite basal plane sheets; grow with particles at the tip; hydrogen is believed to satisfy the valences at cone edges in filaments

- The orientation angle θ (between graphite basal planes and tube axis) increases with increasing hydrogen concentration

- When θ = 0, MWNTs. These are filaments with no graphite edges, requiring no valence-satisfying species such as hydrogen

- Nolan et al provide evidence (all thermal CVD) that material produced with CO disproportionation (without any H_2) was MWNTs; addition of H_2 produced filaments; as % of H_2 ↑, θ ↑ up to 30°

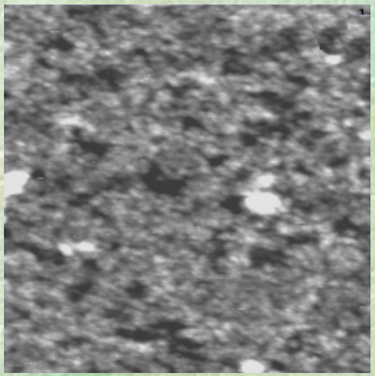
- Better to call these structures as MWNFs (filaments) instead of graphitic carbon fibers (GCFs) or vapor grown carbon fibers (VGCFs) both of which denote solid cylinders

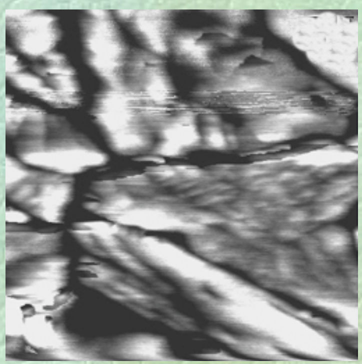


Nolan et al, JPC, B, 1998

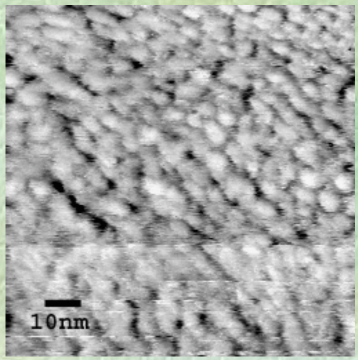
Catalyst Characterization

- Catalyst surface characterized by AFM (with SWNT tip) and STM.
- AFM image of as-sputtered 10 nm iron catalyst (area shown is 150 nm x 150 nm). Also, the same surface after heating to 750° C (and cooled) showing Fe particles rearranging into clusters.



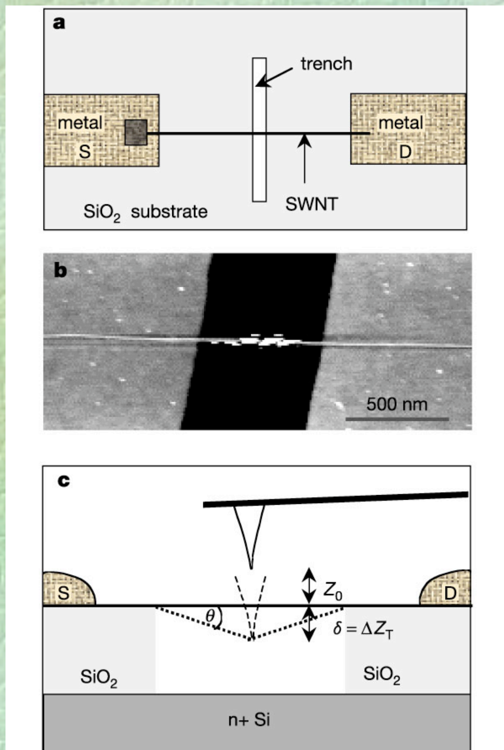


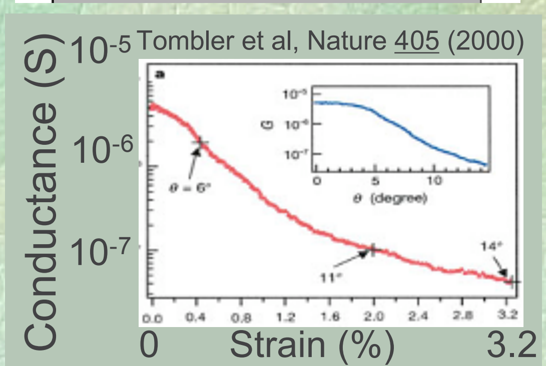
- STM image of a nickel catalyst showing nanoscale particles

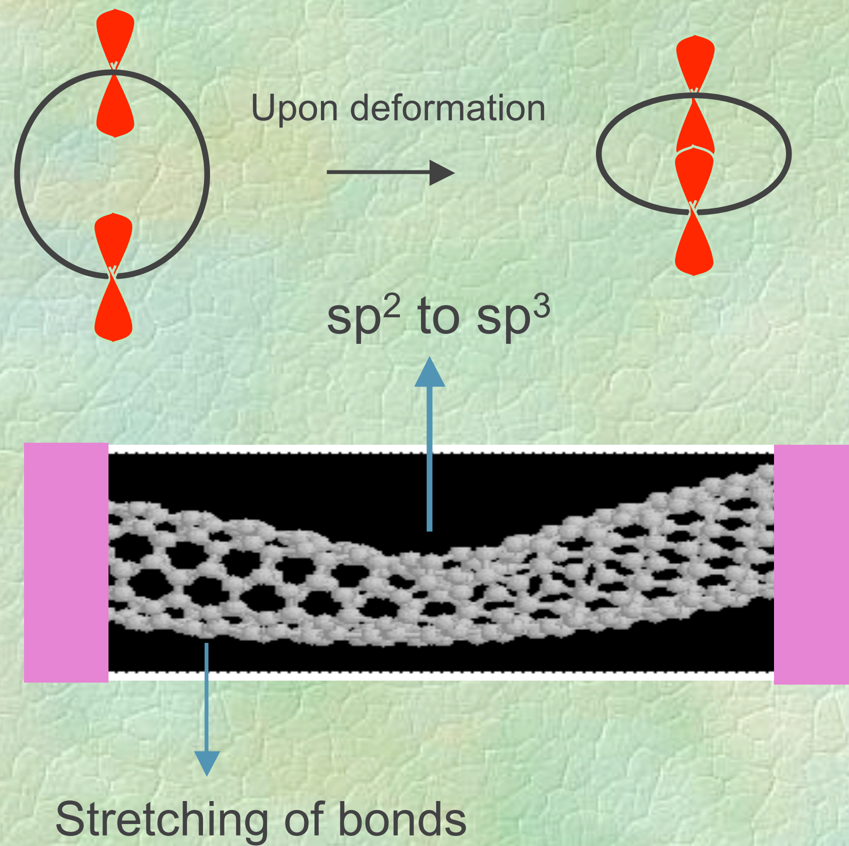


- These results are consistent with high resolution TEM showing particles as small as 2 nm.

Electromechanical Properties

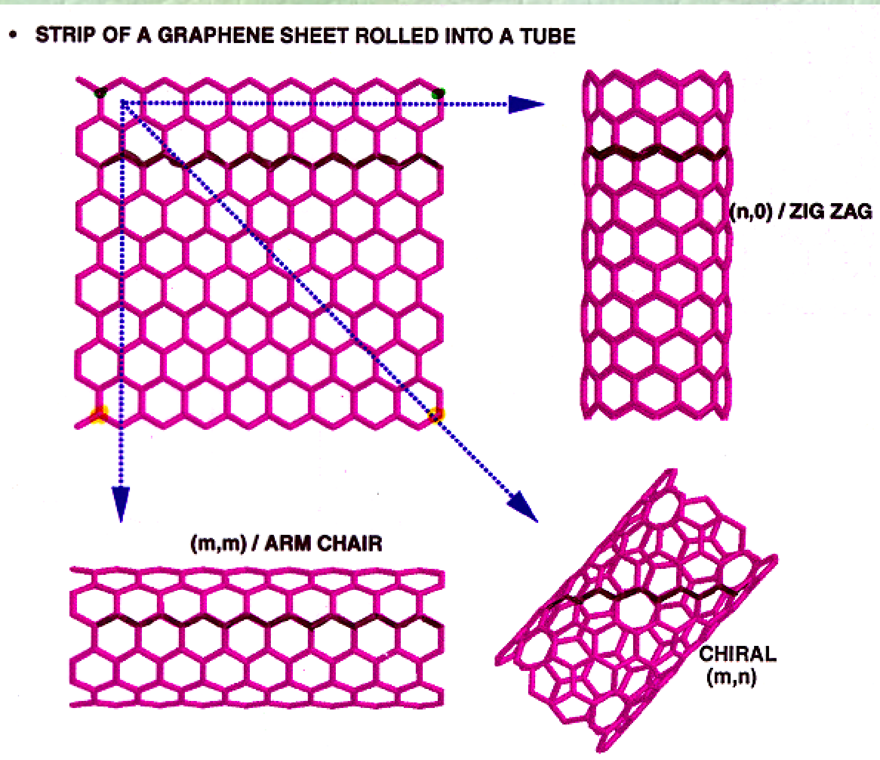


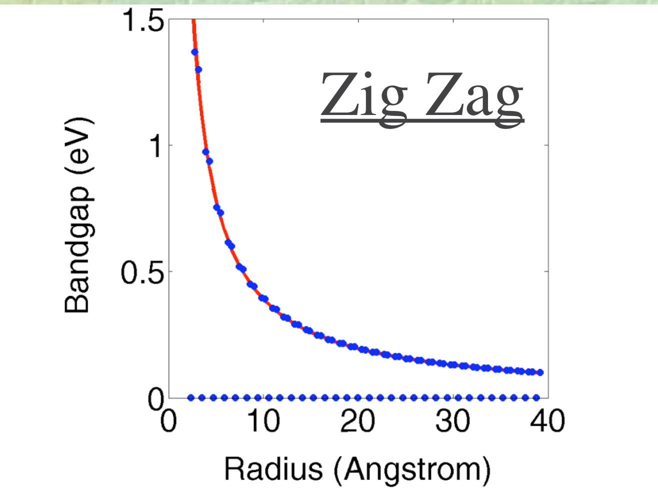




What is the conductance decrease due to?

2. Properties
SWNT Electronics



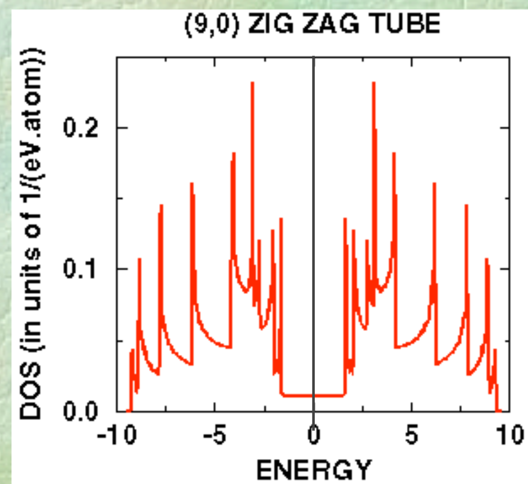


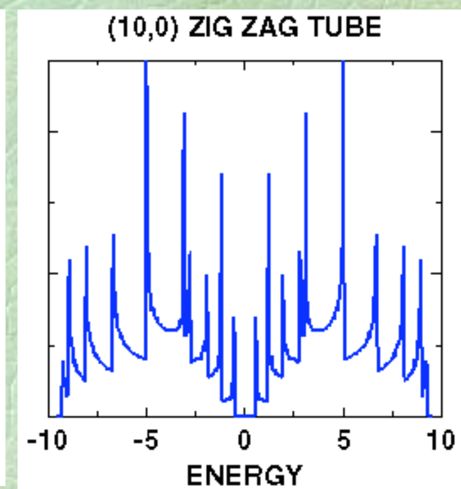
Chiral Tubes are Semiconducting - Nanoelectronics

Armchair tubes do not develop a band gap

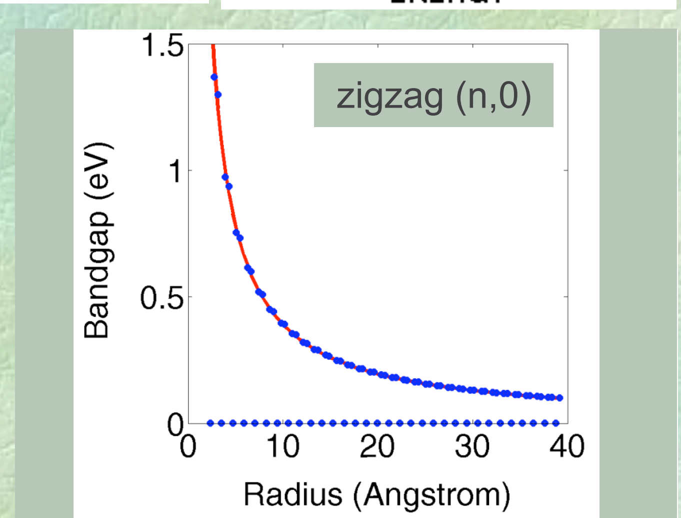
Summary of SWNT Electronic Properties

- Metallic nanotubes:
  n-m = 3*integer





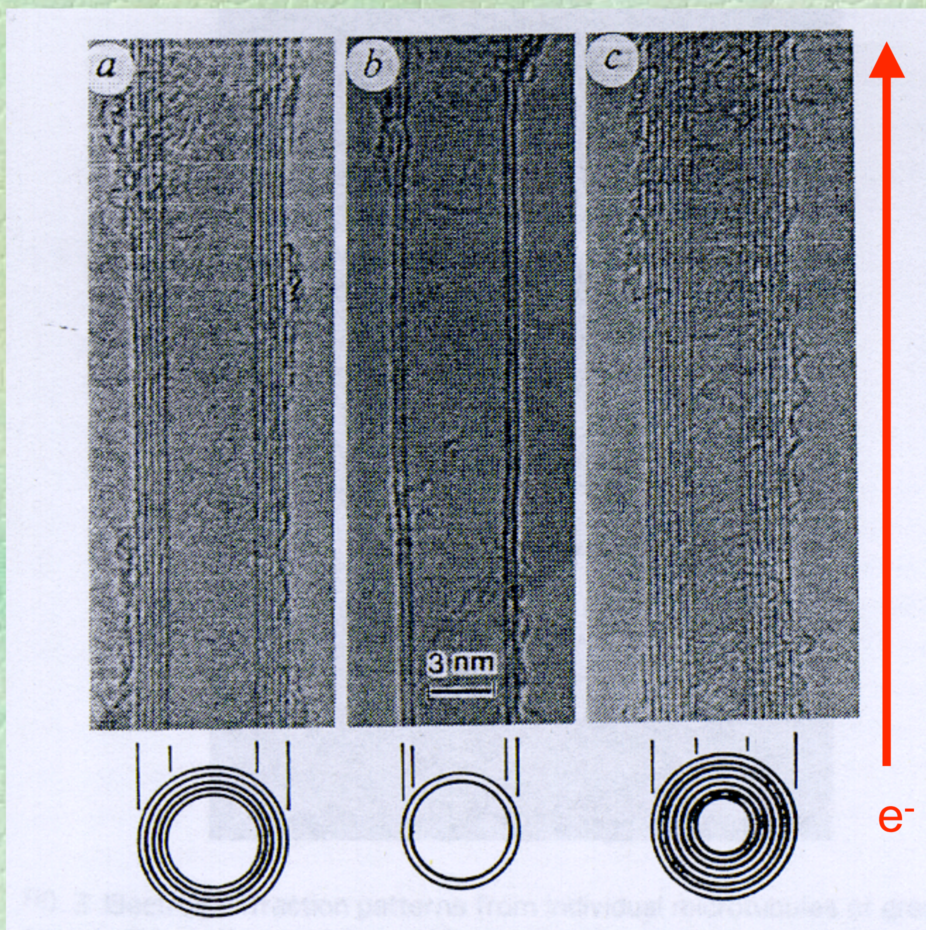
- Semiconducting tubes:
  Bandgap α 1/Diameter



- Armchair tubes are truly metallic

- Other metallic tubes have a tiny curvature induced bandgap

MWNT Properties: electronics, themal, and mechanical



-ballistic conductors

quantum conductance

G_0=1/(12.9 kOhm)

mean free path ~microns

-high current carrying capacity

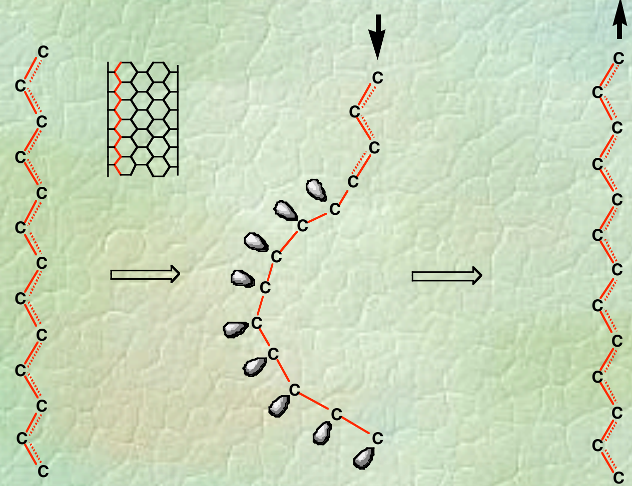
10^7 to 10^9 A/cm^2

-high thermal conductivity

1200 W/m-K and above at room temperature

-high mechanical strength

Mechanical Property



-Graphitic sp^2 C-C Bonds

Sp^2 C=C 152 Kcal/mole
sp^3 C-C 88 Kcal/mole

$k_B=3Y\pi(r_o^4-r_i^4)/4L^3$ Force constant for bending response

$k_C=Y\pi(r_o^2-r_i^2)/L$ Force constant for compression response

3. Applications: Structural, Mechanical

- High strength composites
- Cables, tethers, beams
- Multifunctional materials
- Functionalize and use as polymer back bone
- 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

Applications:
Sensors, NEMS, Bio

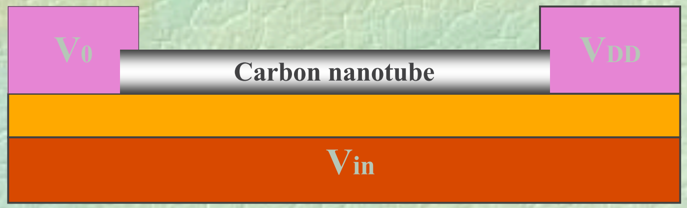
- CNT based microscopy: AFM, STM…
- Nanotube sensors: force, pressure, chemical…
- Biosensors
- Molecular gears, motors, actuators
- Batteries, Fuel Cells: H_2, Li storage
- Nanoscale reactors, ion channels
- Biomedical
  - in vivo real time crew health monitoring
  - Lab on a chip
  - Drug delivery
  - DNA sequencing
  - Artificial muscles, bone replacement, bionic eye, ear...

Challenges

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

Applications: Electronics

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



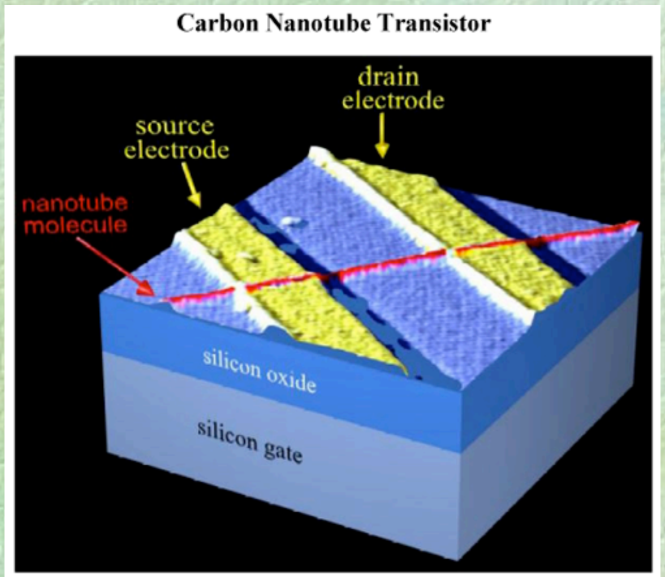
Challenges

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

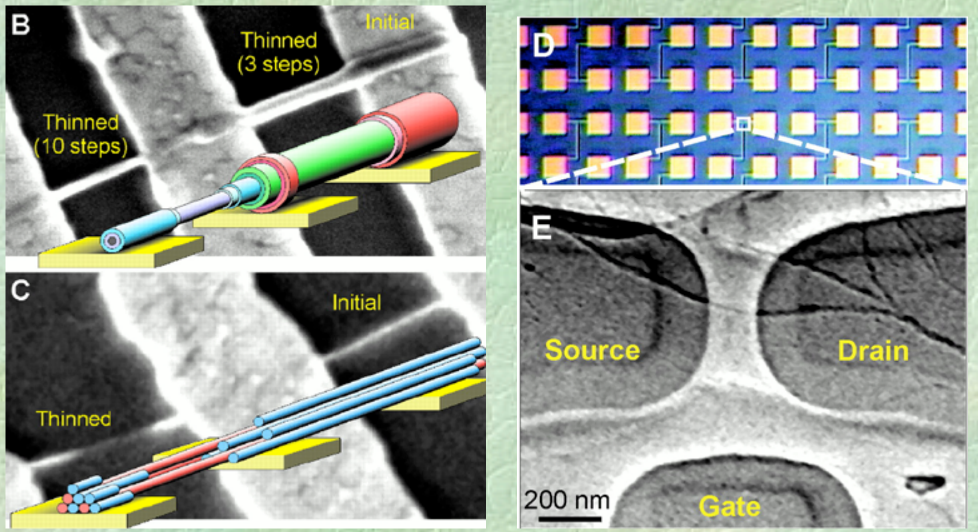
Nanoelectronics Beyond Si Technology

- 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 ± 5%)
- Reliability (operating time > 10 years)
- Very low cost (< 1 μcent/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….

Carbon Nanotube Electronics: FET's



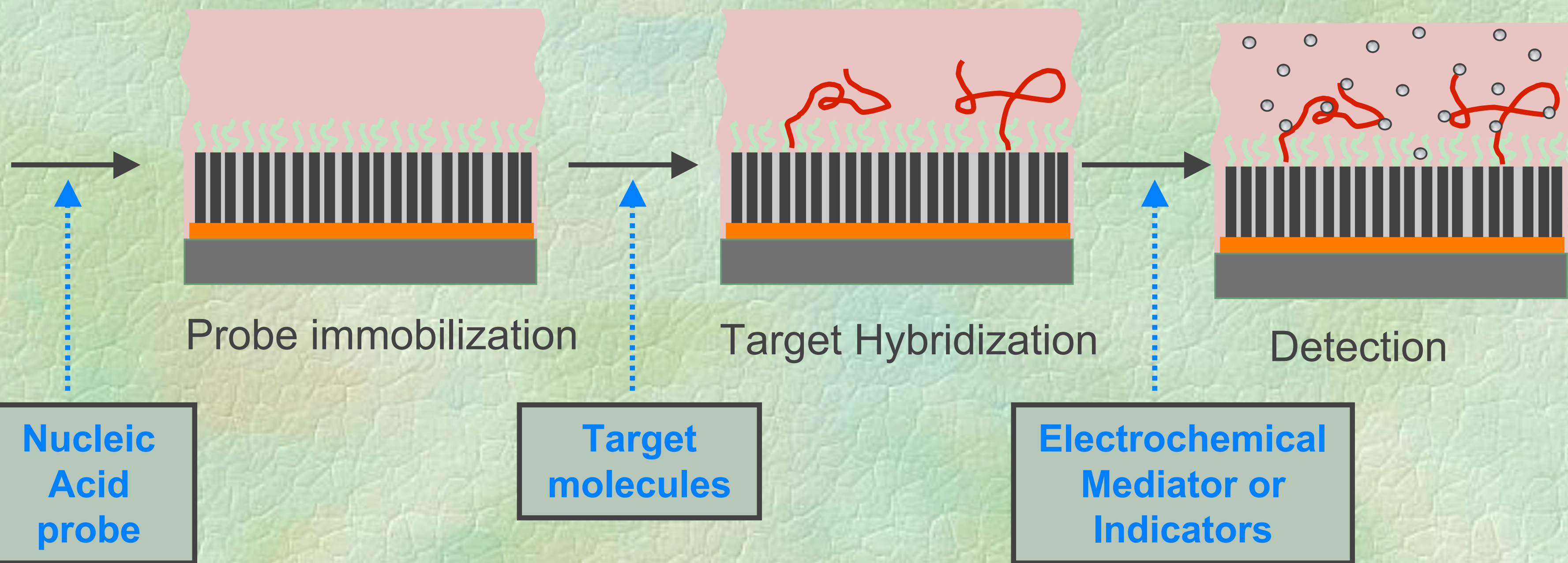
Dekker & coworkers, *Nature* **393**, 49 (1998)



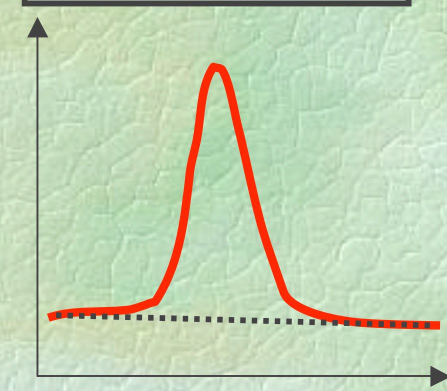
Avouris & coworkers, *Science* **292**, 706 (2001)

- Semiconducting nanotubes can function as field effect transistors with large on/off ratios and relatively high mobility.
- Uncontrolled synthesis of metallic and semiconductor nanotubes places significant constraints on assembly of device arrays.

Carbon Nanotube Biointerface: Biosensor Applications

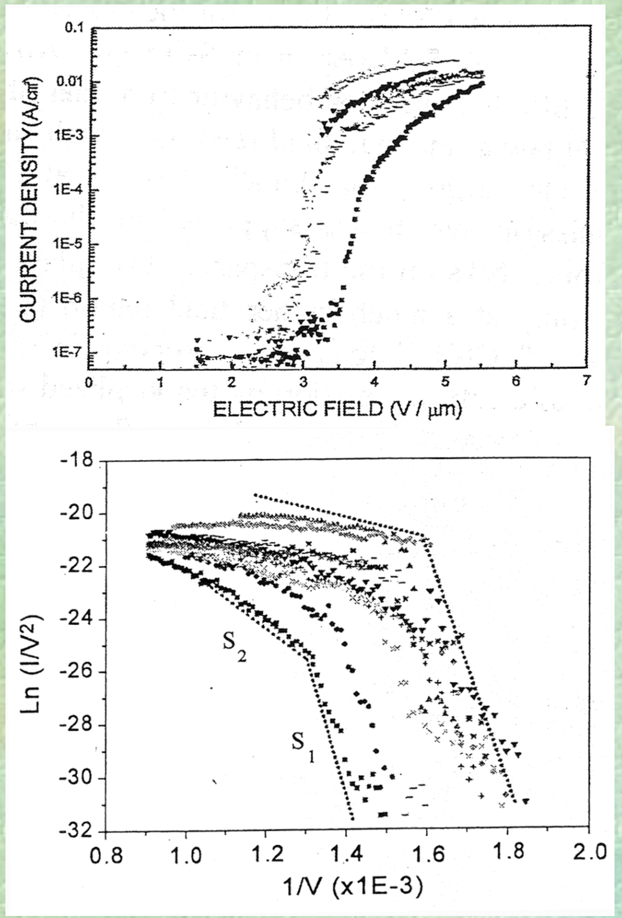


The probe molecules could be proteins (enzymes or antibodies), transition metal complexes (hemes), or nucleic acids



Near-Term Application: 1. Field Emission

- When subjected to high E field, electrons near the Fermi level can overcome the energy barrier to escape to the vacuum level
- Common tips: Mo, Si, diamond
- Applications:
  - Cathode ray lighting elements
  - Flat panel displays
  - Gas discharge tubes in telecom networks
  - Electron guns in electron microscopy
  - Microwave amplifiers



- Fowler - Nordheim equation: $\mathrm{I} = aV^2 \exp(-b\phi^{1.5}/\beta V)$
  ϕ is work function, β is field enhancement factor
- Plot of ln (I/V^2) vs. $(1/V)$ should be linear
- At low emission levels, linearity seen (S2); in the high field region, current saturates (S1)
- Critical: low threshold E field, high current density, high emission site density (for high resolution displays)

Field Emission (cont.)

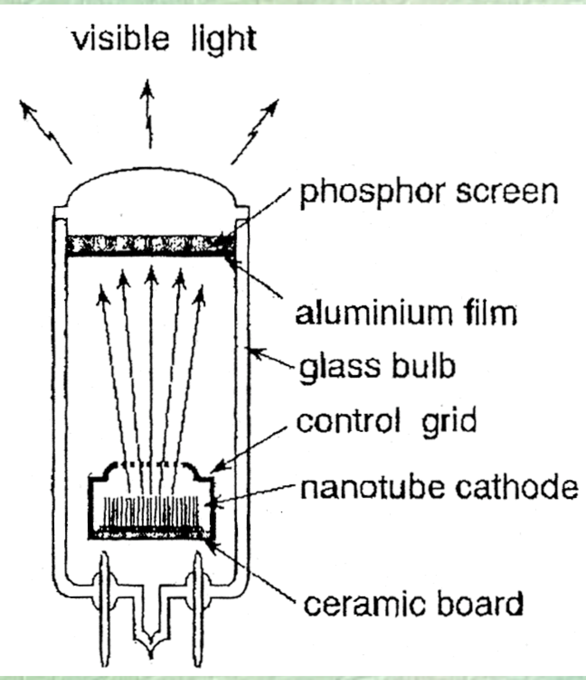
- Needs
  - For displays, 1-10 mA/cm^2
  - For microwave amplifiers, > 500 mA/cm^2

- To obtain low threshold field
  - Low work function (ϕ)
  - Large field enhancement factor (β) $\Rightarrow$ depends on geometry of the emitter; $\beta \simeq 1/5r$

- Threshold field values (in V/μm) for 10 mA/cm^2
  - Mo - 50-100
  - Si - 50-100
  - P-type diamond - 130
  - Graphite Powder - 17
  - Carbon nanotubes - 1-3 (stable at 1 A/cm^2)

Field Emission Test Apparatus

- Cathode and anode enclosed in an evacuated cell at a vacuum of 10^{-9} - 10^{-8} Torr
- Cathode: glass or polytetrafluoroethylene substrate with metal-patterned lines
  - nanotube film transferred to substrate or grown directly on it
- Anode located 20-500 μm from cathode
- Turn-on field: electric-field required to generate 1 nA
  - should be small
- Threshold field: electric field required to yield 10 mA/cm^2



Flat Panel Displays

- Working full color flat panel displays and CRT-lighting elements have been demonstrated in Japan and Korea

- Display
    - Working anode, a glass substrate with phosphor coated ITO stripes
    - Anode and cathode perpendicular to each other to form pixels at the intersection
    - Phosphors such as Y_2O_2S: Eu (red), Zns: Cu, Al (green), ZnS: Ag, Cl (blue)
    - 40” display showing a uniform and stable image

- Lighting Element
    - Phosphor screen printed on the inner surface of the glass and backed by a thin Al film (~100 nm) to give electrical conductivity
    - Lifetime testing of the lighting element shows a lifespan over 10000 hrs.

Near-Term Application: 2. Polymer Nanocomposites

- Carbon nanotubes viewed as the "ultimate" nanofibers ever made
- Carbon fibers have been already used as reinforcement in high strength, light weight, high performace composites:
    - Expensive tennis rackets, air-craft body parts…
- Nanotubes are expected to be even better reinforcement
    - C-C covalent bonds are one of the strongest in nature
    - Young's modulus ~ 1 TPa ⇒ the in-plane value for defect-free graphite
- Problems
    - Creating good interface between CNTs and polymer matrix necessary for effective load transfer

WHY?

❶ CNTs are atomically smooth; h/d ~ same as for polymer chains

❷ CNTs are largely in aggregates ⇒ behave differently from individuals

- Solutions
    - Breakup aggregates, disperse or cross-link to avoid slippage
    - Chemical modification of the surface to obtain strong interface with surrounding polymer chains

Conducting Polymers Based on Carbon Nanotubes

- High aspect ratio allows percolation at lower compositions than spherical fillers (less than 1% by weight)

- Neat polymer properties such as elongation to failure and optical transparency are not decreased.

- ESD Materials: Surface resistivity should be 10^{12} - 10^{5} Ω/sq
  - Carpeting, floor mats, wrist straps, electronics packaging

- EMI Applications: Resistivity should be < 10^{5} Ω/sq
  - Cellular phone parts
  - Frequency shielding coatings for electronics

- High Conducting Materials: Weight saving replacement for metals
  - Automotive industry: body panels, bumpers (ease of painting without a conducting primer)
  - Interconnects in various systems where weight saving is critical

Smart Materials, Special Coatings

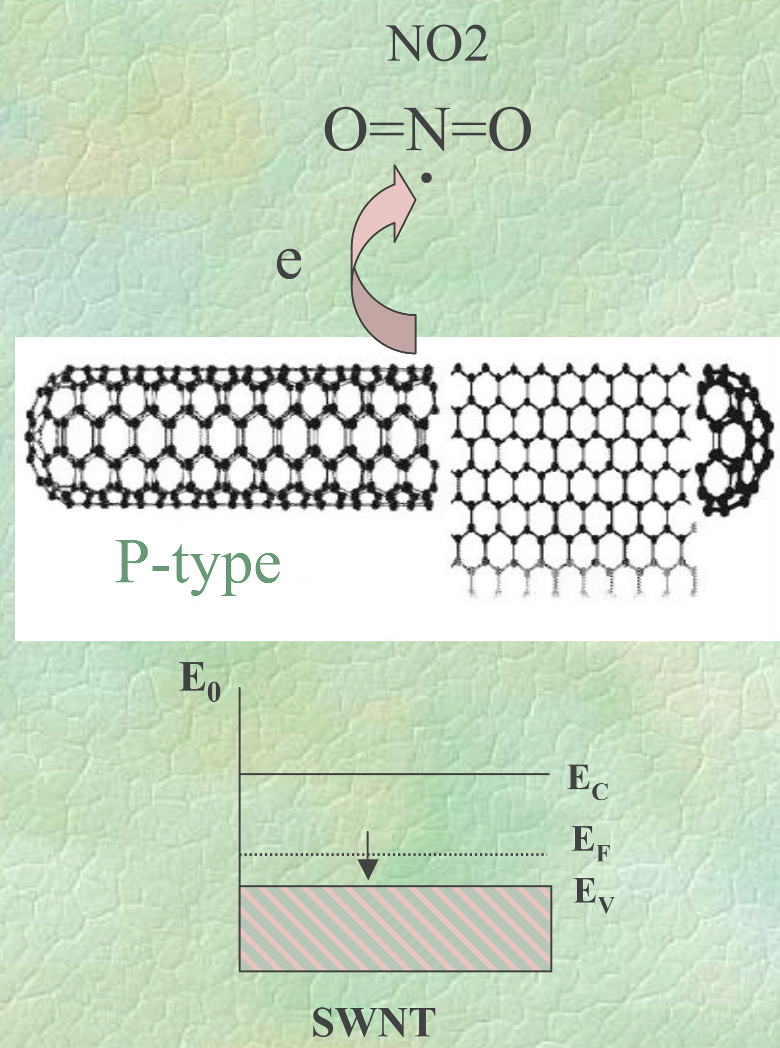
- Carbon nanotubes can be embedded in high performance composites as reinforcing agents and strain sensors allowing for nondestructive monitoring and distributed sensing of large structures

- SWNT/PVOH fibers with 60% wt SWNT $\Rightarrow$ tensile strength similar to spider silk
  - These fibers can be woven into textiles to create garments with sensing and EMI shielding capabilities.

- Thermally conductive coatings (with nanotubes incorporated into polymers)
  - Deicing aircrafts in cold weather by applying current to the coatings

Near-Term Application: 3. Chemical Sensors

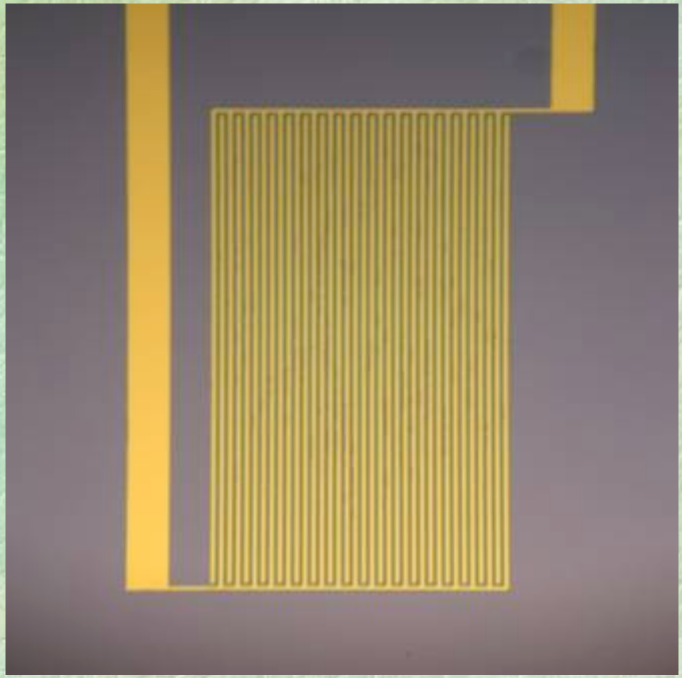
- Every atom in a single-walled nanotube (SWNT) is on the surface and exposed to environment
- Charge transfer or small changes in the charge-environment of a nanotube can cause drastic changes to its electrical properties

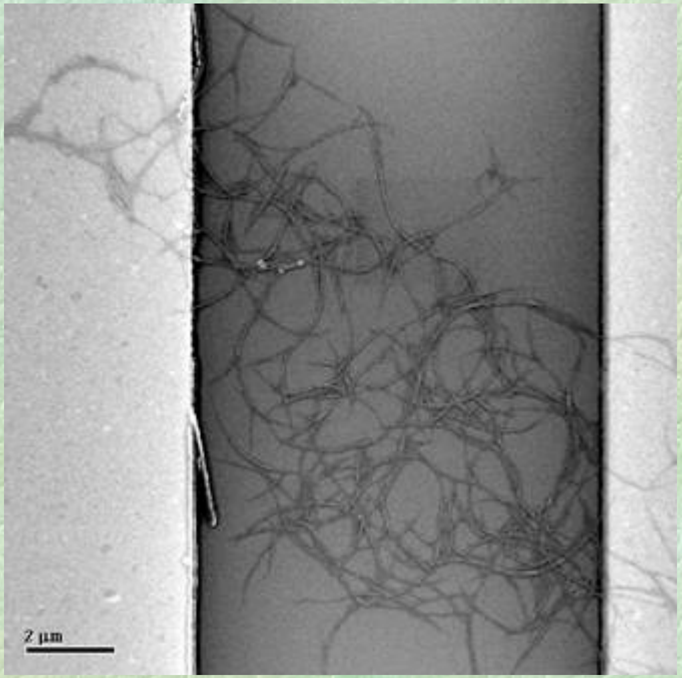


SWNT Chemiresistor

Sensor fabrication:

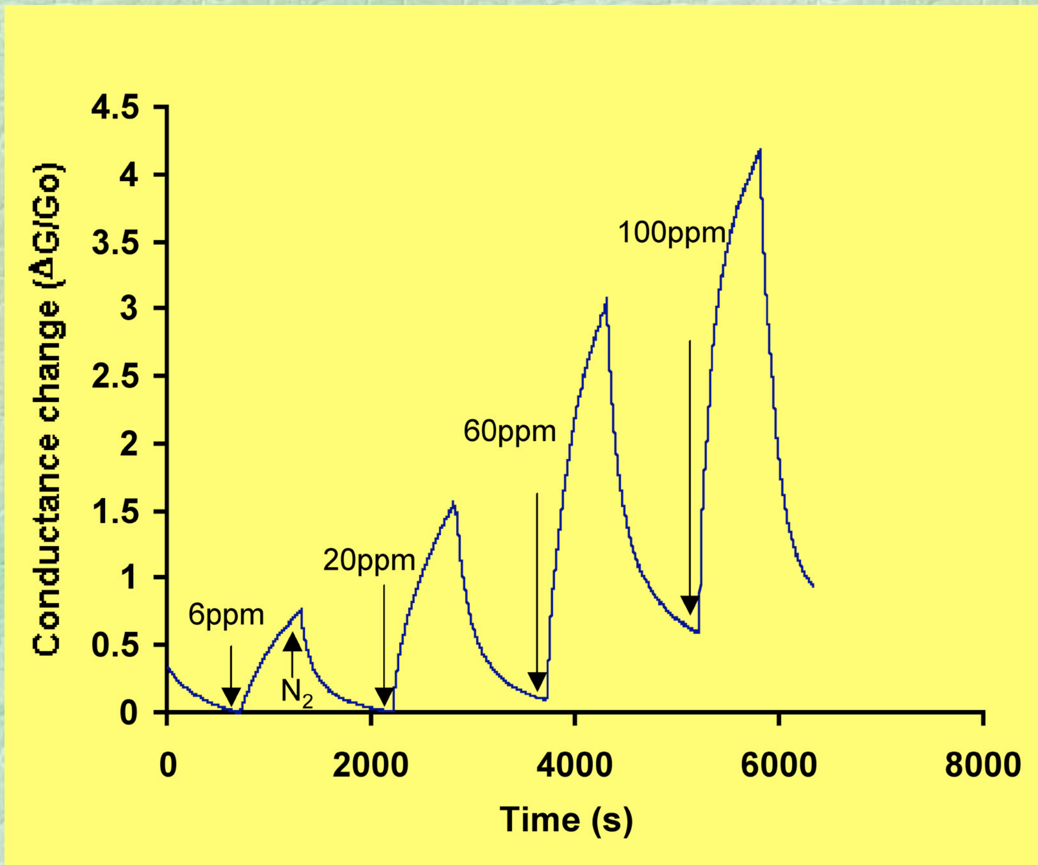
1. SWCNT dispersions--Nice dispersion of CNT in DMF
2. Device fabrication--(see the interdigitated electrodes below)
3. SWCNT deposition—Casting, or in-situ growth

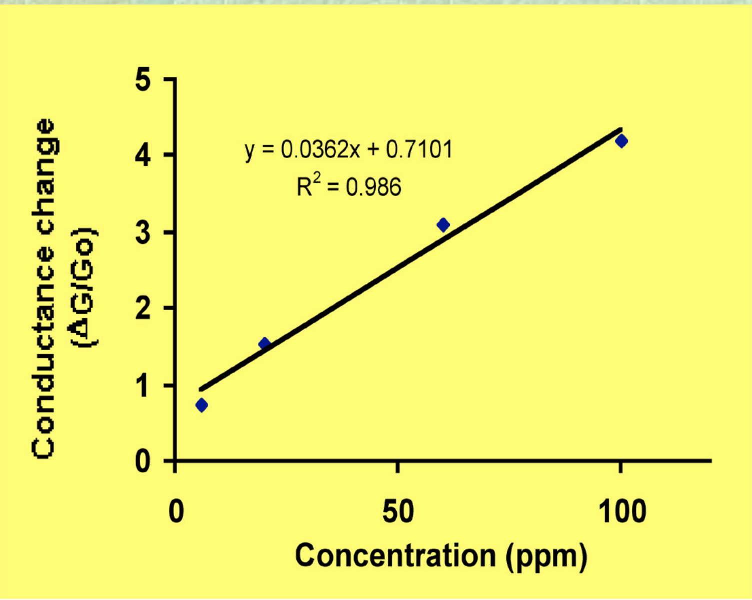




Jing Li et al., Nano Lett., **3**, 929 (2003)

SWNT Sensor Responding to NO2

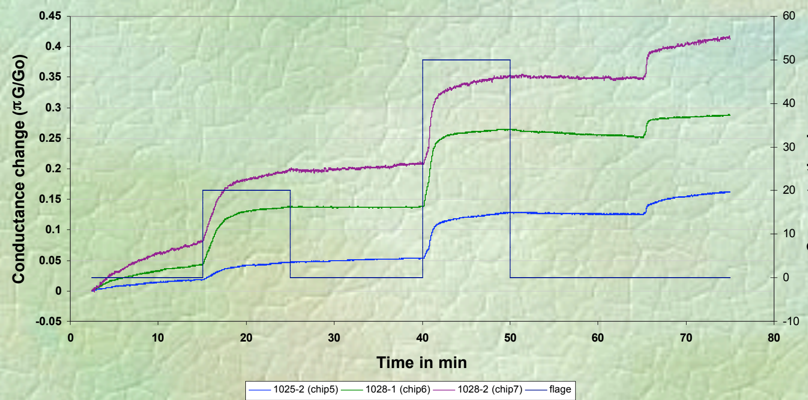




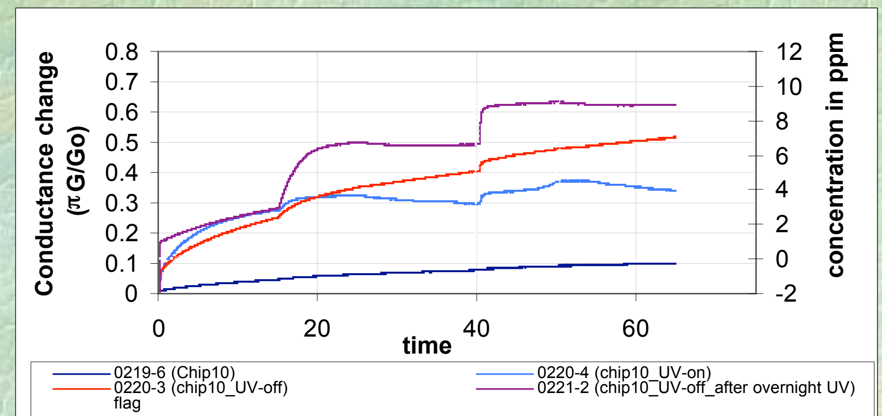
Detection limit for NO2 is 44 ppb.

Sensors for Gases

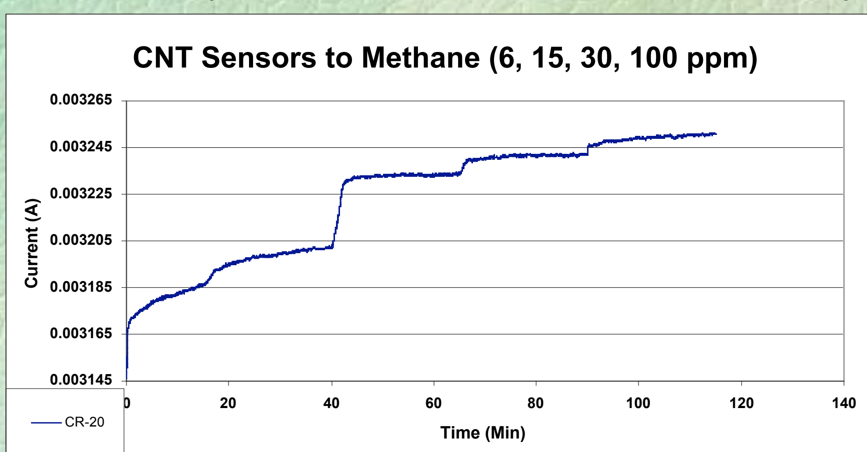
Benzene

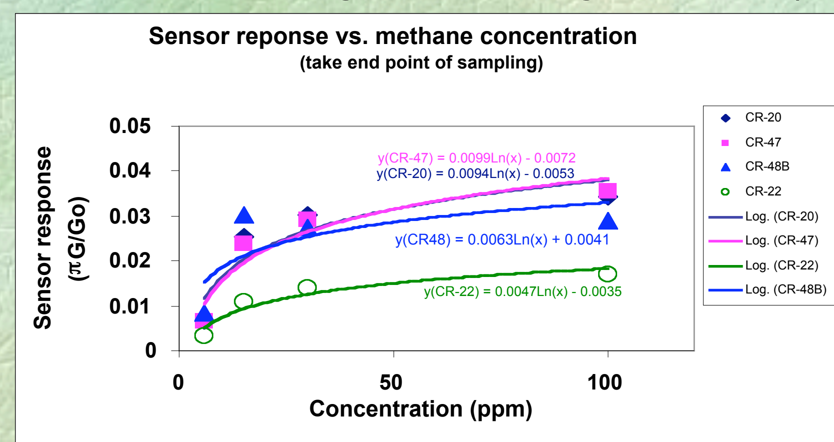


Acetone

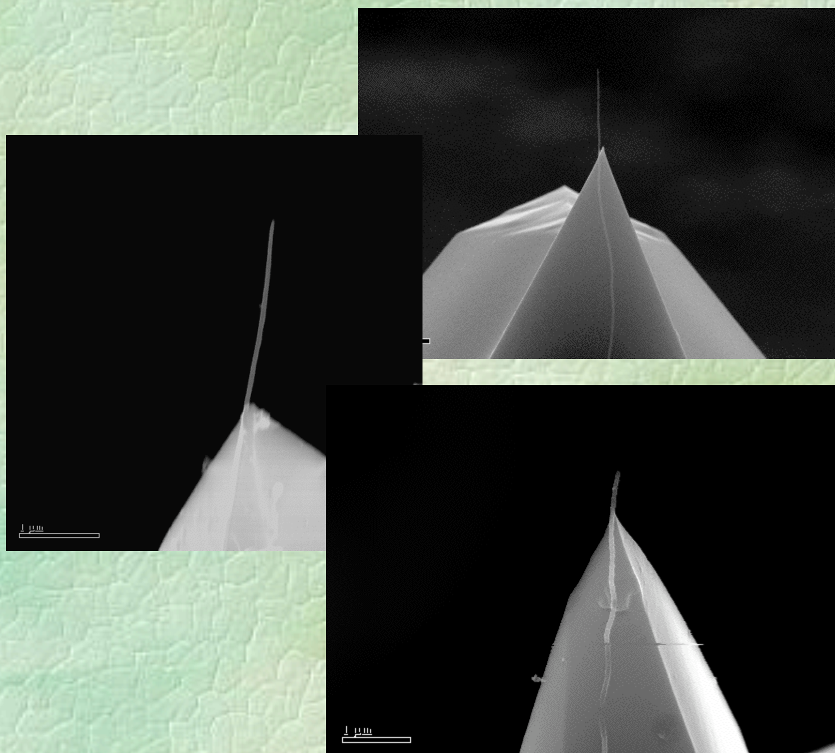


Methane (CNT is not sensitive to CH4, only CNT doped with Pd give following response)

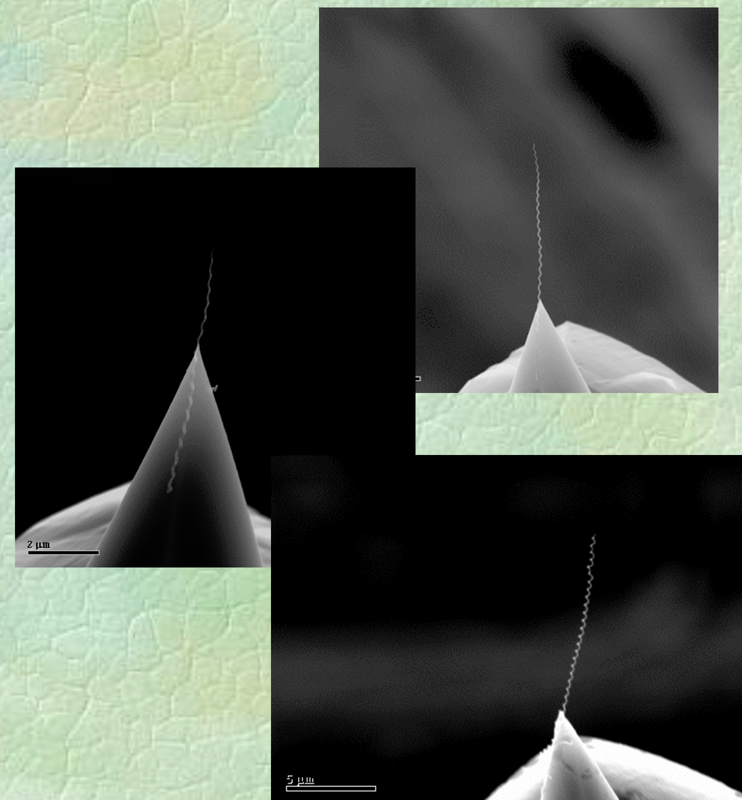




Near-term Application:
4. CNT Tip Scanning Probe Microscopy

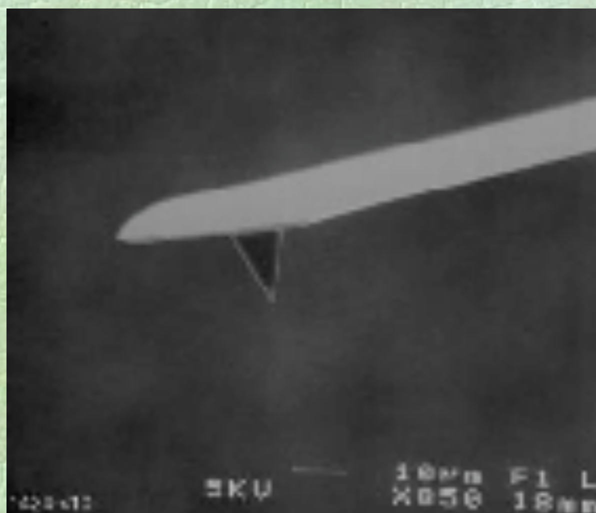


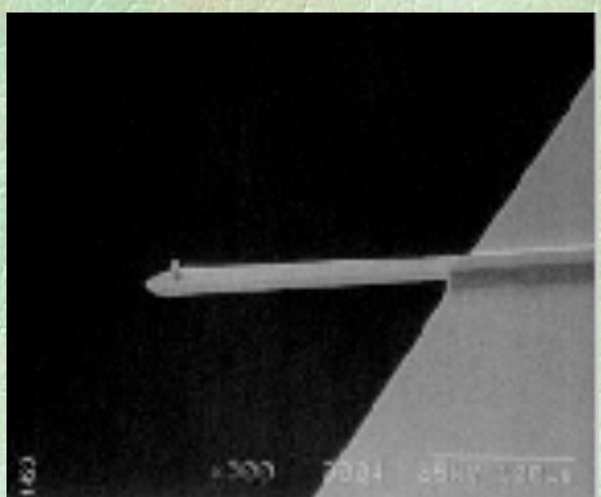
straight tube with high aspect ratio



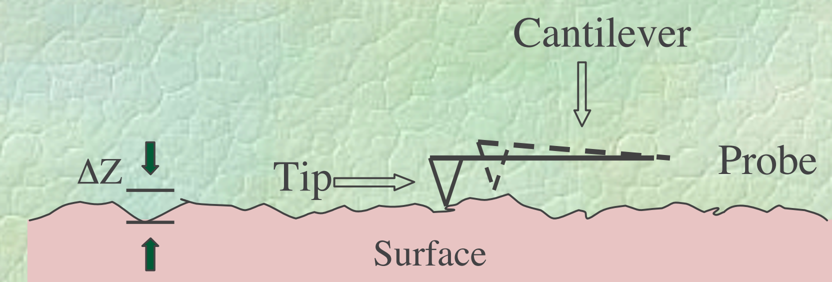
specialized coiled tube

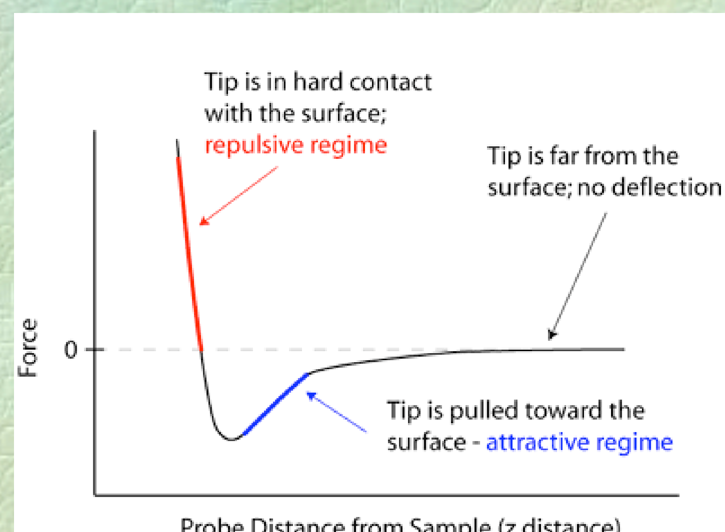
4. CNT Tip for Nanocharacterization and Nanofabrication



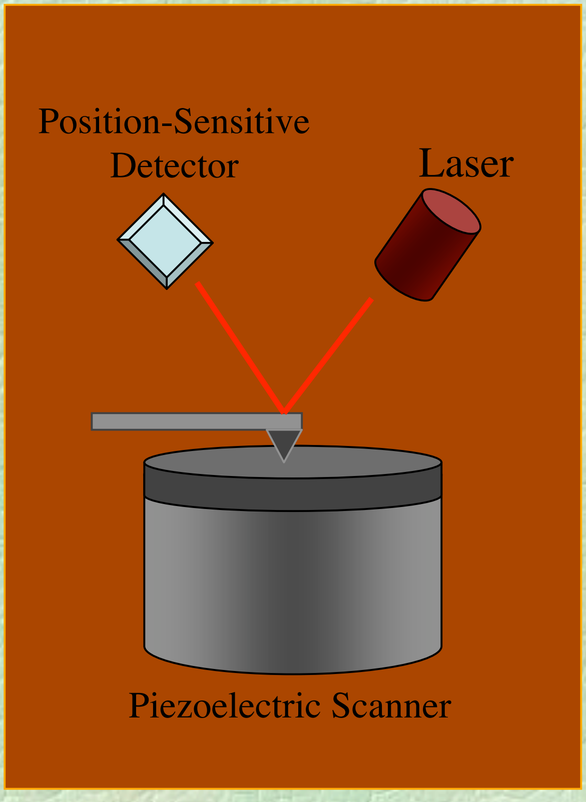


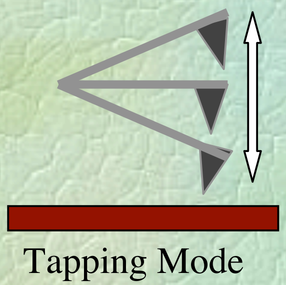
Atomic Force Microscope (AFM)

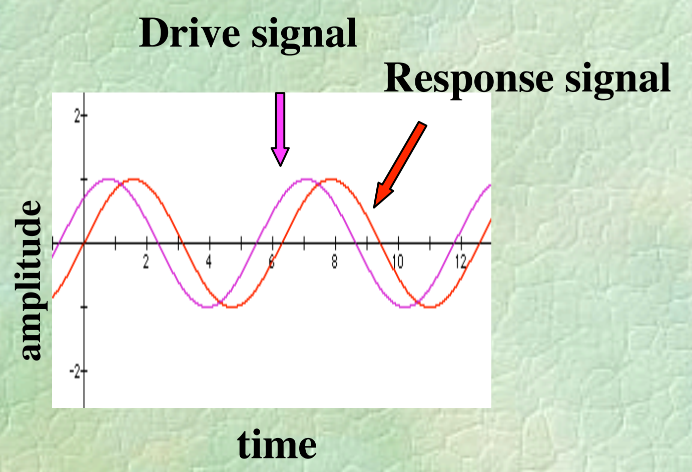




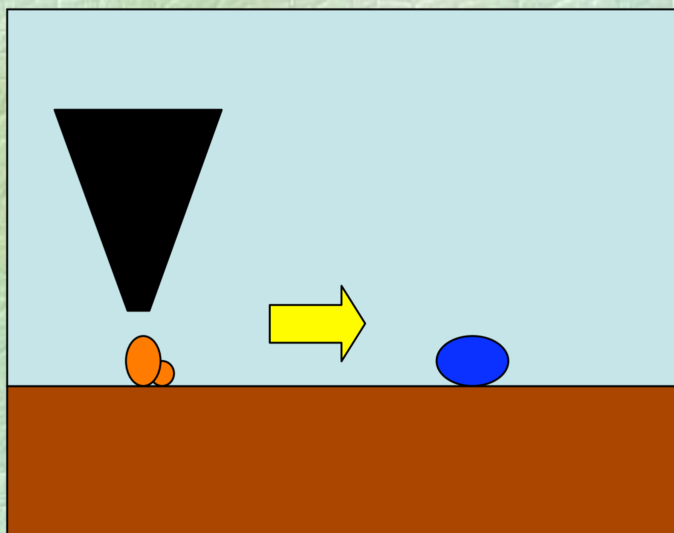
Method of Detection



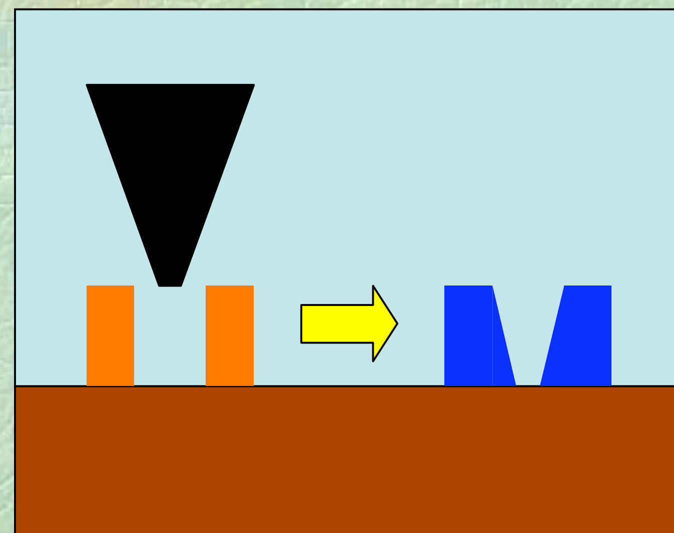




Limitation of Microfabricated Silicon Probes

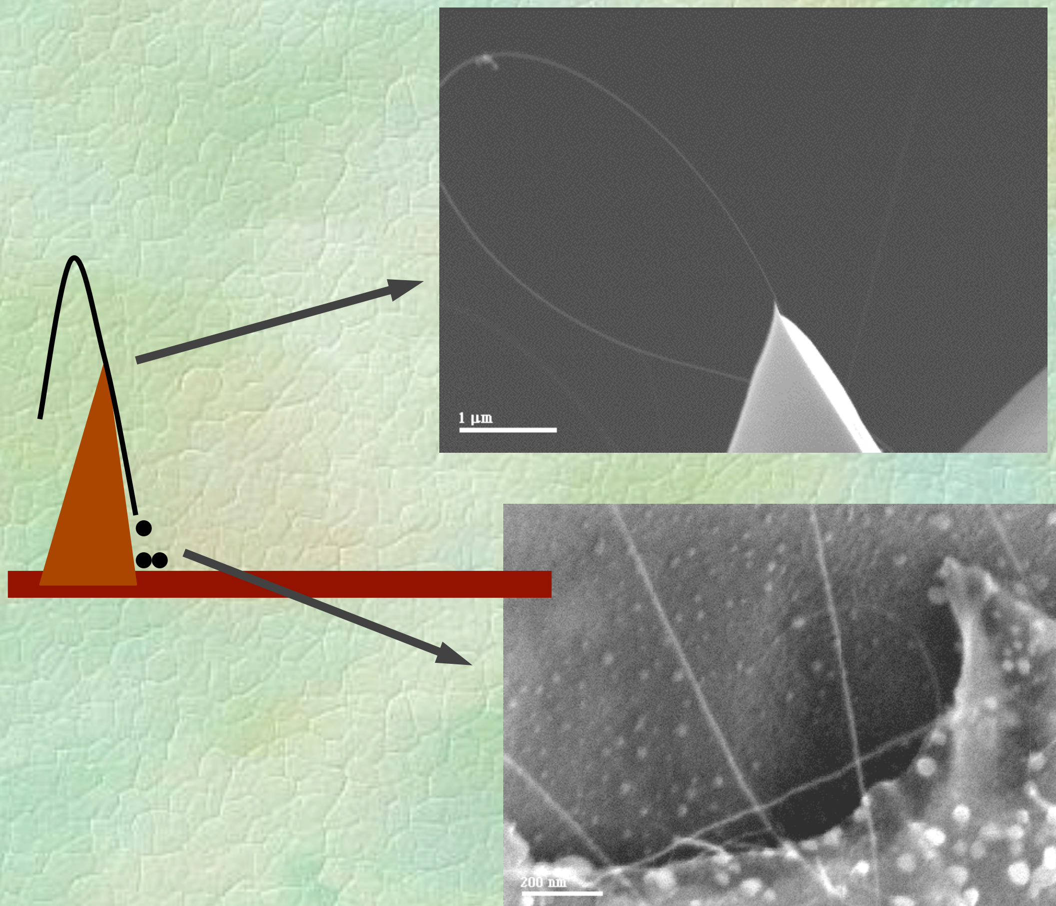


Lateral Resolution



High Aspect Ratio Imaging

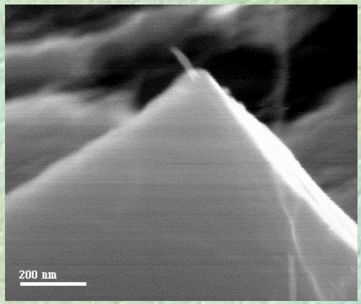
Growth of SWNT Tip by CVD

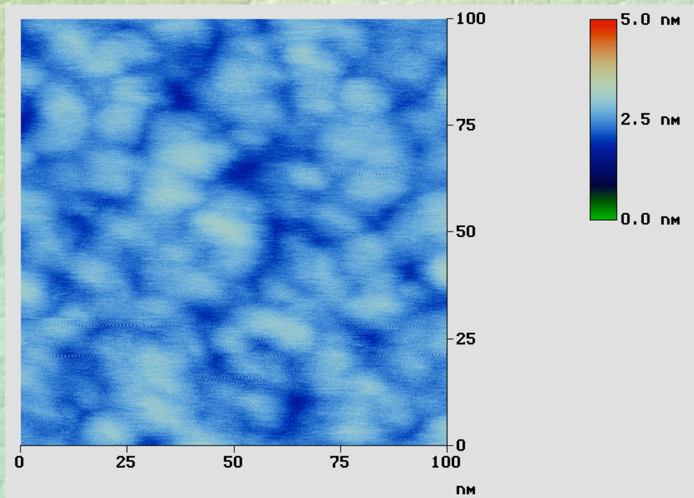


Growth of SWNTs from catalyst island at the base of the Si tip

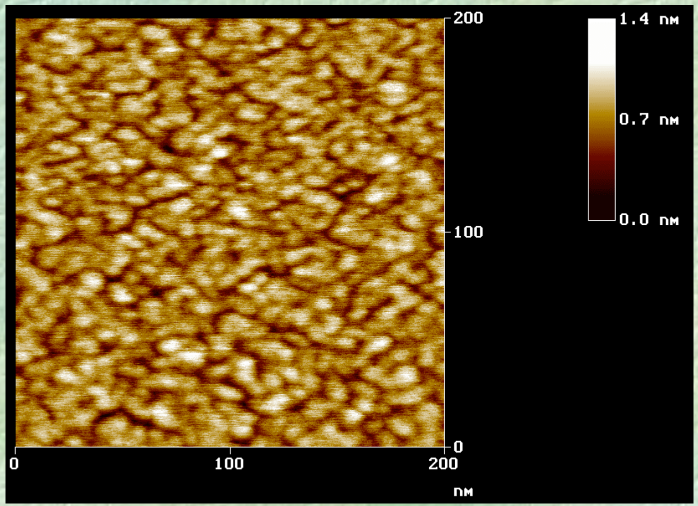
van der Walls force for the interaction of SWNTs with Si surface

High Lateral Resolution Imaging with SWNT Scanning Probes



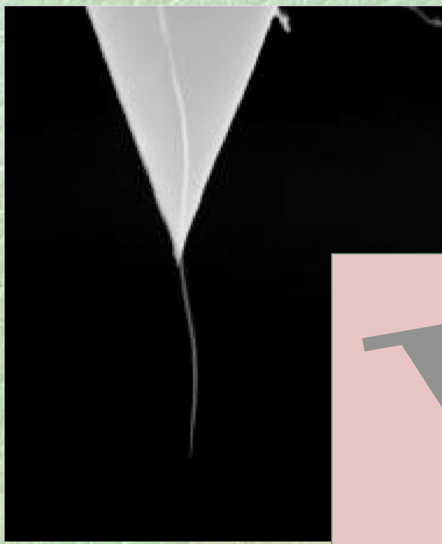


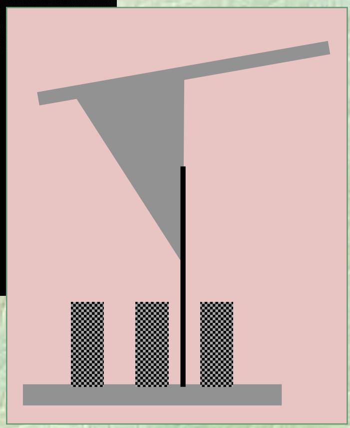
Si_3N_4 on Silicon Substrate



Ion-beam sputtered 2 nm Ir film on mica

Profilometry
MWNT tips for high aspect ratio lithography

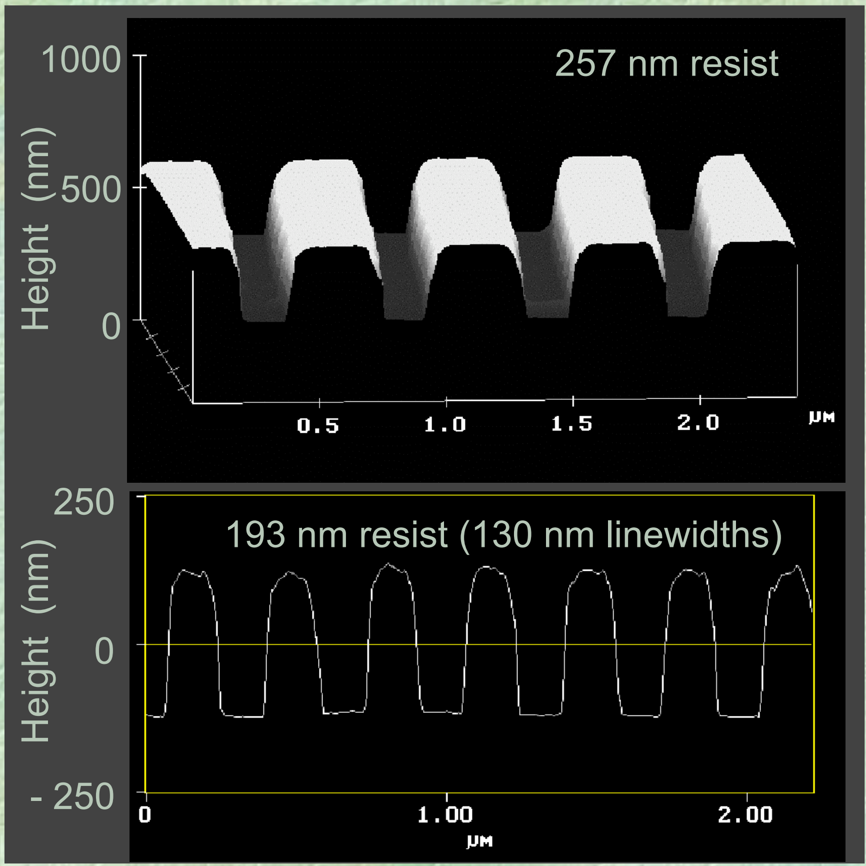




$$l^3_m/l^3_s = r^4_m Y_m/r^4_s Y_s$$

For X_m<0.5 nm

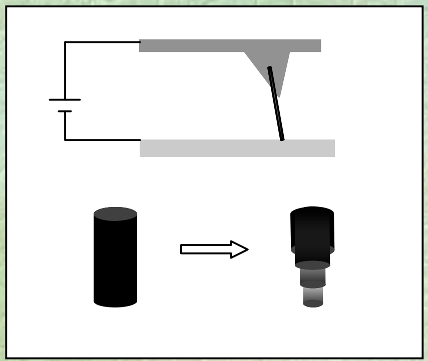
L_m >1 µm (MWNT with r =10 nm)

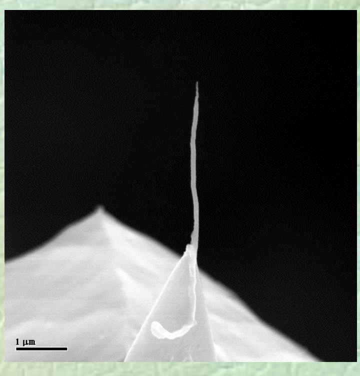


Samples from M. Sanchez and W. Hinsberg of IBM Almaden

Nguyen, C.V et al., Appl. Phys. Lett. **81,** 901 (**2002**)

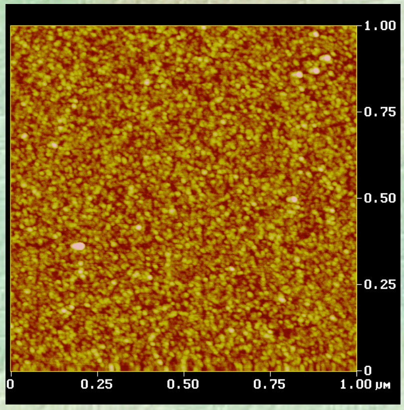
Sharpened MWNT Probes

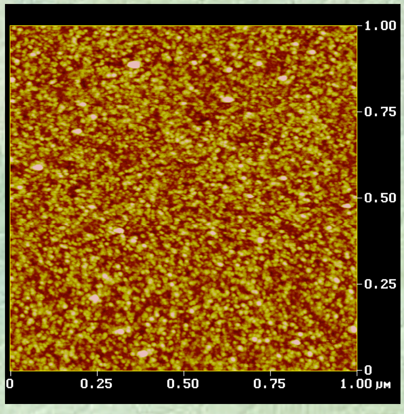




Improve lateral resolution
Radius of curvature < 5 nm

CVD HfO_2 on Si Surface

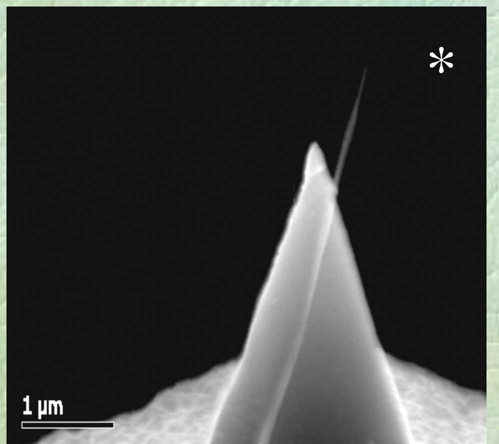


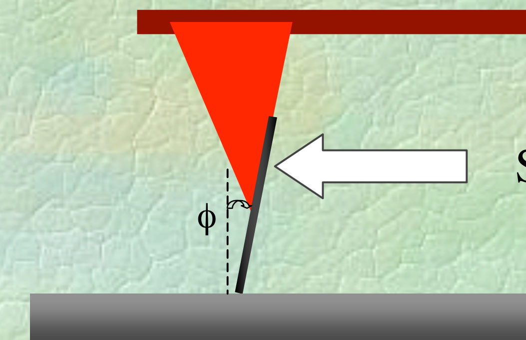


1st scan 56th scan

- RMS roughness values remain the same: 0.562 and 0.564 nm for The 1st and 56th scans, respectively.
- Control: For Si Probes, the RMS roughness values decreased with more number of scans (0.42 to 0.32 after the 12th scan)
- Sharpened MWNT tip retain the graphitic structure and therefore it is robust.

MWNT Probes Are Stable





- More forgiven than SWCNT probes because of its stiffness:

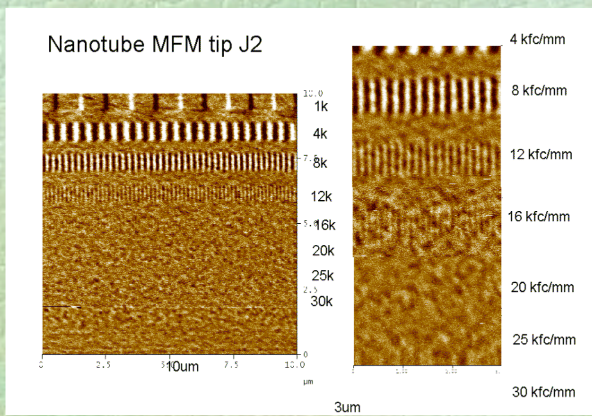
$$Rr \sim 4/3\ (L^2/r_o^2)\ \tan(\phi)$$

Rr = ratio of bending response to compression response

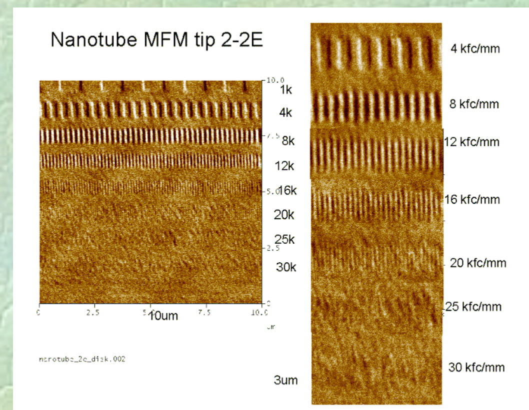
Larger radius (r_o) tube along the length of the MWCNT, smaller Rr (less bending response) and therefore less contact of CNT sidewall with sample

* Hudspeth, Q.M. et al, *Surface Science* **515**, 453-462 (**2002**)

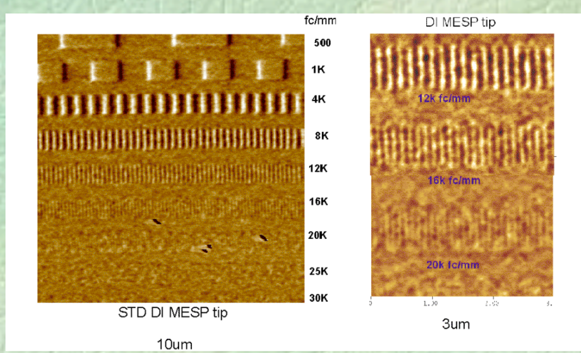
Magnetic Force Microscopy with MWNT Probes



MWNT probe w/
500 A Co coating



MWNT probe w/
300 A Co coating



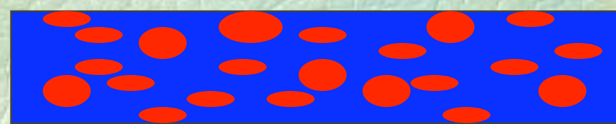
Standard MFM probe

- Optimization of Co coating

Collaboration:
Terris, B., Best, M. of IBM Almaden Research Center

Polymeric Hybrids for Low-k Dielectric On-chip Interconnects

<u>Spin-on film of porogens and MSSQ</u>



= porogens (PEO)

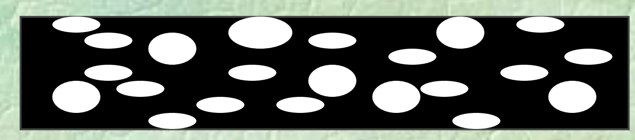
= MSSQ as the matrix material

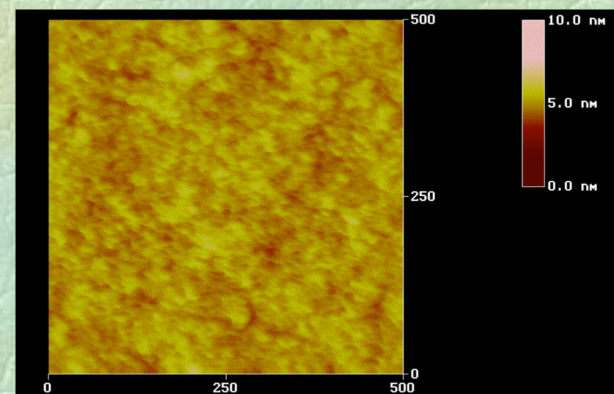
Cross-link MSSQ at 200°C

<u>Film of organic/ inorganic hybrid</u>

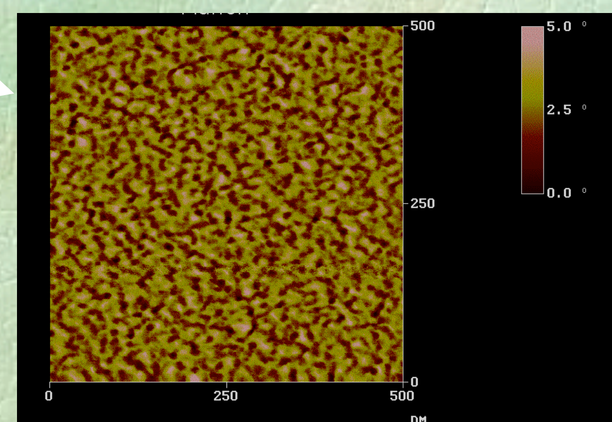
Decompose porogens at 400°C

<u>Porous poly(MSSQ) film</u>





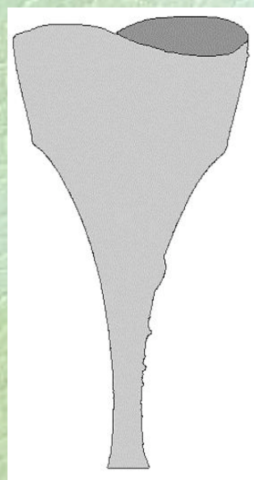
Height image



Phase image

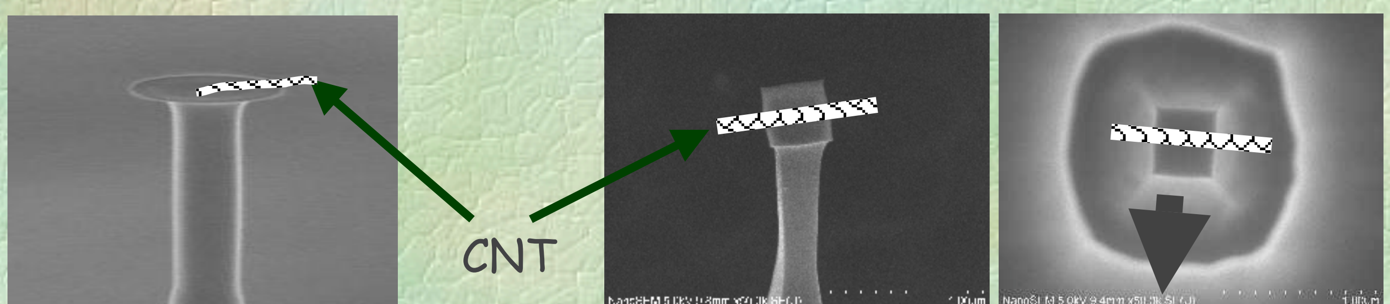
* Samples from Bob Miller and Willi Volksen of IBM Almaden Research Center

CD-AFM and Line Edge Roughness



Boot shaped/Flared Tip

- Sizes range from 70 nm to 2500 nm in diameter
- Large size prevents acquisition of high frequency roughness (This is due to averaging as opposed to dilation or "convolution").
- Currently cannot be used for dense lines smaller than 70 nm (1:1 ratio)

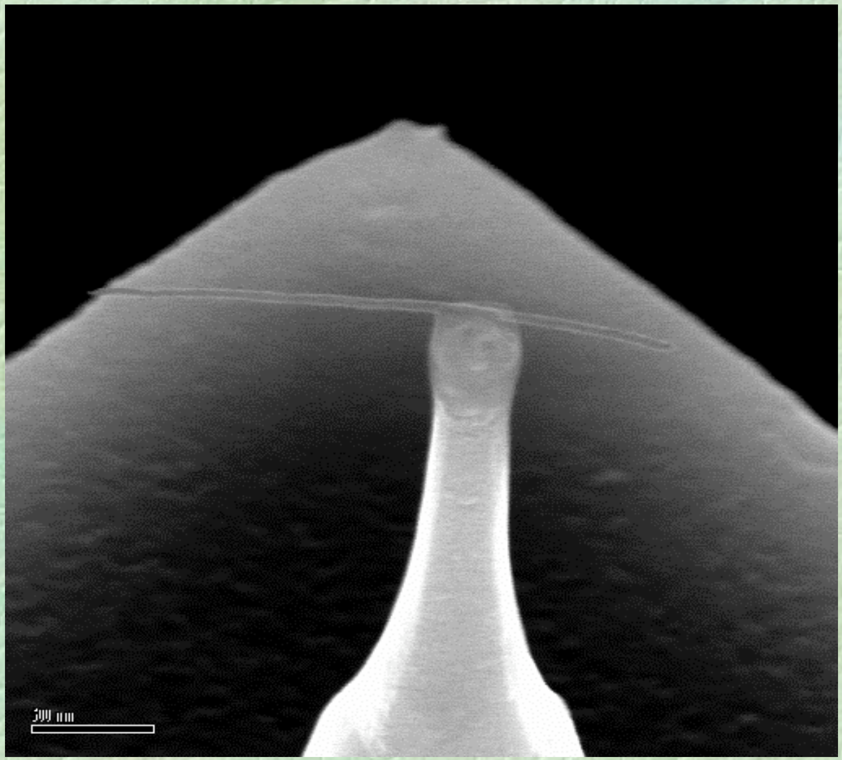


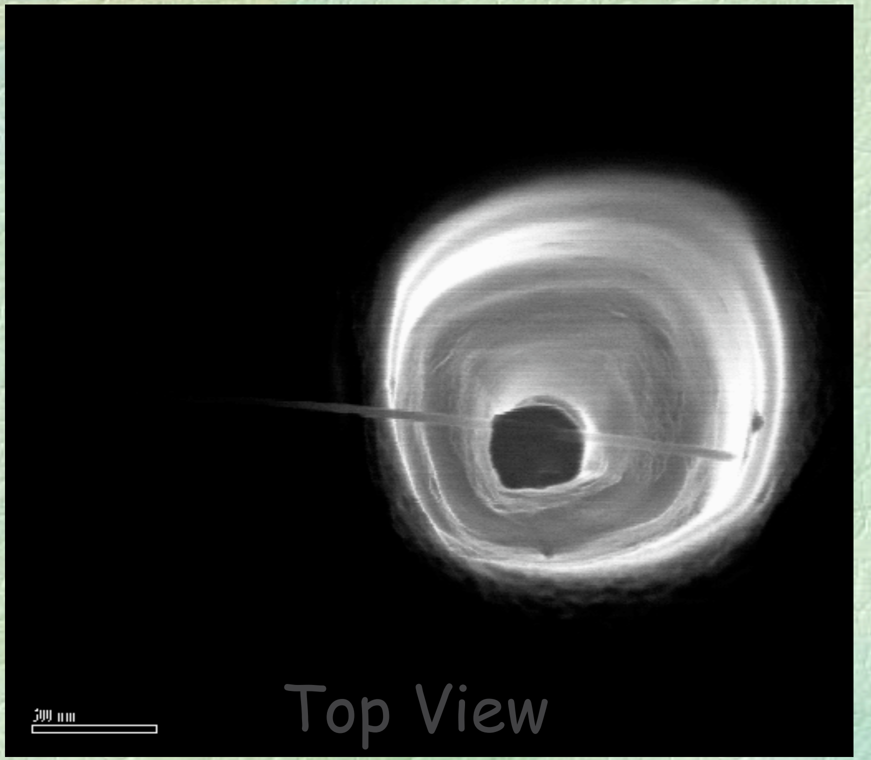
One Side

Two Sides

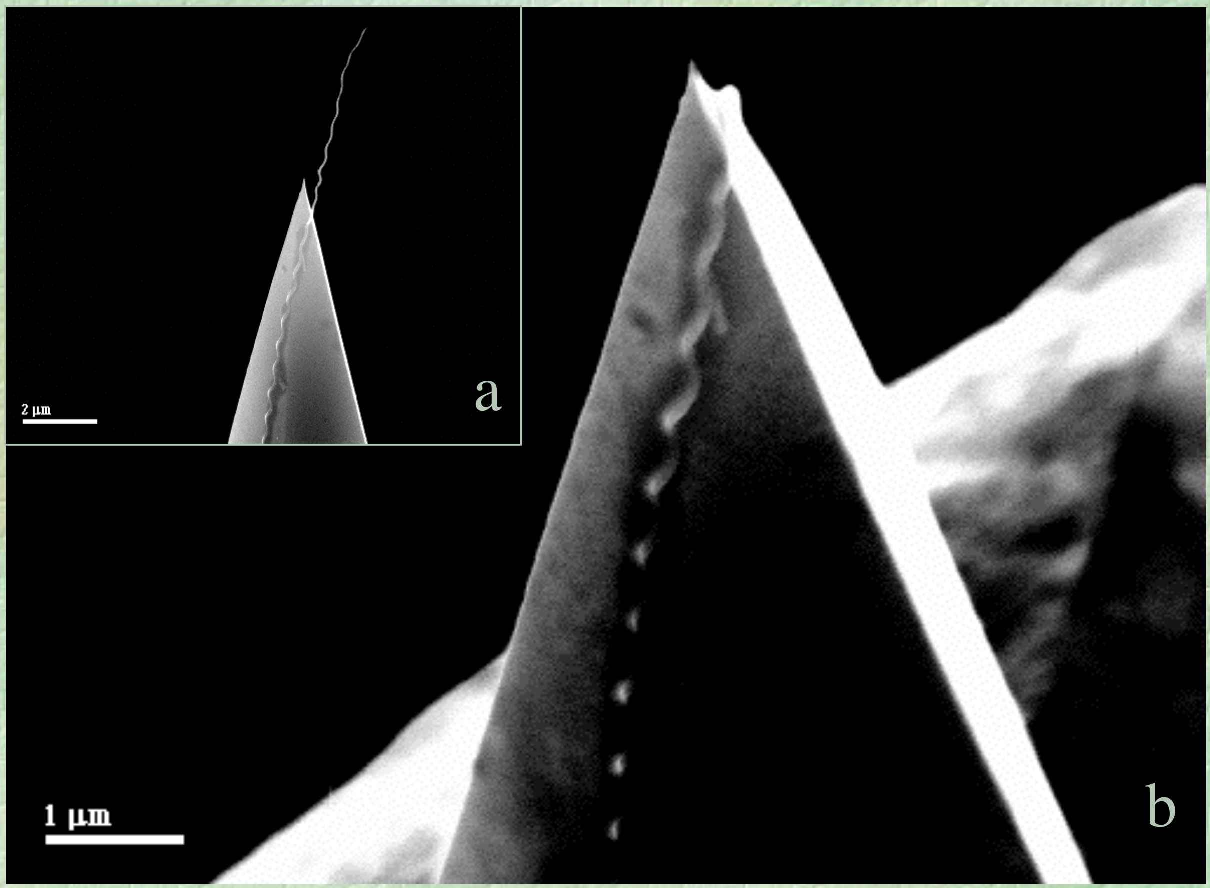
Collaboration: Theodore Vorburger, Joe Fu and George Orji (NIST)

MWNT tip for Line Edge Roughness



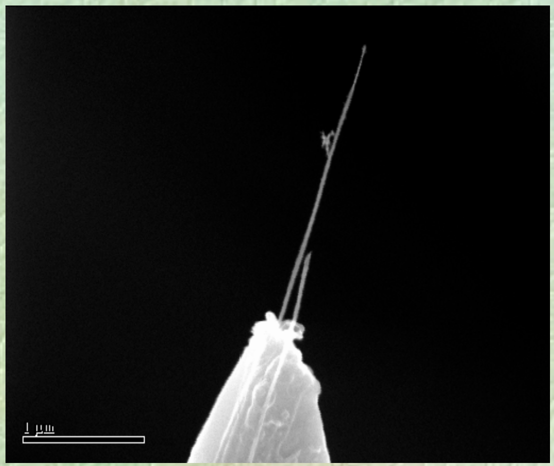


Biological Imaging In Liquid Environment

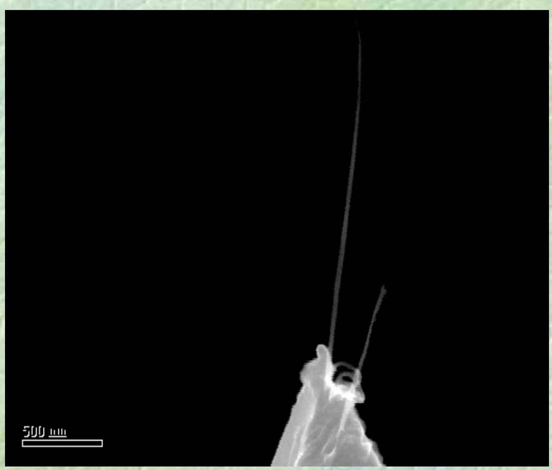


a) MWNT probe. b) MWNT probe after immersion in H_2O.
MWNT is folded back against the underlying Si probe where it is pinned against this surface by Van der Waals forces.

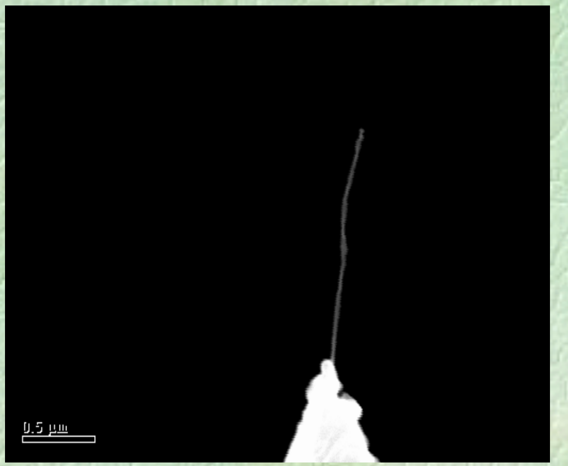
Oxygen Plasma Treatment for Imaging In Liquid



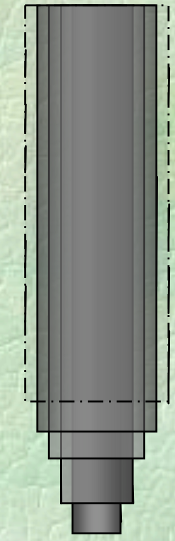
T=0 min



T=5 min, 50w, 500mtorr



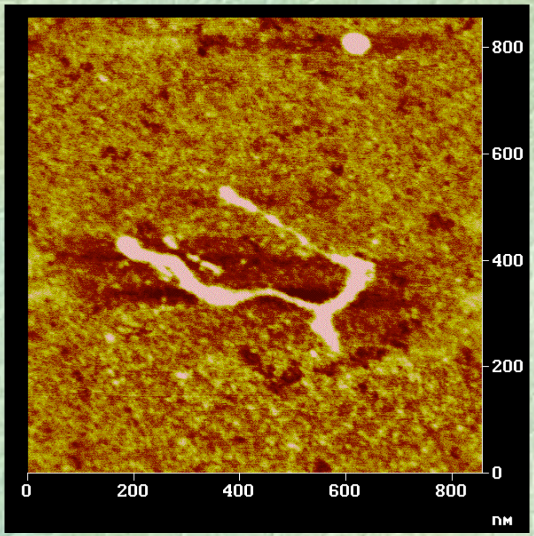
T=10 min, 50w, 500mtorr

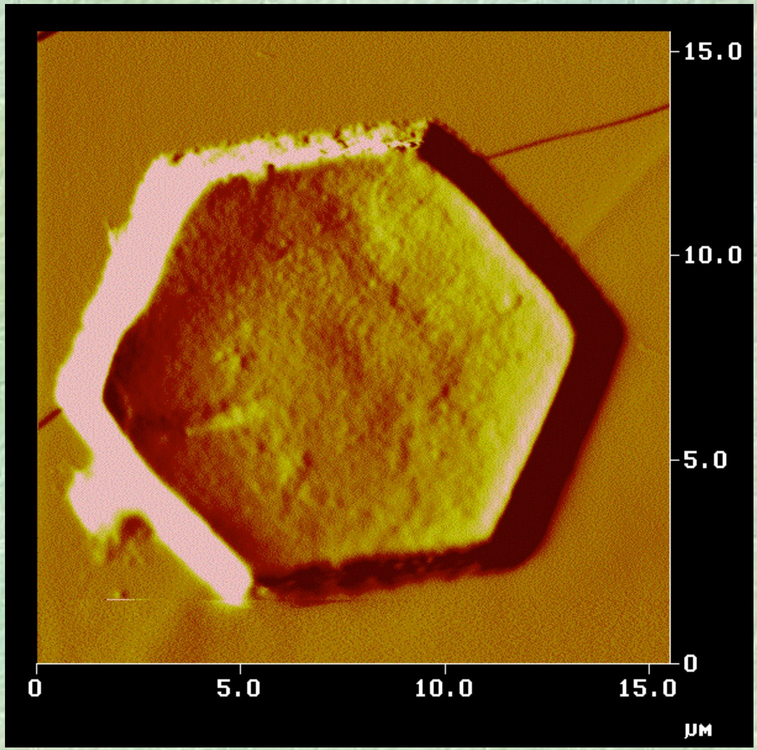


T= 1-2 minutes: Formation of hydrophilic chemical groups such as quinones, phenols and carboxylic acids.

Aqueous Biological Imaging

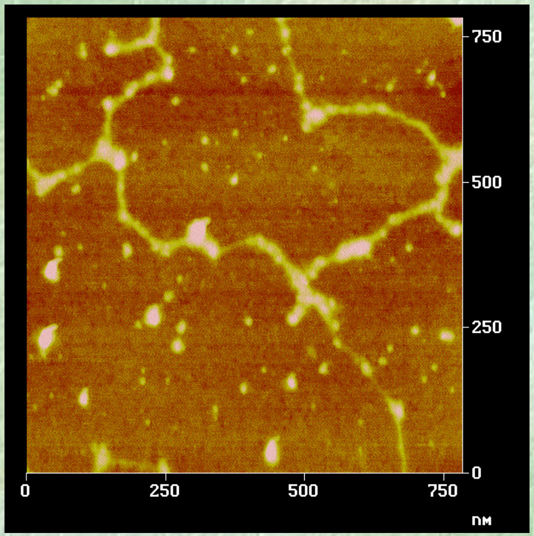
DNA on
APTES
coated mica





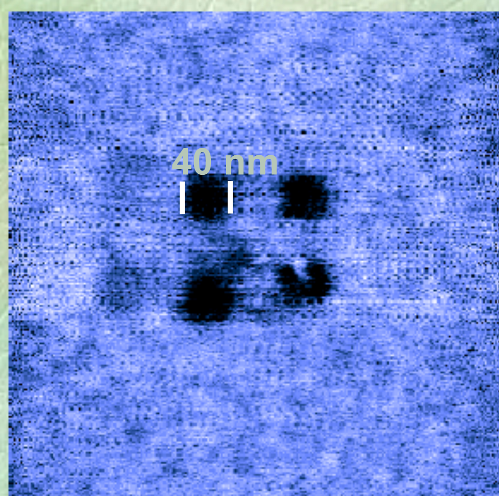
HSP 60 protein crystal imaged using
MWCNT probe in air.

DNA on
mica

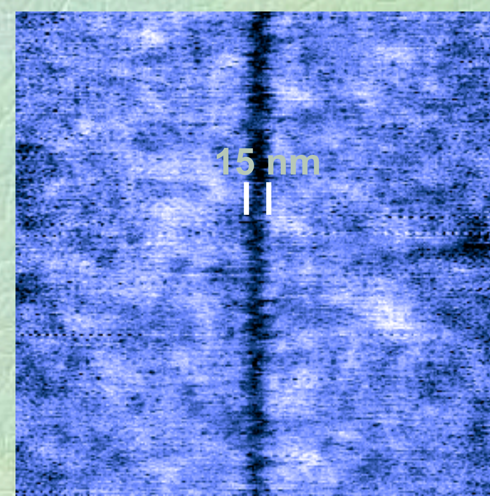


Dip-pen Nanolithography with MWNT Probes

LFM images show Octadecanethiol Patterned on Au(111) surface



0 nm 500



0 nm 350

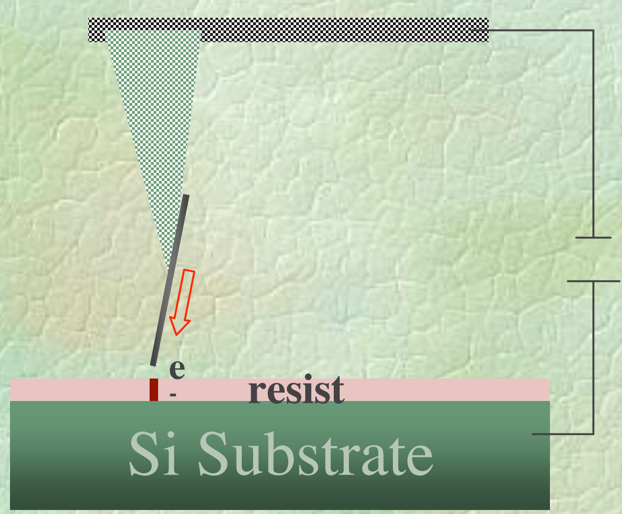
- Slower transfer rate of materials from tip to substrate

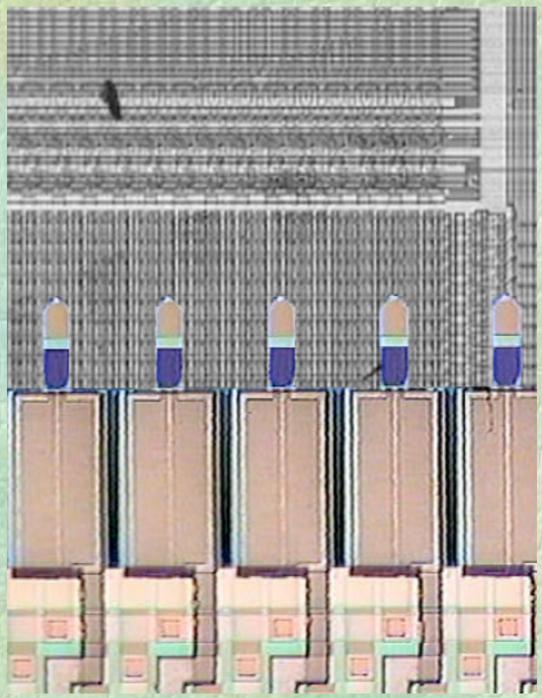
* Khalid Salaita, David S. Ginger and Chad Mirkin, Northwest Univeristy

SPL Nanofabrication

Use CNT probes for scanning probe lithography

- Excellent registry and alignment
- No proximity effect (e-beam lithography)





-**SPL offers great control over positioning, and dense structures (circumvents proximity effect in EBL)**

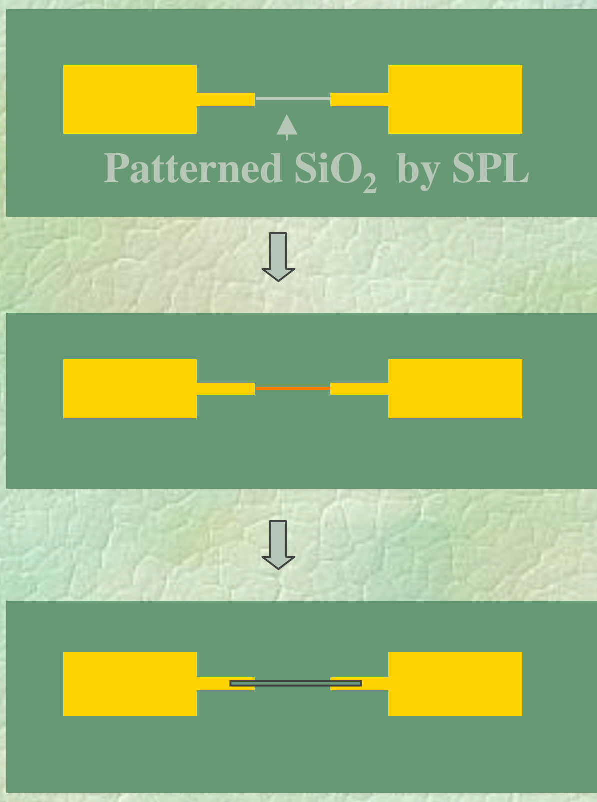
- Improve resists, optimized for SPL applications

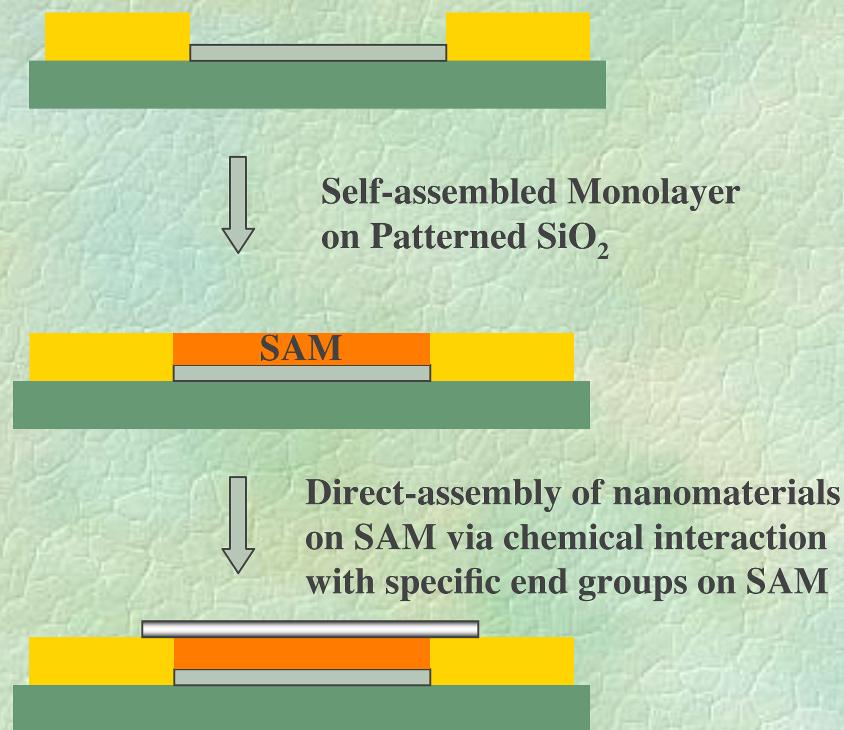
-**Multi-probes AFM (i.e. IBM millipedes)**

higher throughput

Minne, S.C. et al. *Appl Phys Let*. **73**, 1742 (1998)

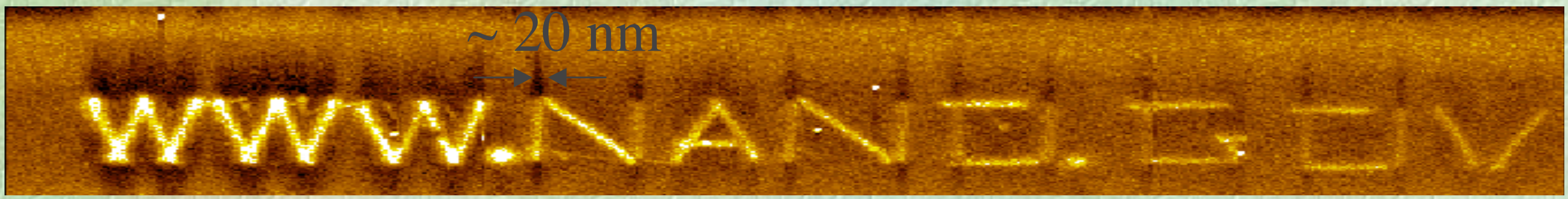
Chemical Nanopatterning for Directed Self-Assembly





Nanolithography

Anodization of hydrogen-passivated silicon surface with MWNT probe by applying a DC field (-17 V) between tip and substrate in air



- Due to strong binding energy for carbon atoms (14.5 eV and 12.5 eV for hexagon and pentagon, respectively) carbon nanotube tip under strong applied field (20V/nm) won't field evaporate atoms

Acknowledgements

M. Meyyappan and NASA for financial support

Ramsey M. Stevens
Lance Delziet
Philippe Sarrazin
Brett Cruden
Alan Cassell
Jing Li
Laura Ye

And You for your attention….

5. Summary and Perspectives

- Much progresses have been made, resulting in real near-term benefits.

Perspectives:

Opportunities for science and industry

- Si CMOS is maturing, but it can be combined nanotechnology for many more important and commercial important applications
- Require integration for functional materials (biomolecules with nanomaterials)
- Nanoscale fabrication must be achieved. It is the key to opening applications