Carbon Nanotubes and Their Potential Applications

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International Congress of Nano Bio Clean Tech

Outline

1. Carbon Nanotubes
   A. Structures and properties
   B. Synthetic Techniques
2. Applications
   A. Bio and Chemical Sensors
   B. Multifunctional Nano-polymer composites
   C. Field emission Applications
3. 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 ato

(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.

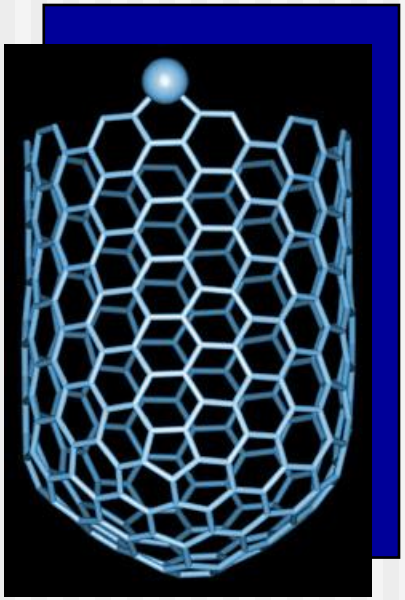
Use Knowledge of Biology, Chemistry, Physics, Engineerin to develop useful technologies.

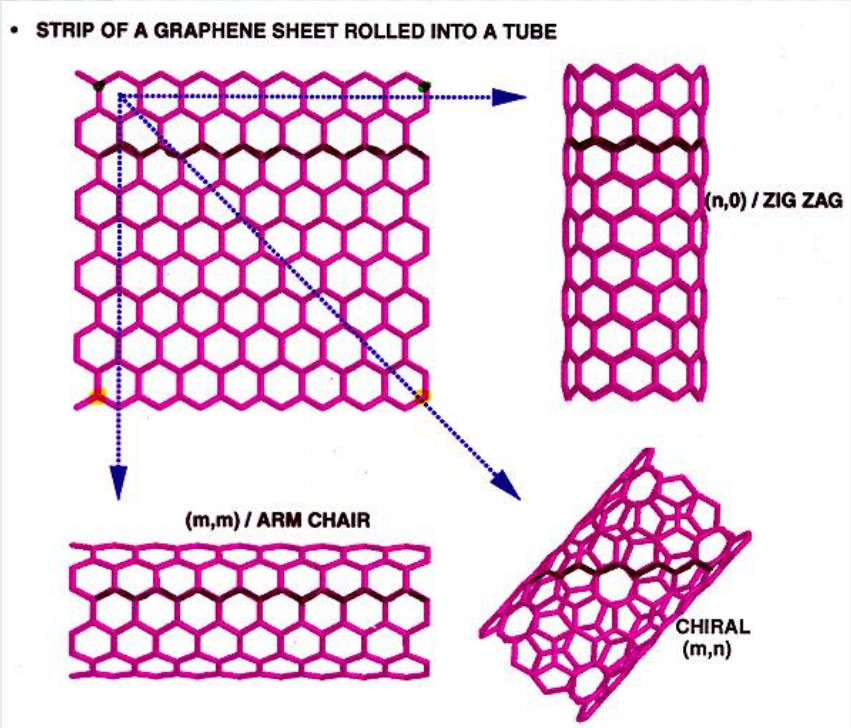


Sensors - combination of CMOS and Bio Chemistry.

1. Carbon Nanotube

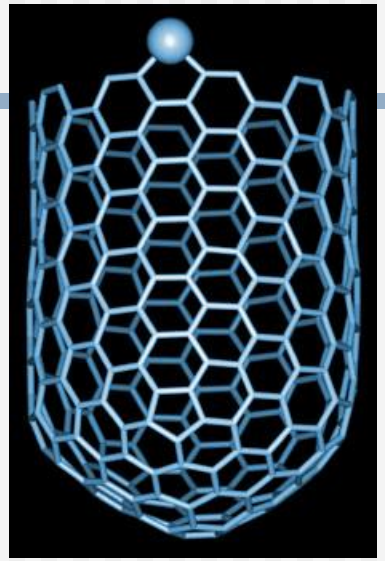
- CNT is a tubular form of carbon with diameter as small as nm.
- Length: few nm to microns.
- CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.



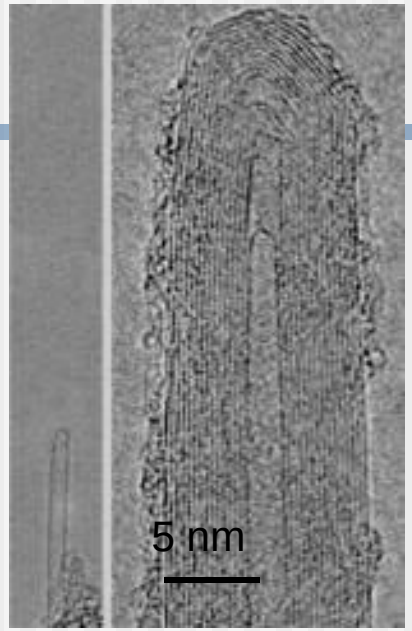


- CNT exhibits extraordinary mechanical properties: Young's modulus over 1 Tera Pascal.
- CNT can be metallic or semiconducting, depending on chirality.

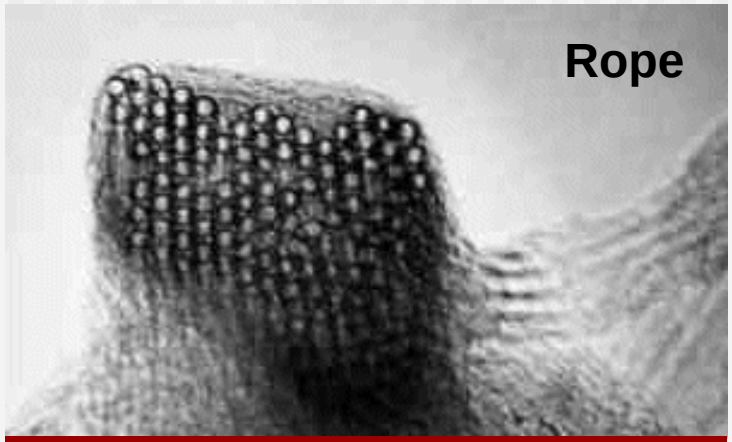
Nanotube Images



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



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

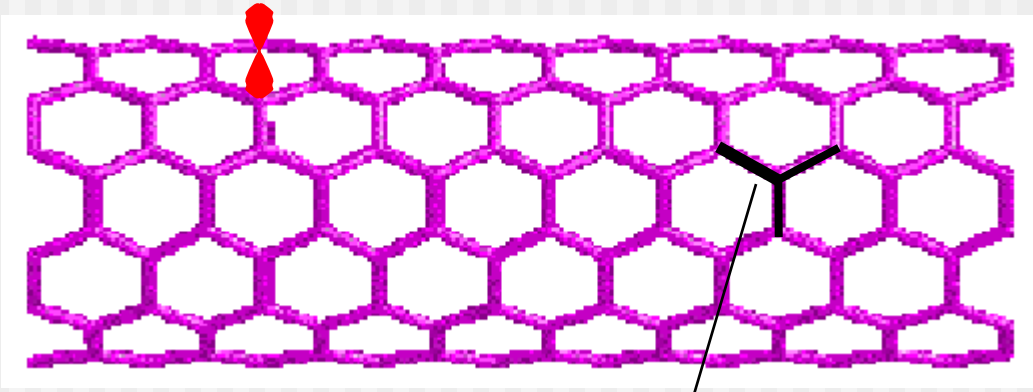


Thess et. al, Science (1996)

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

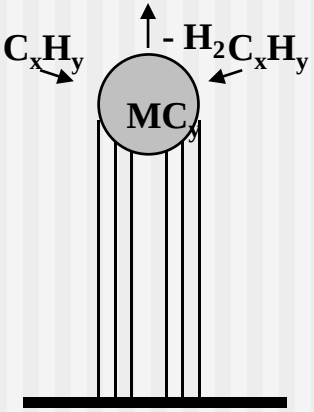
- CNT has been grown by laser ablation (pioneered at Rice) and carbon arc process (NEC, Japan) - early 90s.
  - SWNT, high purity, purification methods

- 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

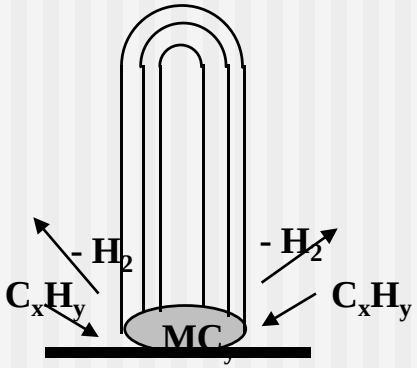


CVD Growth Mechanisms For Carbon Nanotubes

- 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 growt mechanism
- Growth stops when graphitic overcoat occurs on the growth front - “catalyst poiso



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

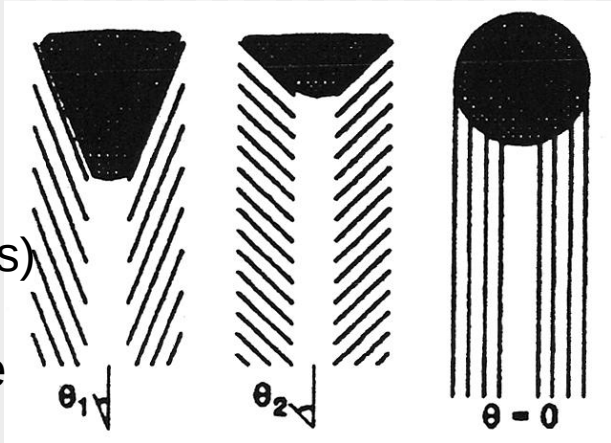
- Filaments consist of stacked-cone arrangement of graphite basal plane sheets; grow with particles at the tip; hydrogen is believed to satisfy the valences at cone edges in filaments

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

- When $\theta = 0$, 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°

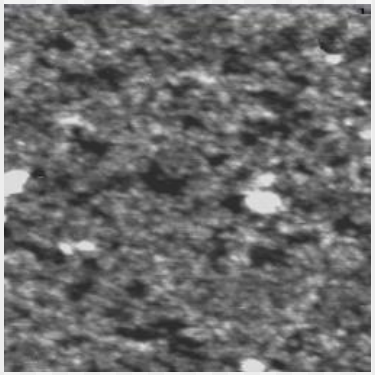
- Better to call these structures as MWNFs (filaments) instead of graphitic carbon fibers (GCFs) or vapor grown carbon fibers (VGCFs) both of which denote solid cylinders

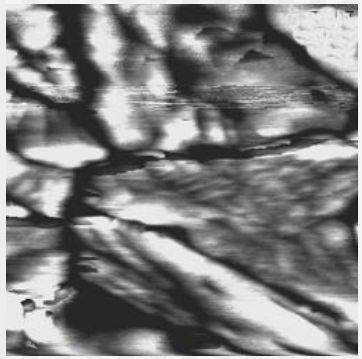


Nolan et al, JPC, B, 1998

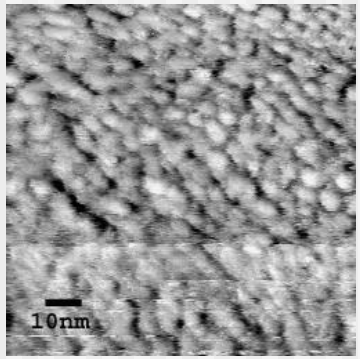
Catalyst Characterization

- 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.



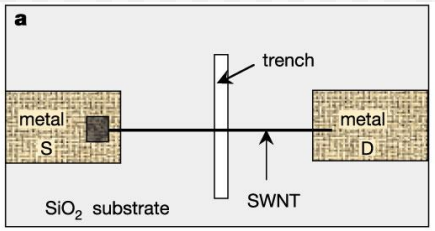


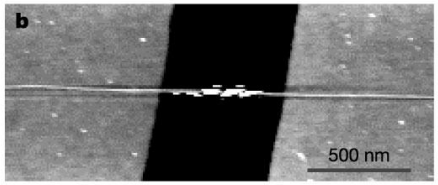
- STM image of a nickel catalyst showing nanoscale particles

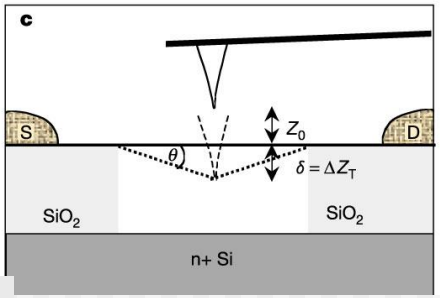


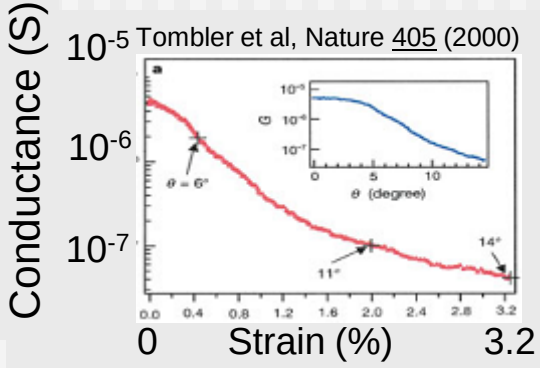
- These results are consistent with high resolution TEM showing particles as small as 2 nm.

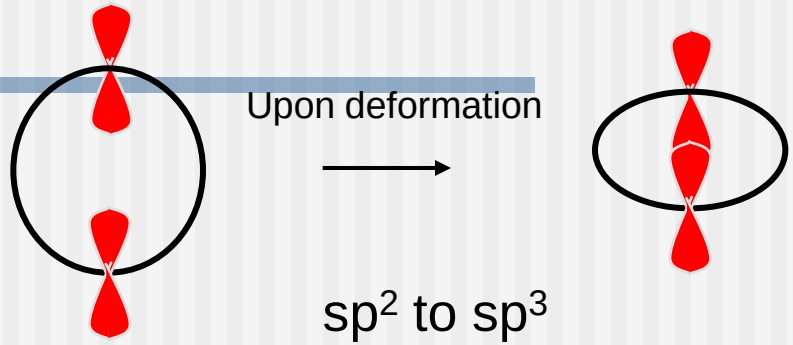
Electromechanical Properties



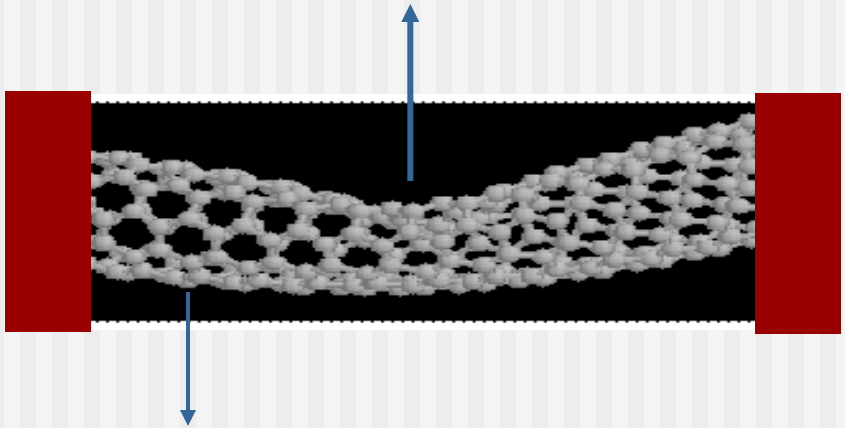








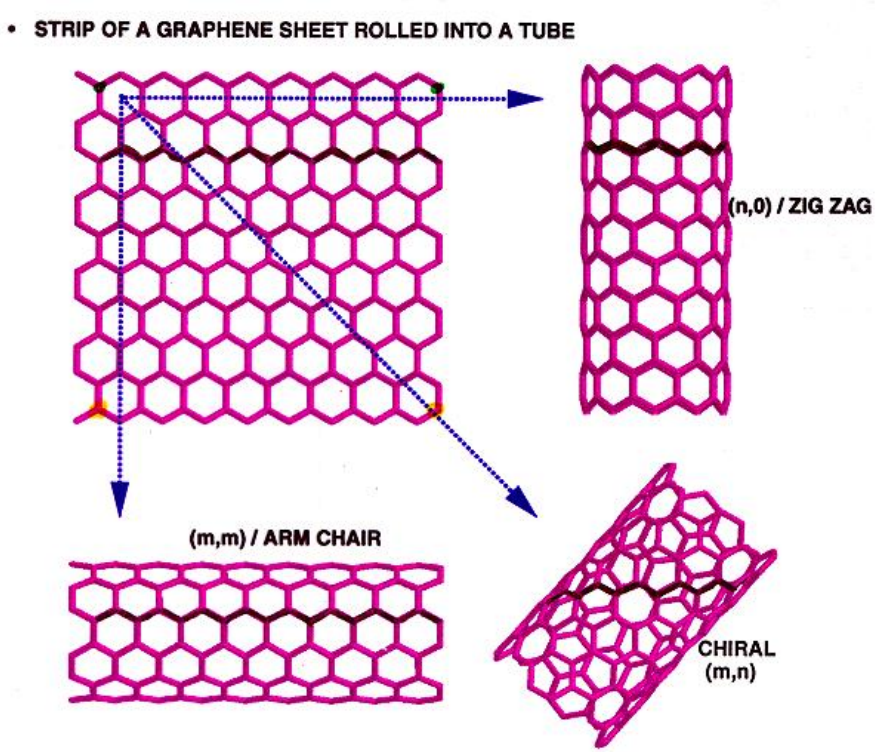
sp^2 to sp^3

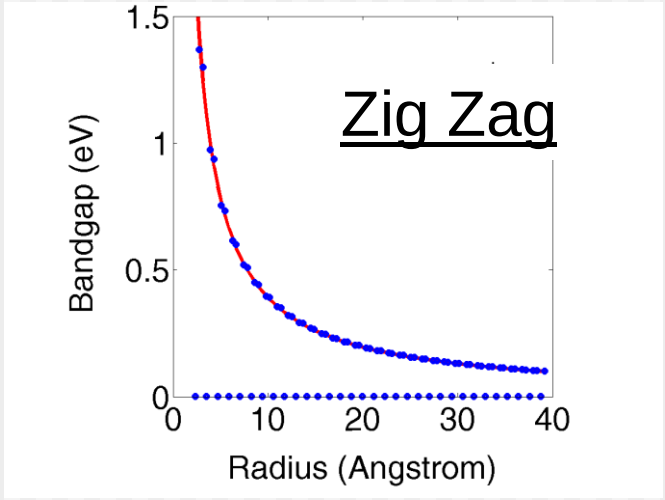


Stretching of bonds

What is the conductance decrease due to?

2. Properties
SWNT Electronics





Chiral Tubes are Semiconducting - Nanoelectronics

$$d = [3(n^2+nm+m^2)]^{1/2} a_{c\text{-}c}/\pi$$

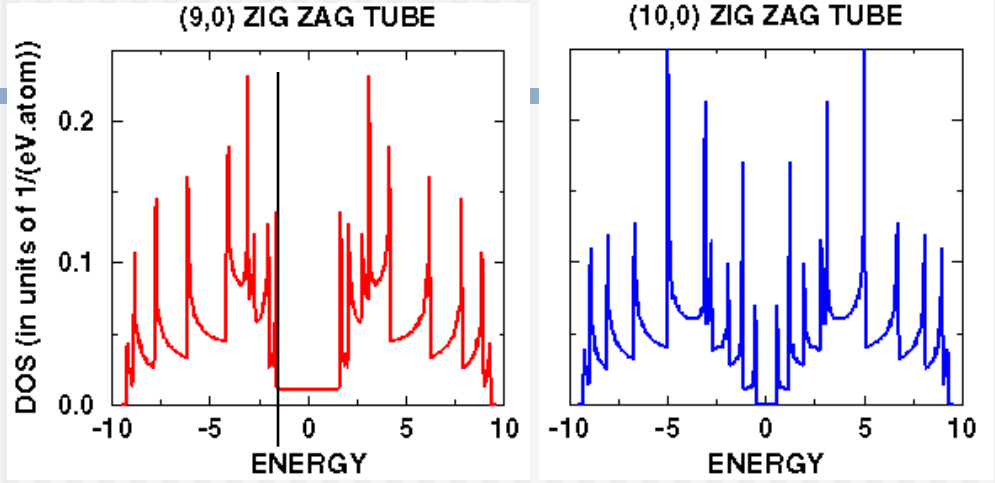
- semiconducting [(n-m), 3] ≠0

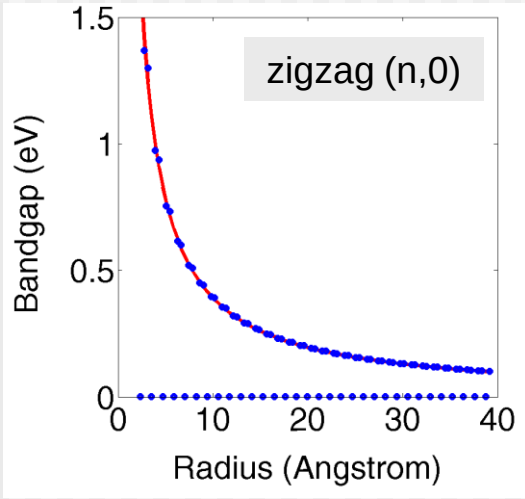
- metallic [(n-m), 3] = 0

Armchair tubes do not develop a band gap

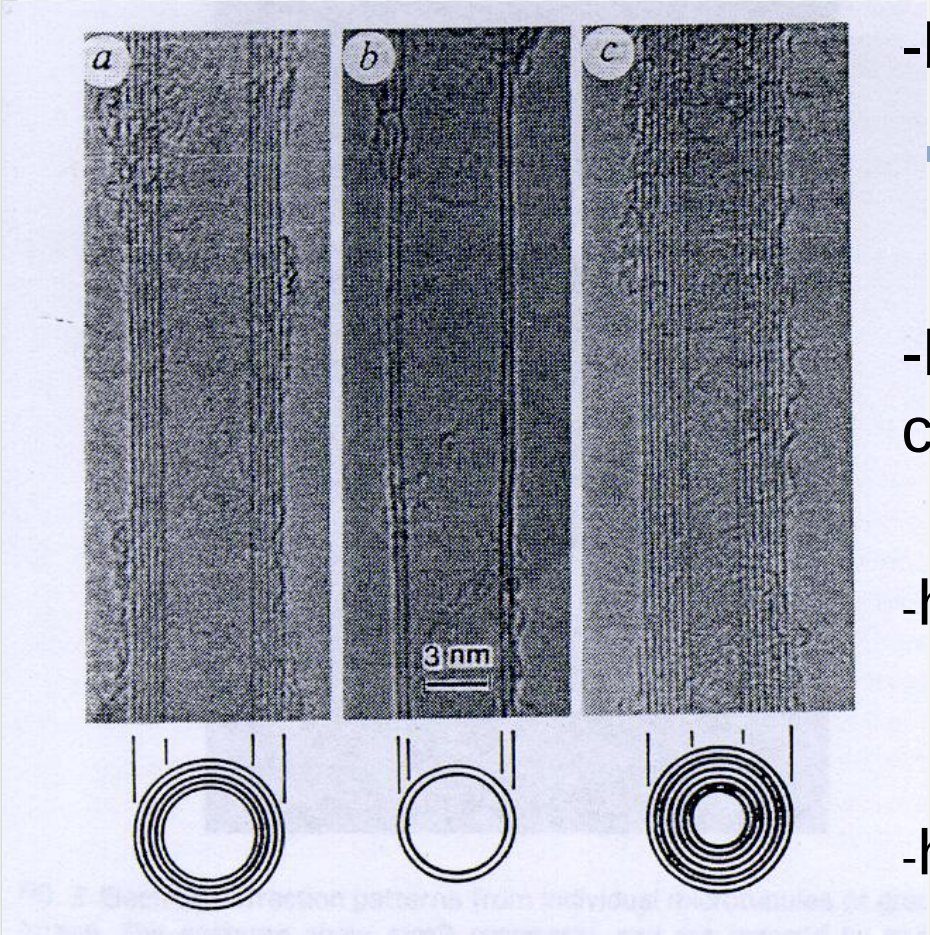
Summary of SWNT Electronic Properties

- 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, Thermal, 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

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

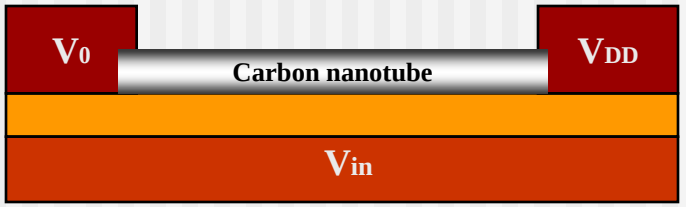
- CNT based microscopy: AFM, STM…
- Nanotube sensors: force, pressure, chemica
- Biosensors
- Molecular gears, motors, actuators
- Batteries, Fuel Cells: H_2, Li storage
- Nanoscale reactors, ion channels
- Biomedical
  - in vivo real time crew health monitoring
  - Lab on a chip
  - Drug delivery
 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

Challenges

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

Applications: Electronics

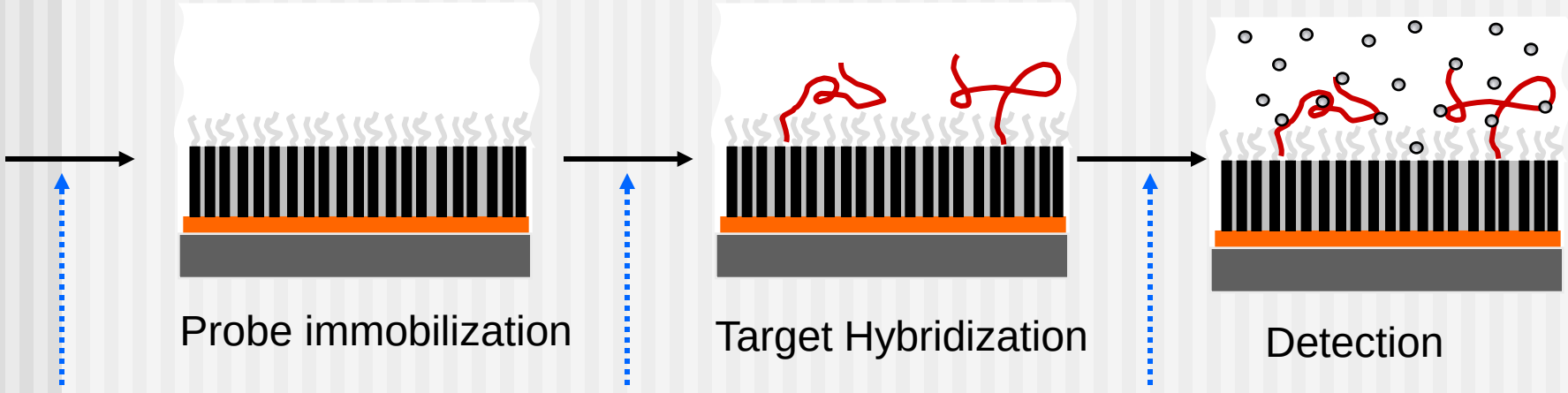
- CNT quantum wire interconnects
- Diodes and transistors for computing
- Capacitors
- Data Storage
- Field emitters for instrumentation
- Flat panel displays
- THz oscillators



Challenges

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

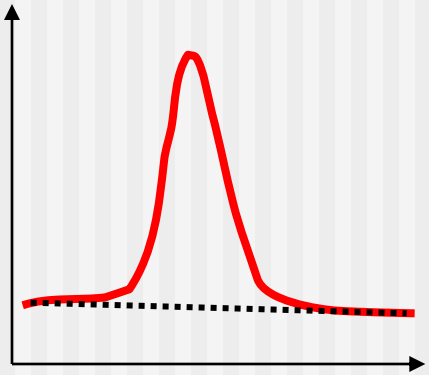
Carbon Nanotube Biointerface: Biosensor Applications



Nucleic Acid probe

Target molecules

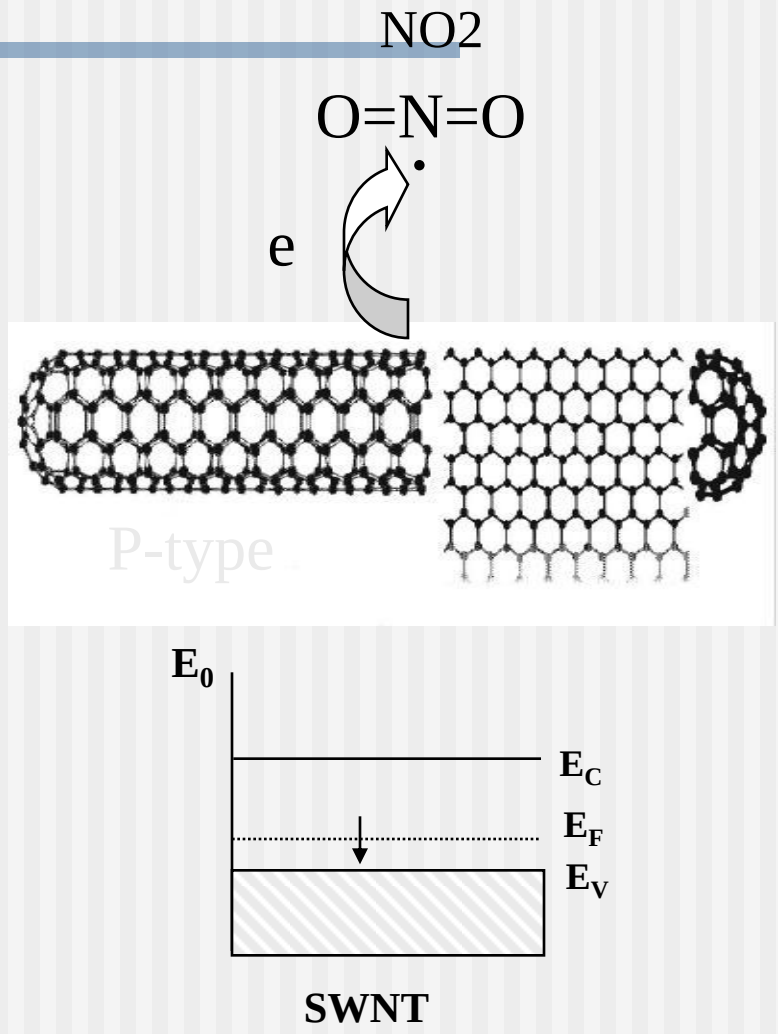
Electrochemical Mediator or Indicators



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

Application: Chemical Sensors

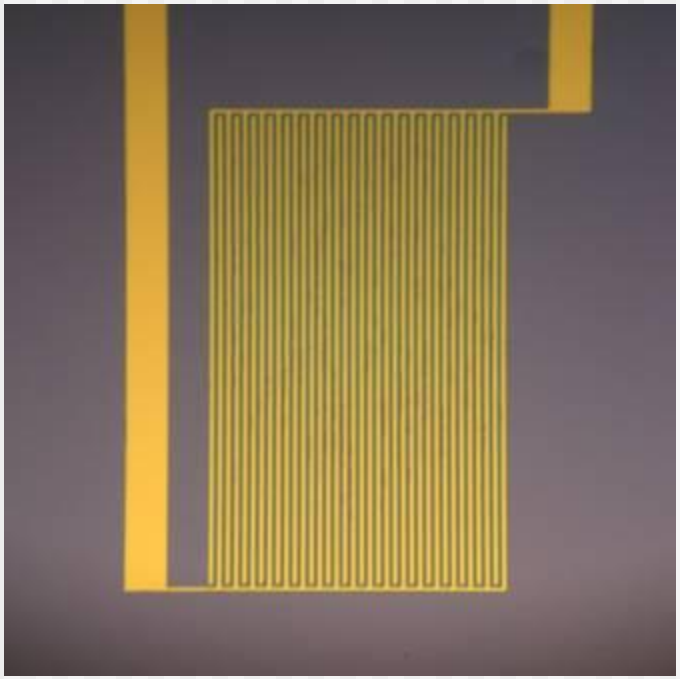
- Every atom in a single-walled nanotube (SWNT) is on the surface and exposed to environment
- Charge transfer or small changes in the charge-environment of a nanotube can cause drastic changes to its electrical properties

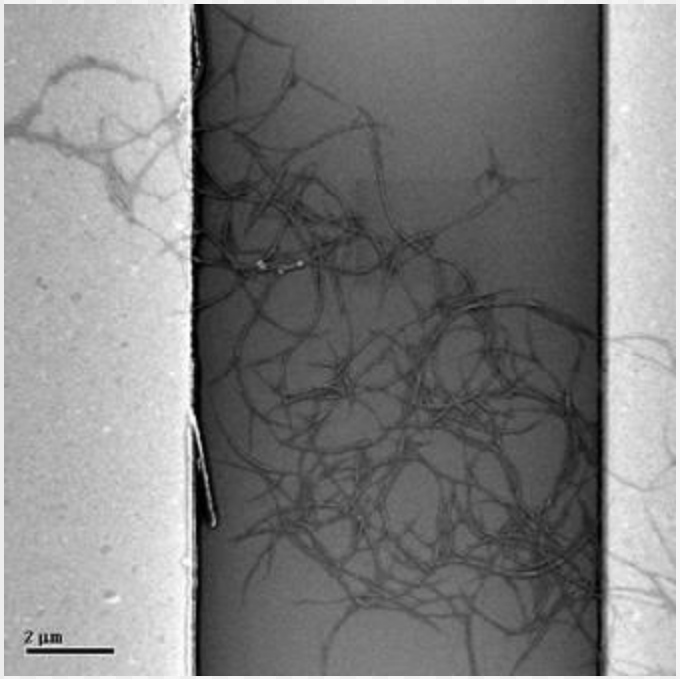


SWNT Chemiresistor

Sensor fabrication:

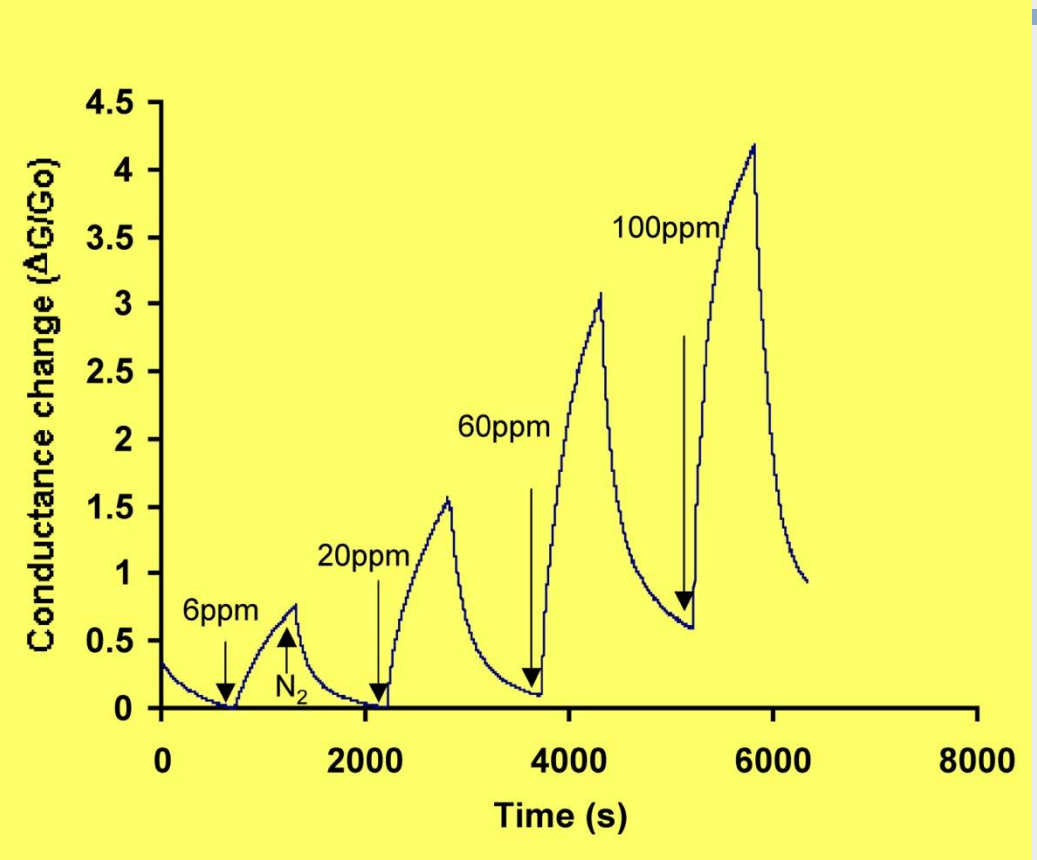
1. SWCNT dispersions--Nice dispersion of CNT in DMF
2. Device fabrication--(see the interdigitated electrodes below)
3. SWCNT deposition—Casting, or in-situ growth

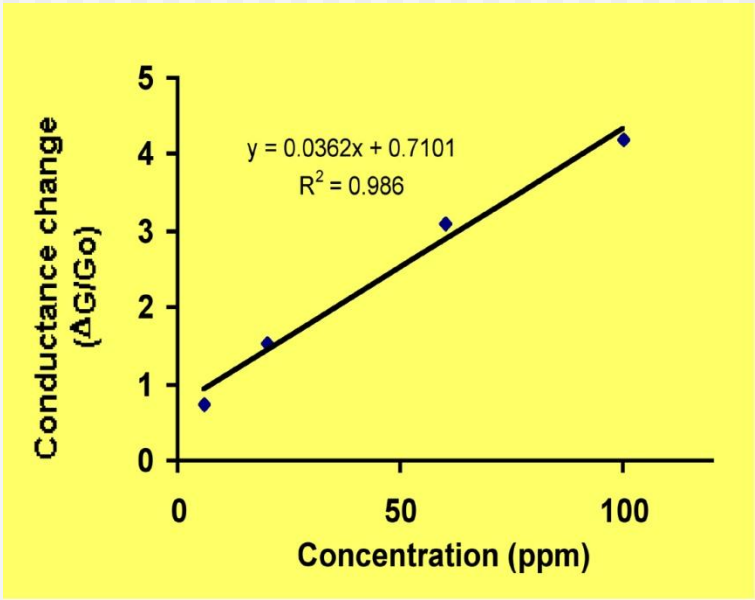




Jing Li et al., Nano Lett., **3**, 929 (2003)

SWNT Sensor Responding to NO2

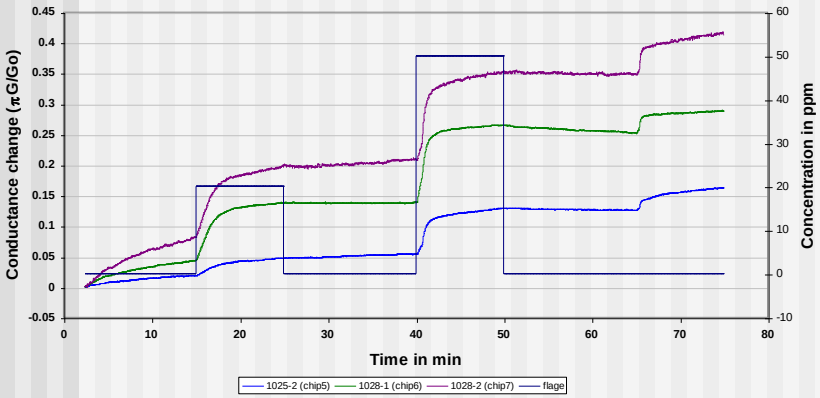




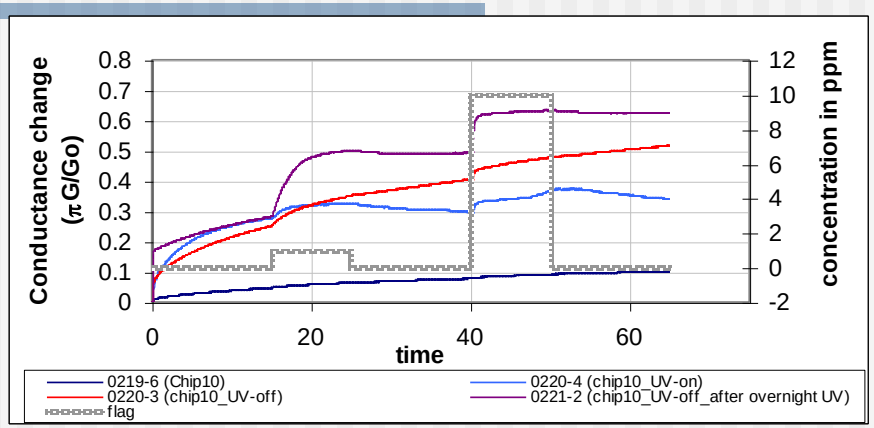
Detection limit for NO2 is 44 ppb.

Sensors for Gases

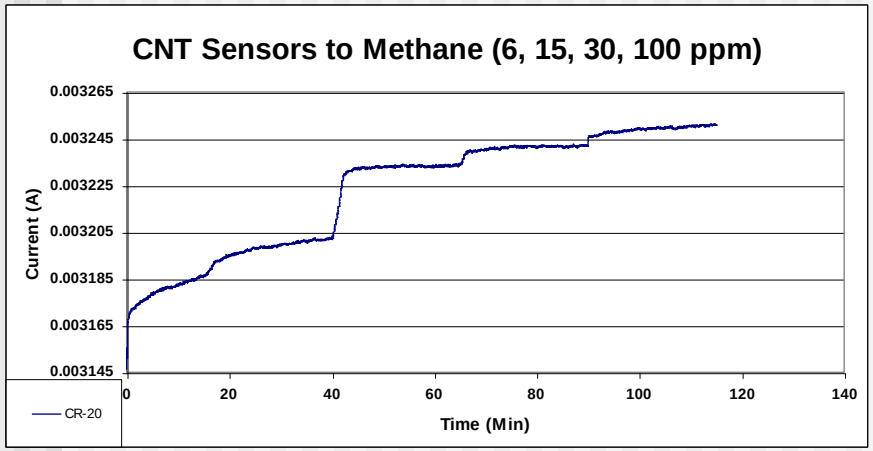
Benzene

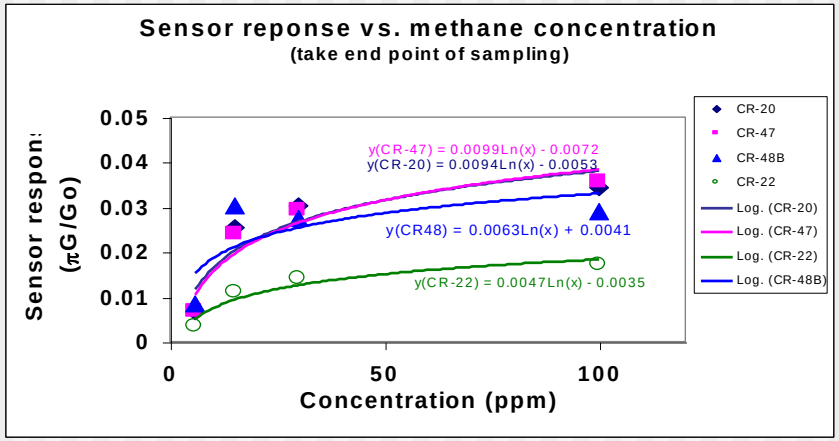


Acetone

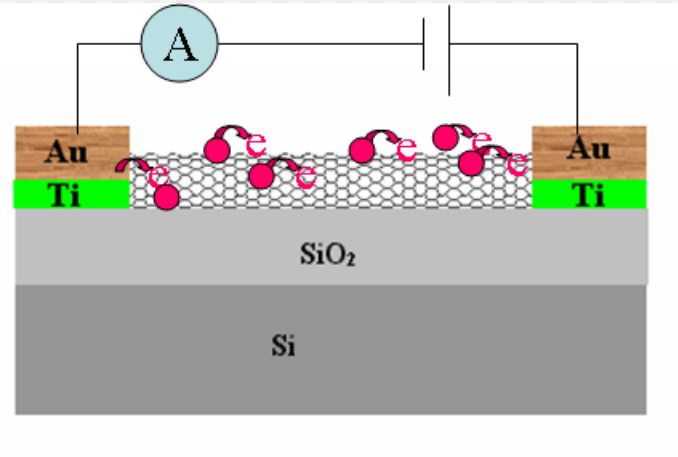


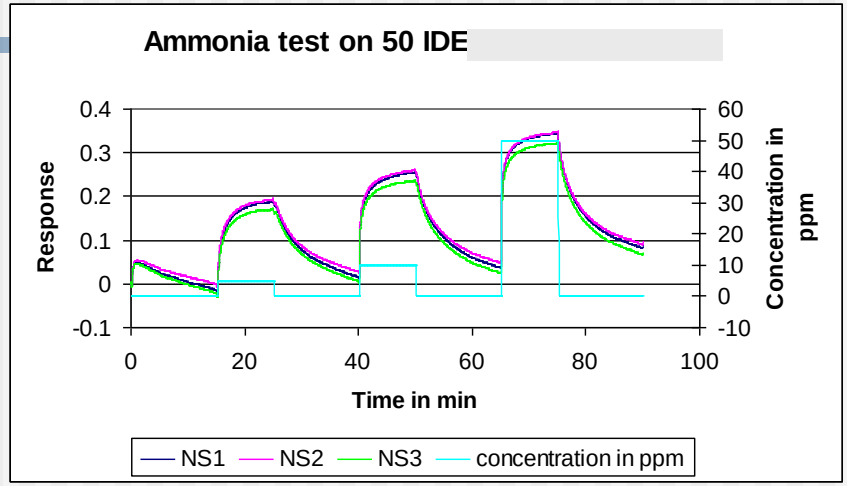
Methane (CNT is not sensitive to CH4, only CNT doped with Pd give following response)

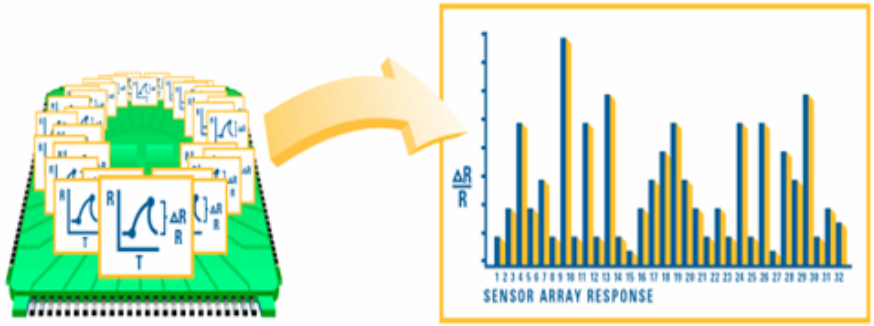




Nanosensing Technology







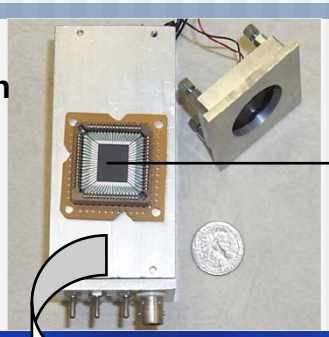
Using pattern matching algorithms, the data is converted into a unique response pattern

Operation:

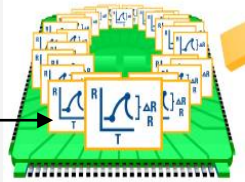
1. The relative change of current or resistance is correlated to the concentration of analyte.
2. Array device "learns" the response pattern in the *training* mode.
3. Unknowns are then classified in the *identification* mode.

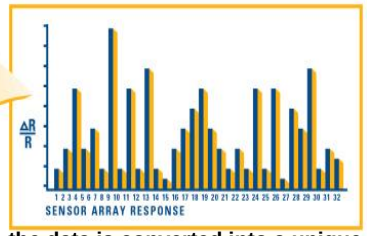
Screening at the Airport

A chemical detector that can be installed in the x-ray scanner



A sensor chip

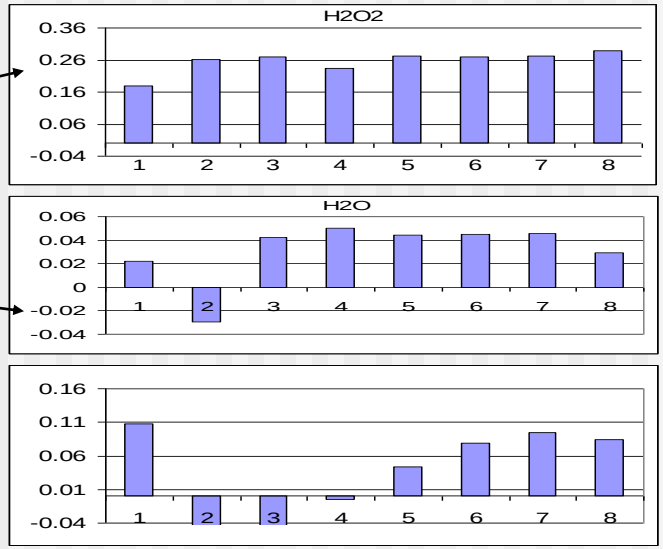




Using pattern matching algorithms, the data is converted into a unique response pattern



An x-ray screening machine



Pattern recognition differentiates H_2O_2 (top) from H_2O (middle), Methanol (bottom)

Application: 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?

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

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 fil (less than 1% by weight)

- Neat polymer properties such as elongation to failure and optical transparer 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 withou 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

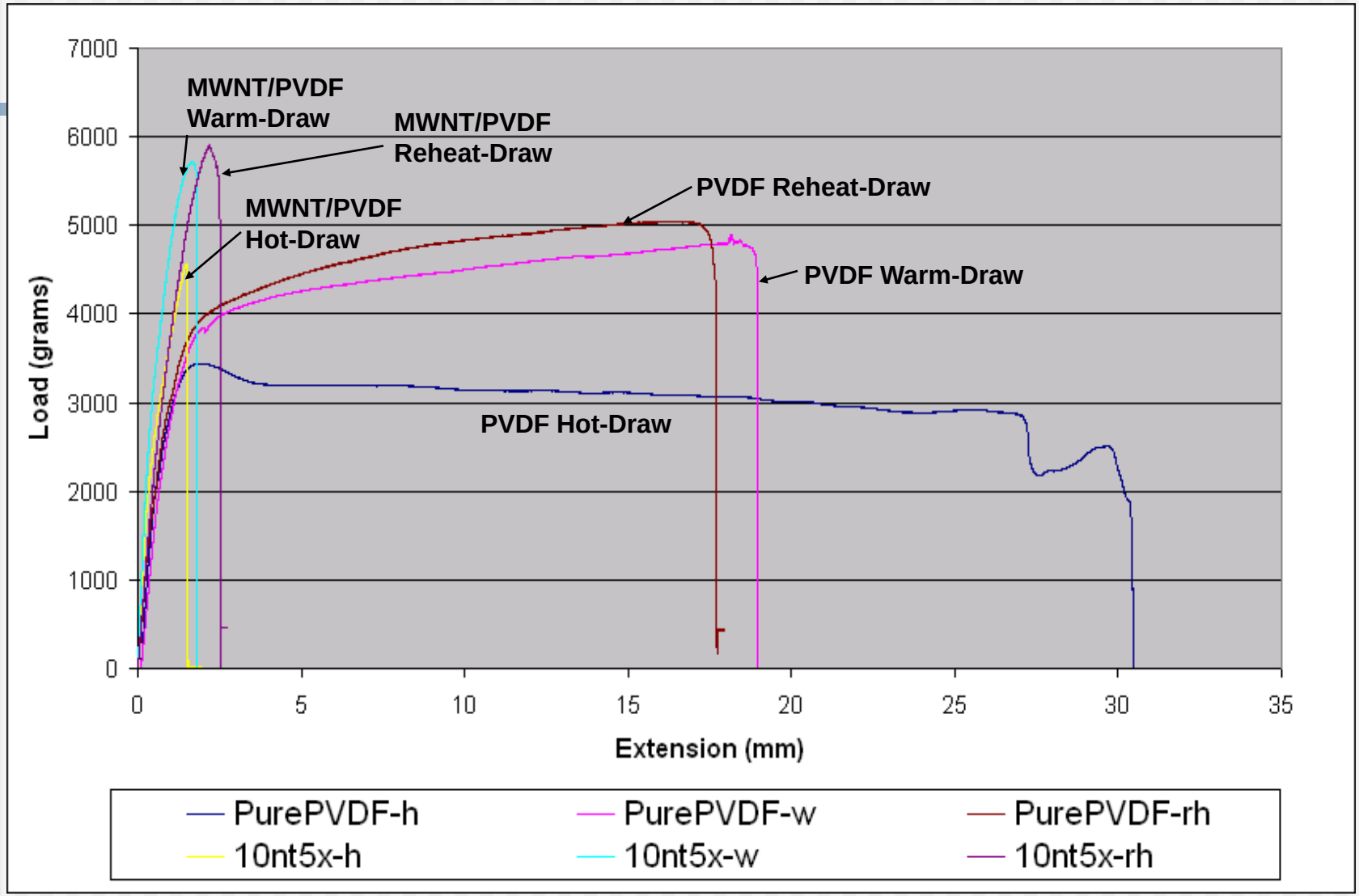
- SWNT/PVOH fibers with 60% wt SWNT $\Rightarrow$ tensile strength similar to spider silk
  - These fibers can be woven into textiles to create garments with sensing and EMI shielding capabilities.

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

MWNT/PVDF Reheat-Draw

- Same mixing and extrusion process
- Cool extruded samples (without draw) to room temp.
- Reheat samples in oven and draw at 150-155ºC
- Tensile yield strength @ 65.1MPa (~49%), similar to warm-draw results
- Images are similar to warm-draw
- Provides flexibility as a 2-step processing

MWNT/PVDF Dry Mix Tensile Data

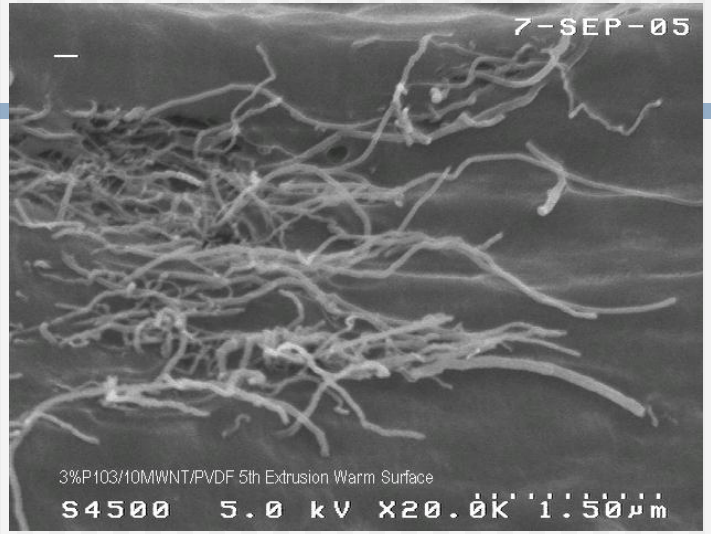


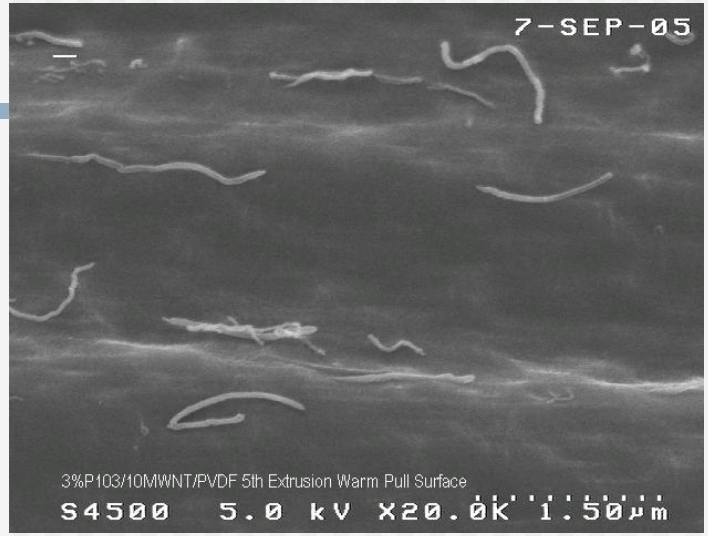
Surfactant/MWNT/PVDF Warm-Draw

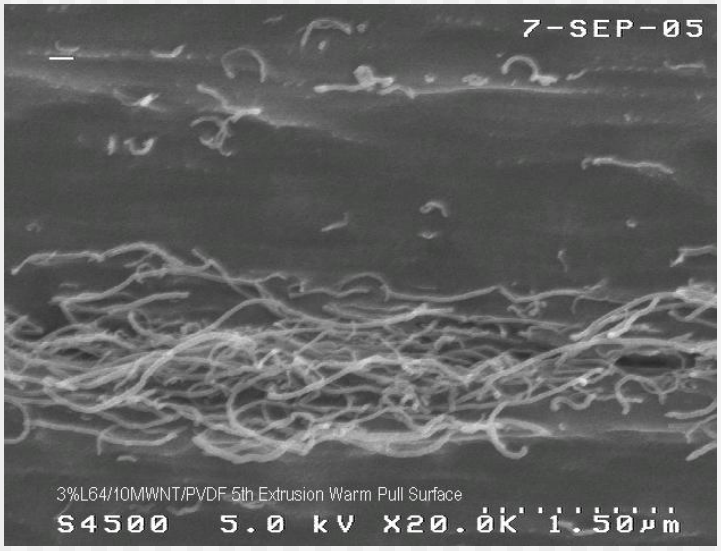
- Mix surfactant in acetone then add MWNT then add PVDF
- Tried Pluronic P103 and Pluronic L64: 3%P103/10%MWNT/PVDF and 3%L64/MWNT/PVDF
- Allow 30 hours for acetone to evaporate
- Same extrusion and warm-draw processing as previous MWNT/PVDF Warm-draw
- Able to perform warm-draw on 1st extrusion, indicating that dispersion is improved
- Tensile yield strength increase with # of extrusion:
  - P103: 1X @ 37.8MPa to 5X @ 52.4MPa (~20%+)
  - L64: 1X @ 45.2MPa to 5X @ 50.3MPa (~15%+)

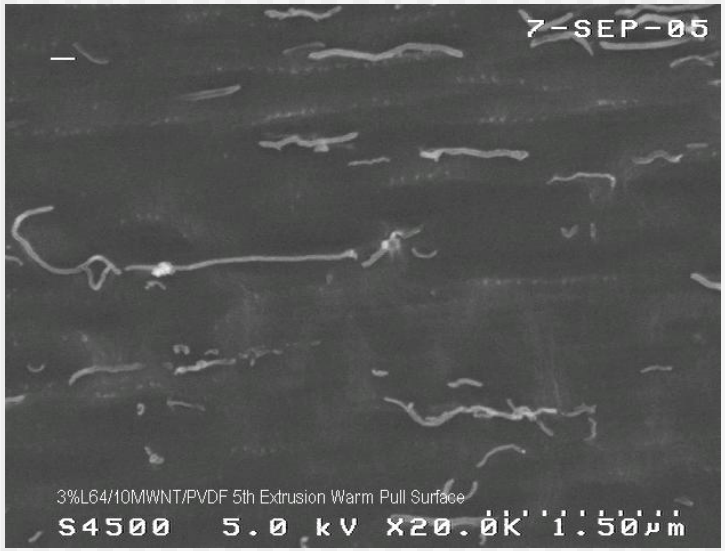
Surfactant/MWNT/PVDF Warm-Draw

Surface image With P103







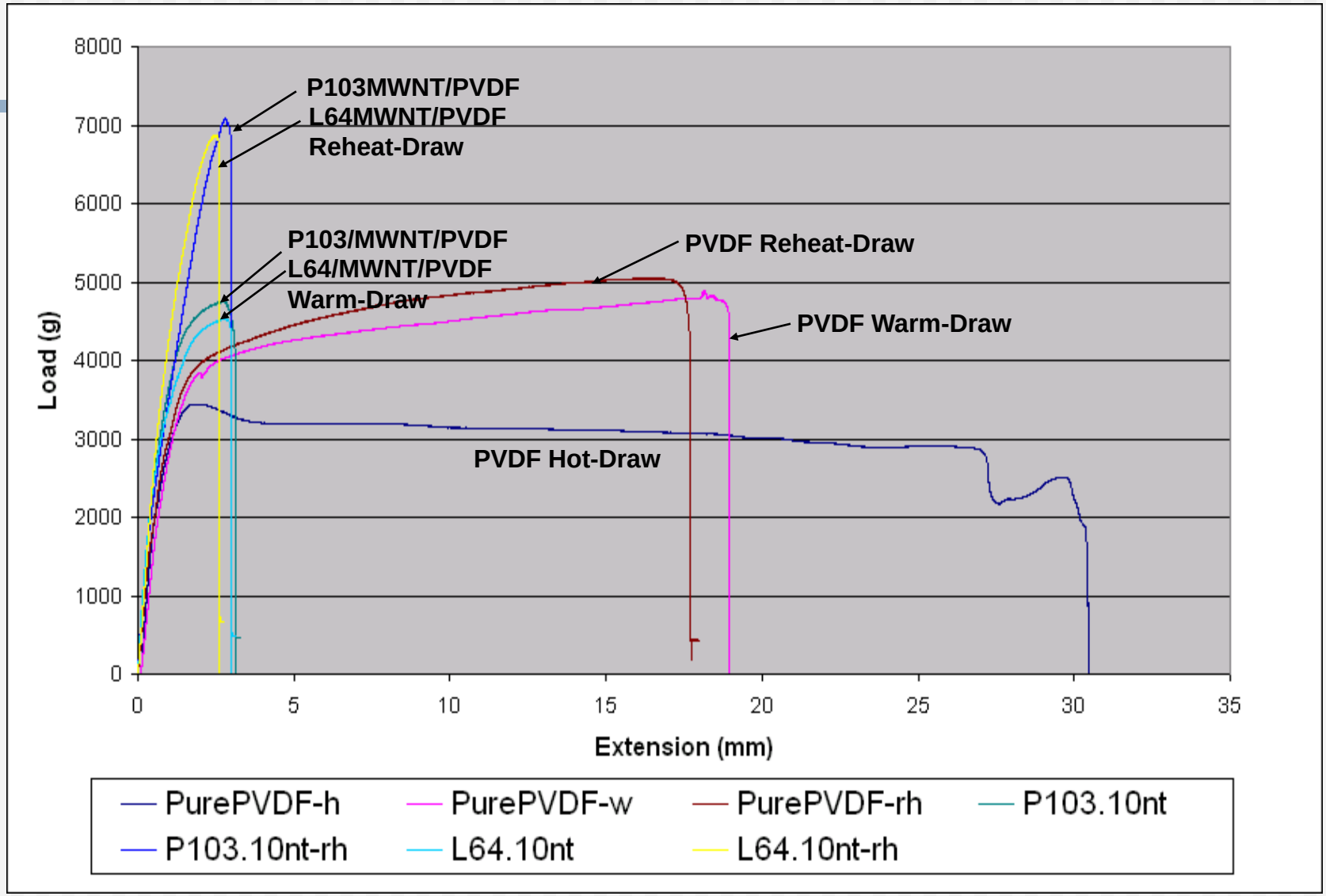


Surface image With L64

Surfactant/MWNT/PVDF Reheat-Draw

- Same mixing and extrusion process
- Cool extruded samples (without draw) to room temp
- Reheat samples in oven to 200ºC for 10min and draw at 150-155ºC
- Tensile yield strength increase:
  - P103: 82.3MPa (~88%+)
  - L64: 79.0MPa (~81%+)
- Images are similar to warm-draw samples with surfactant

Surfactant/WMNT/PVDF Tensile Data



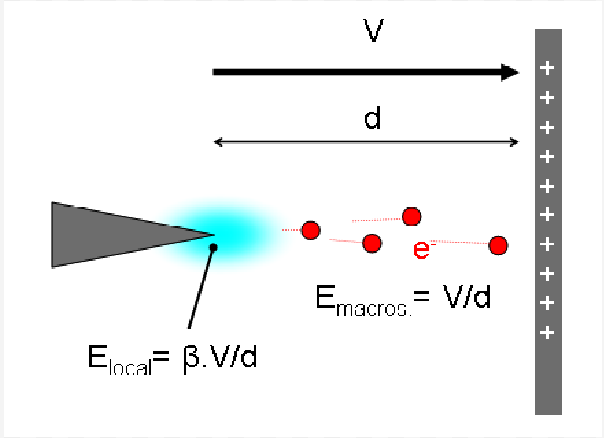
Tensile Data Summary

	σ-yield	%	Delta Ly	σ-max	%	Delta Lm	σ-draw	Delta Ld
Pure PVDF (hot draw)	41.2 MPa	-	0.78 mm	51.0 MPa	-	1.54 mm	57.9 MPa	3.30 mm
Pure PVDF (warm draw)	43.7 MPa	6%	1.48 mm	48.4 MPa	-5%	2.20 mm	107.8 MPa	4.70 mm
Pure PVDF (Reheat draw)	44.3 MPa	7.6%	1.36 mm	49.5 MPa	2.2%	2.02 mm	112.6 MPa	4.75 mm
5%MWNT/PVDF (hot draw) 5X	41.8 MPa	2%	0.88 mm	45.8 MPa	-10%	0.97 mm		
5%MWNT/PVDF (warm draw) 5X	56.2 MPa	29%	1.75 mm	58.0 MPa	20%	2.15 mm		
10%MWNT/PVDF (hot draw) 5X	52.2 MPa	27%	1.15 mm	55.6 MPa	9%	1.46 mm		
10%MWNT/PVDF (warm draw) 5X	63.7 MPa	46%	1.17 mm	79.4 MPa	64%	1.76 mm		
10%MWNT/PVDF 5X Reheat Pull	65.1 MPa	49%	1.78 mm	73.7 MPa	52%	2.22 mm		
3%P103 10%MWNT/PVDF 1X.	37.8 MPa	-13%	1.1 mm	44.7 MPa	-8%	2.35 mm		
3%P103 10%MWNT/PVDF 5X	52.4 MPa	20%	1.38 mm	58.7 MPa	21%	2.32 mm		
3%L64 10%MWNT/PVDF 1X	45.2 MPa	3%	1.75 mm	52.1 MPa	8%	4.87 mm		
3%L64 10%MWNT/PVDF 5X	50.3 MPa	15%	1.65 mm	58.0 MPa	20%	2.85 mm		
3%P103 10%MWNT/PVDF 5X Reheat	82.3 MPa	88%	2.25 mm	89.2 MPa	84%	2.79 mm		
3%L64 10%MWNT/PVDF 5X Reheat	79.0 MPa	81%	1.96 mm	85.9 MPa	77%	2.71 mm		

CNT Field Emission and Applications

- When subjected to high E field, electrons near the Fermi level can overcome the energy barrier to escape to the vacuum level

- Compare to thermionic emission, where the source is heated to ~ 1000º C to give the electrons the energy required to overcome the surface potential barrier: currently X-ray sources use thermionic emission.

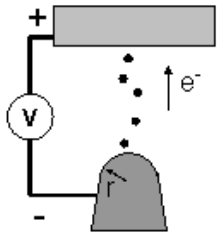


- Common tips: Mo, Si, diamond
- Applications:
  - Cathode ray lighting elements
  - Flat panel displays
  - Gas discharge tubes in telecom networks
  - Electron guns in electron microscopy

Courtesy: P. Sarrazin

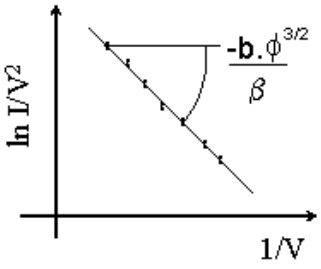
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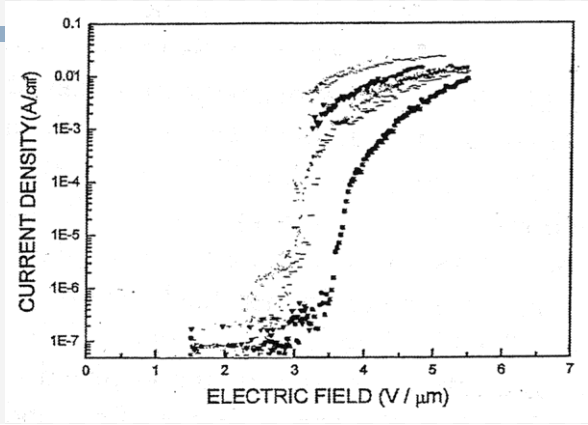
Field Emission Model



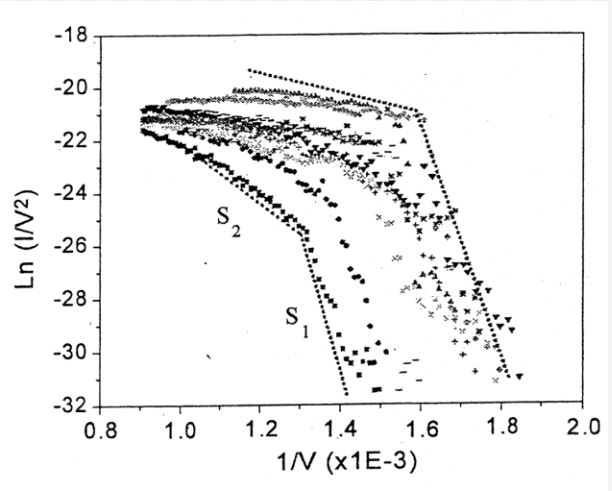
$$I = a \cdot V^2 \cdot e^{\left(\frac{-b \cdot \phi^{3/2}}{\beta \cdot V}\right)}$$

Field enhancement factor $\beta \sim 1/r$



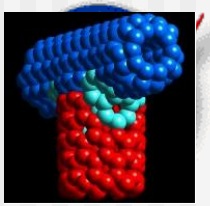


- Fowler - Nordheim equation
  ϕ is work function, β is field enhancement factor
- Plot of ln (I/V^2) vs. ($1/V$) should be linear
- At low emission levels, linearity seen; in the high field region, current saturates
- Critical: low threshold E field, high current density, high emission site density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



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Field Emission (cont.)



- Needs
  - For displays, 1-10 mA/cm^2
  - For traveling wave tube amplifiers (TWTA) > 500 mA/cm^2
- To obtain low threshold field
  - Low work function (ϕ)
  - Large field enhancement factor (β) $\Rightarrow$ depends on geome of the emitter; $\beta \sim 1/5r$
- 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)

Cold Cathode Field Emission Fundamental

- **Field enhancement factor (β)** $F_{tip} = \beta V_{applied}$

$\beta = 1.2\ (2.15 + h/R)^{0.9}\ d$

with electric field F_{tip}, applied voltage $V_{applied}$, distance d between the extractor and substrate surface, nanotube height h, and base radius R

Small $R \Rightarrow$ Large $\beta \Rightarrow$ Large $F \Rightarrow$ Large J

F_{tip} = ~ 10^9 V/cm for on set of emission current

Length (aspect ratio) of CNT structure also influence the field enchancement factor.

- **Electrostatic screening between emitters**
  1. Electric field at apexes of emitters drops significantly when adjacent nanotubes are closely spaced
  2. Highest current density occurs in finding optimal balance between nanotube density and spacing
  3. Must be considered density of nanotubes for high electron current sources
- **Conditioning of emitters**
  - Removing adsorbed gaseous molecules from vacuum environment
  - Current stability at low vacuum (?)

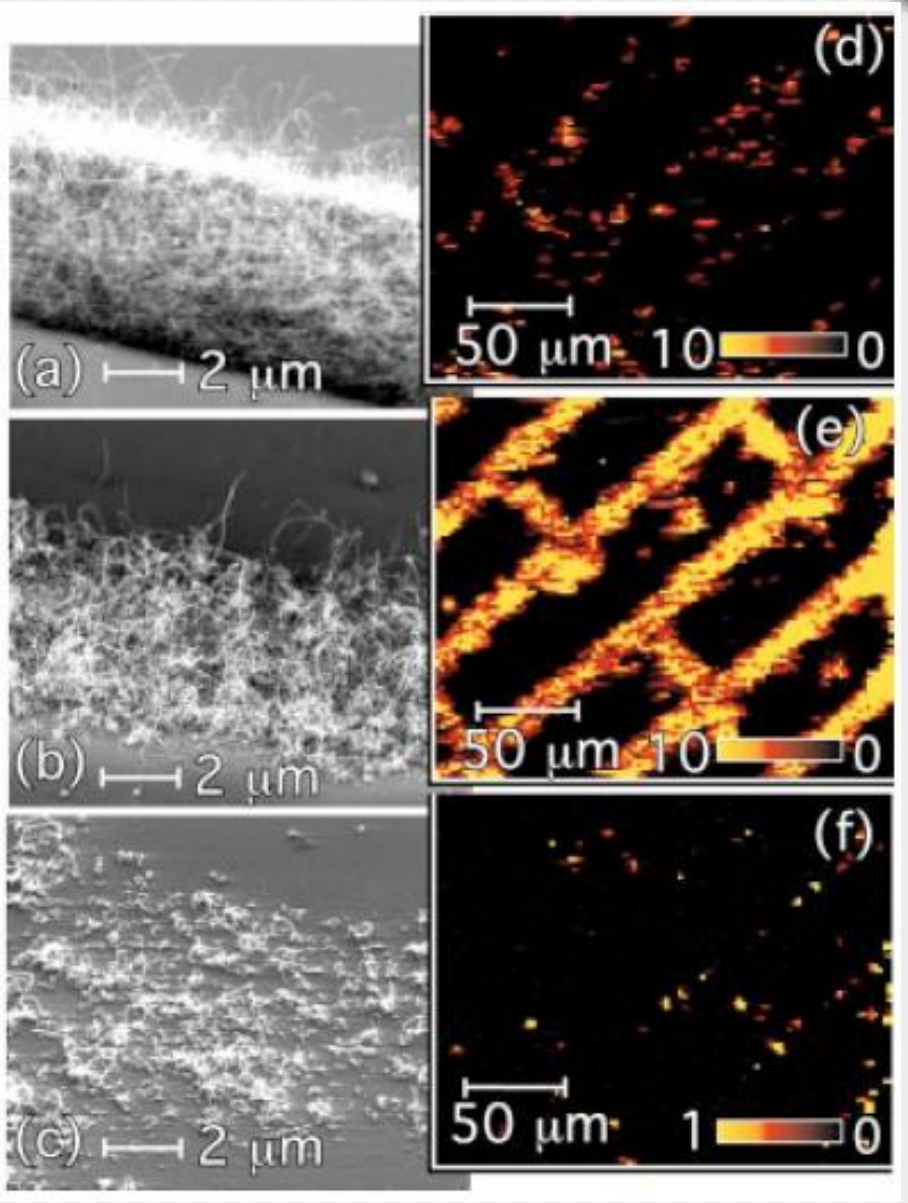
Field Screening Effect

SEM images of patterned CNT films showing regions of (a) high, (b) medium, and (c) low density, with the corresponding FE maps of current density (d)-(f). The films were produced with ethanolic inks of 10 (a), 40 (b), and 60 mM $Fe(NO_3)_3 \cdot 9H_2O$. The FE maps were taken under identical conditions using 100 V in constant voltage mode. The color scale corresponds to 0-10 μA/pixel for images (d), (e); and to 0-1 μA/pixel in image (f).

High density

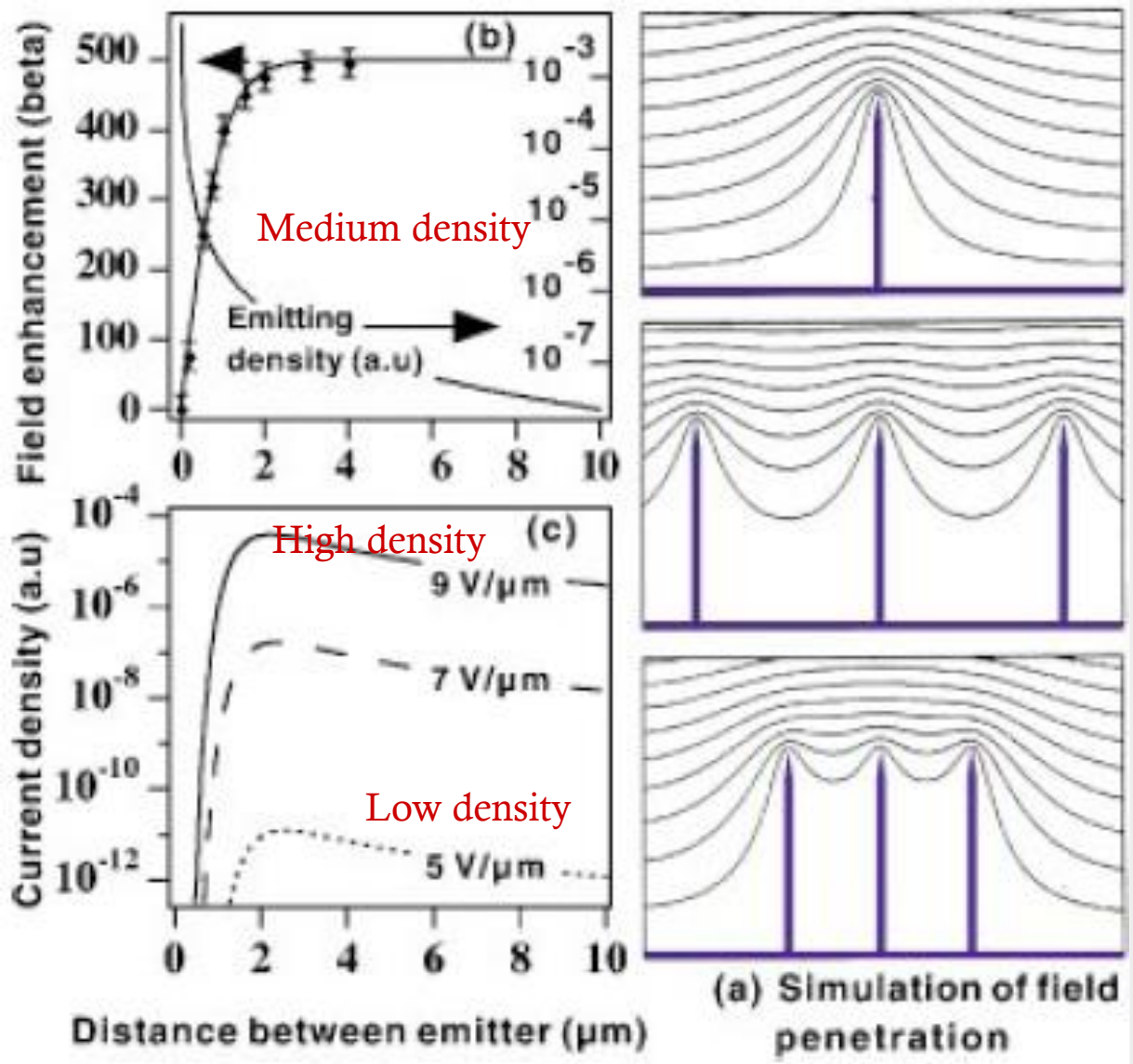
Medium density

Low density



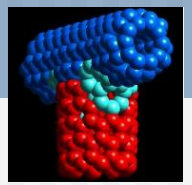
Theoretical Study on Field Screening Effects

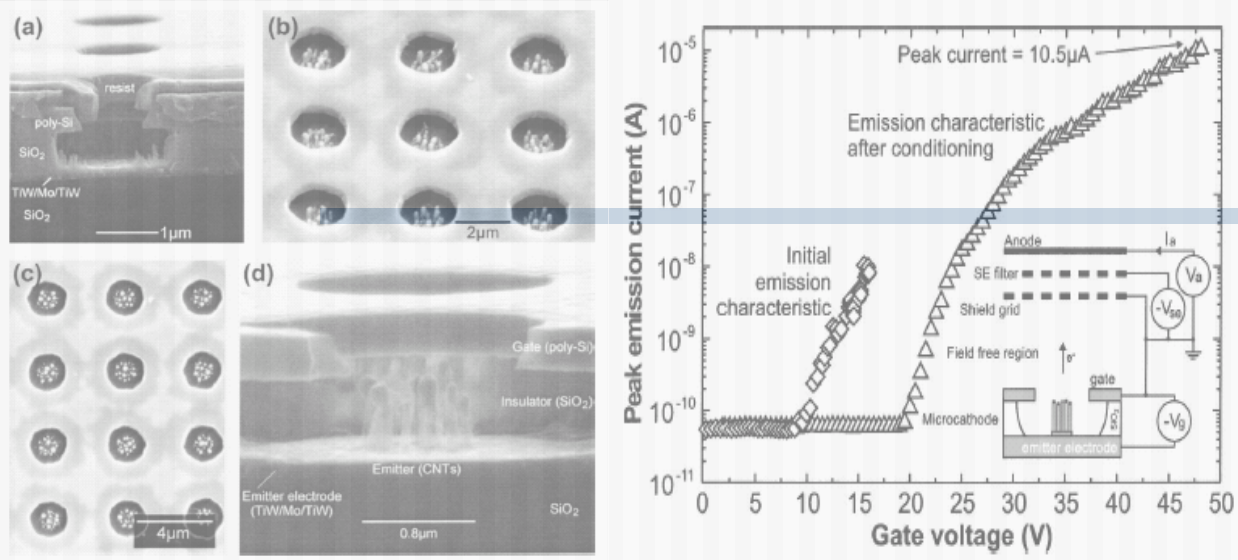
(a) Simulation of the equipotential lines of the electrostatic field for tubes of 1 μm height and 2 nm radius, for distances between tubes of 4, 1, and 0.5 μm; along with the corresponding changes of the field enhancement factor β and emitter density (b), and current density (c) as a function of the distance.



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Field Emission of Gated Carbon Nanofibers





- Carbon Nanofibers have lower stable emission current due to intrinsic high resistance
- Utilizing microfabrication technique is impractical because of cost
- Depending on requirement for current density, other alternative structures of CNT emitters may be sufficient and economically viable

Oakridge National Laboratory/Cambridge University

Efficient field emission from an individual aligned carbon nanotube bundle enhanced by edge effect

Shunjiro Fujii et al. APL, published online 10 April 2007

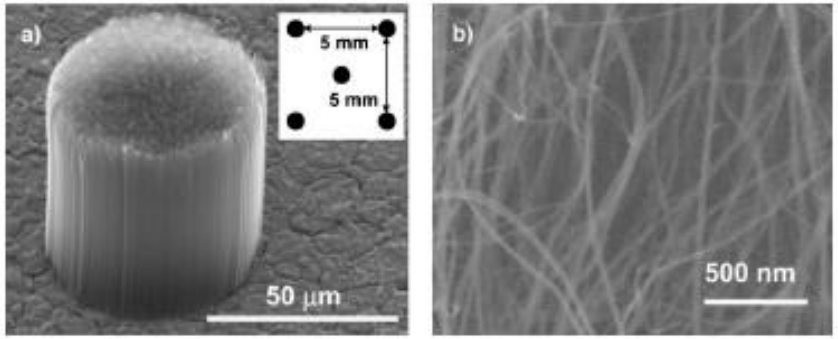


FIG. 1. (a) SEM image of aligned CNT bundle. The inset shows a schematic of an arrangement of five pillar bundles. (b) Enlarged SEM image of the bundle.

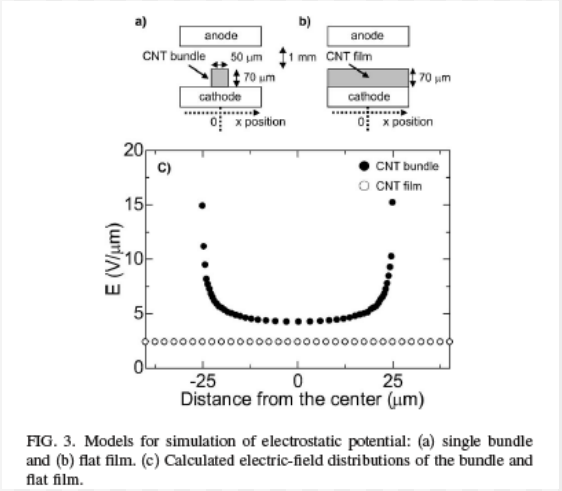
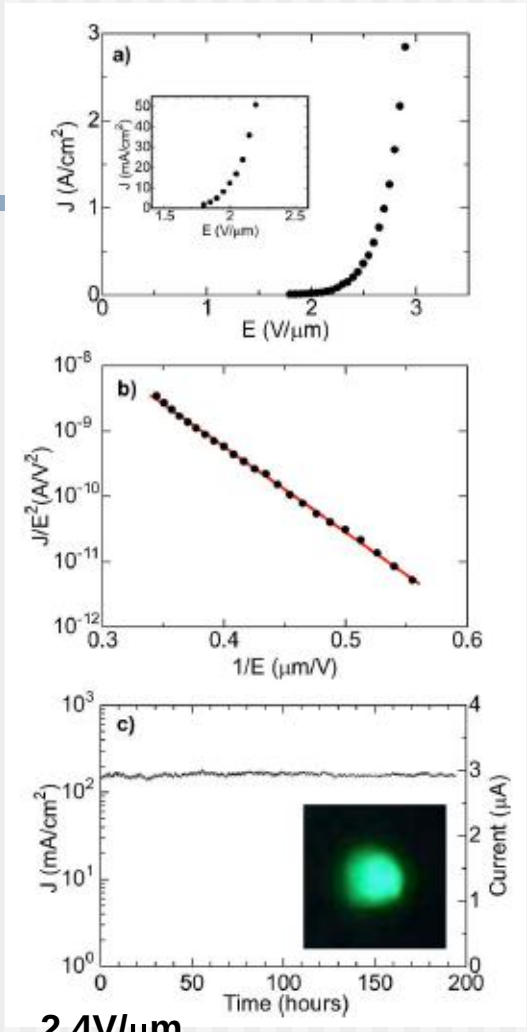


FIG. 3. Models for simulation of electrostatic potential: (a) single bundle and (b) flat film. (c) Calculated electric-field distributions of the bundle and flat film.

***J*=10 mA/cm² at 2.0V/μm**

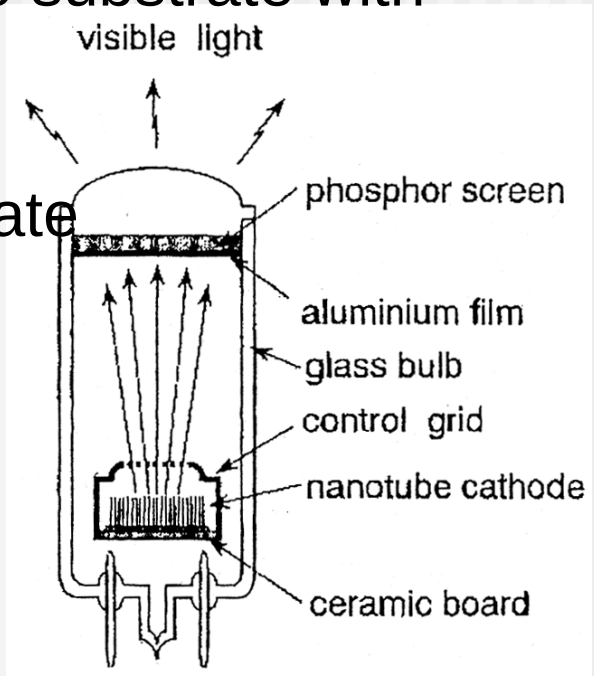
***J*=2.8A/cm² at 2.9V/μm**



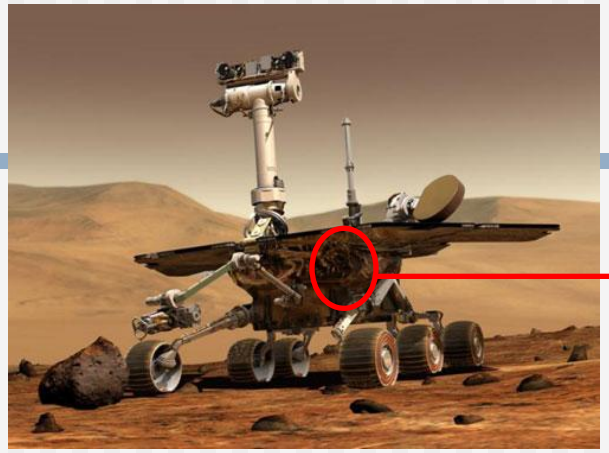
2.4V/μm

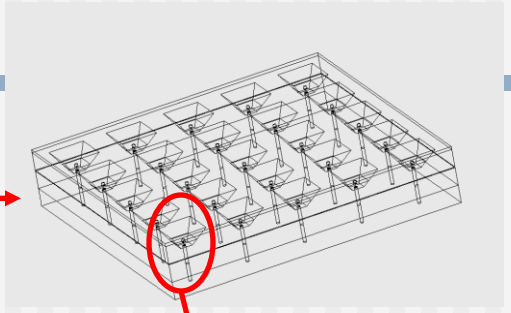
Field Emission Test Apparatus

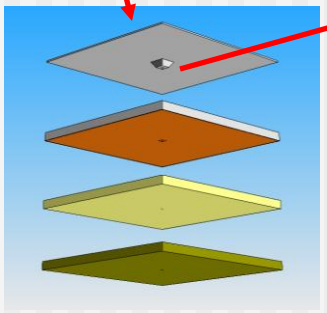
- Cathode and anode enclosed in an evacuated cell at a vacuum of
  10^{-9} - 10^{-8} Torr
- Cathode: glass or polytetrafluoroethylene substrate with metal-
  patterned lines
  - nanotube film transferred to substrate or grown directly on it
- Anode located 20-500 μm from cathode
- Turn-on field: electric-field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

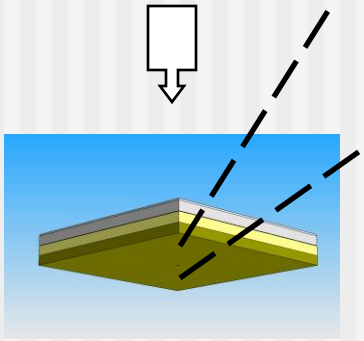


MSEMS: CNT Field Emitter MEMS Based SEM

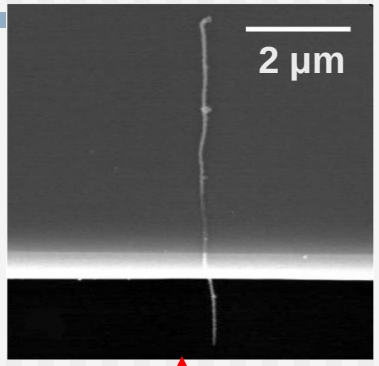


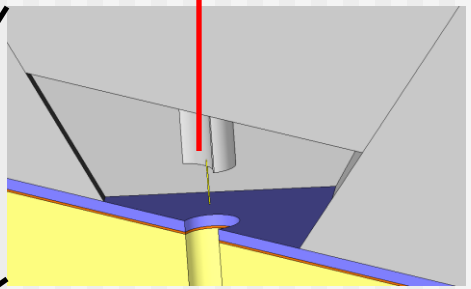






Stable CNT Emitter Demonstrated



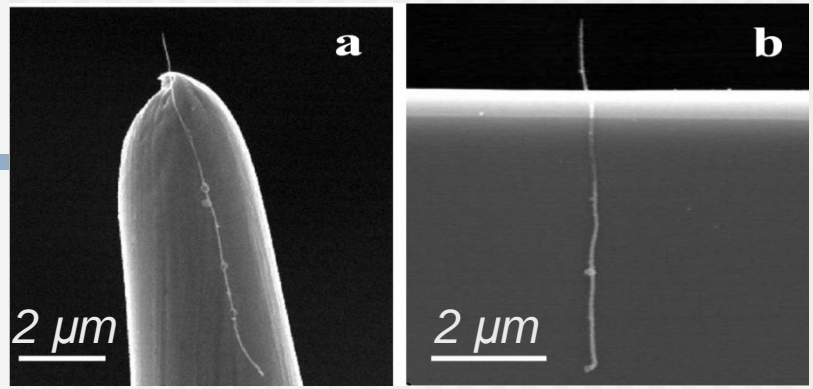


- **Individual CNT field emitters**
  - **Small source (10 nm)**
  - **Low energy spread (0.1-0.5 eV)**
  - **High brightness ($2x10^9$ A/m^2SrV)**
- **MEMS Micro-column integration**
- **Future implementation in a space flight instrument**
- **Redundant multiple electron guns system**
  - **High Throughput e-beam nanolithography**

Template with MEMS
- self alignment
- simple electron optics

* Patent Application

Experimental Emitters and Parameter Extraction



Cathode 1 Cathode 2

- Fowler-Nordheim Eqn.*

$$I = 2\pi R^2 \frac{e^3 F_t^2}{8\pi h (q\phi) t^2(y)} \exp\left\{-\frac{8\pi\sqrt{2m}(q\phi)^{3/2}}{3heF_t} v(y)\right\}$$

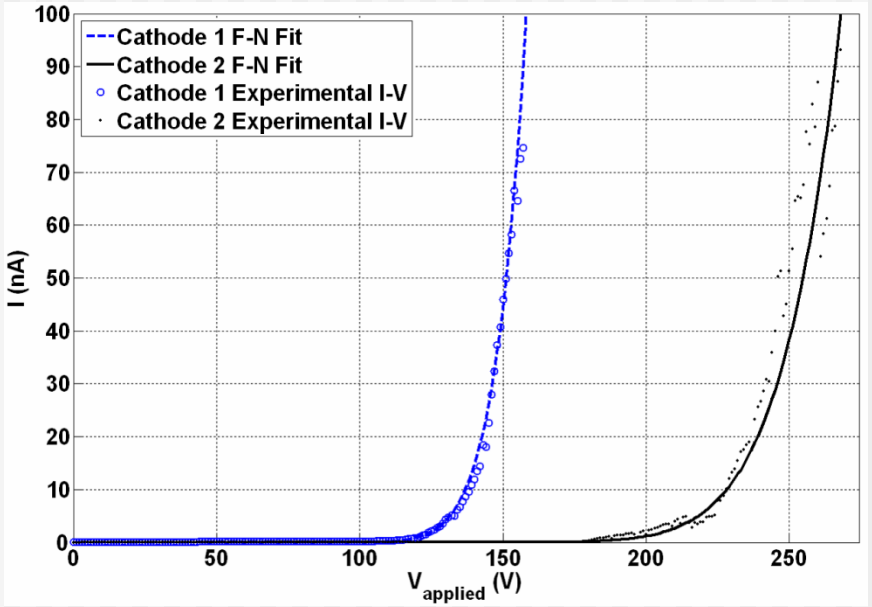
where

$$y = \frac{1}{q\phi}\sqrt{\frac{e^3 F_t}{4\pi\varepsilon_0}}$$

- Extracted parameters
  - Field enhancement factor
  - Work function 5.1 (eV)
  - Radius

    r = 26 nm and r=11 nm

- Experimental turn on voltages 121 V for cathode 1 and 187 V for cathode 2.



Summary and Perspective

- Fundamental Understanding of CNT have been achieved over the last 10 years
- Some CNT applications are well-developed and likely to see in products in the next decade.
  - Sensors
  - Polymer Nano-Composites
  - Field Emission Applications such as lighting, electron microscope.
- Toxicity:
  - Under Investigation (Level of Toxicity to be determined)
  - Non-free forms, e.g.,direct growth on substrates or in binders such as polymer composites, are less problematic.
  - Free forms, naked carbon nanotubes, are airborne. Should be handle with care and with protective equipments.

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Norman Gunther
Bryan Ribaya
Darrell Niemann
Alex Austin
You Li
Setha Yim
Riichiro Ohta
Nathaniel Zuckerman
Jessica Killian

And You for your attention….