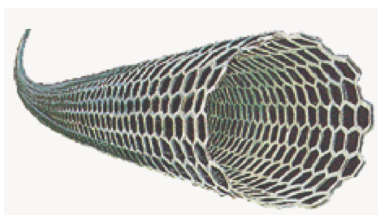
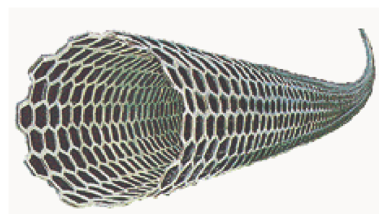
Carbon Nanotubes

Prof. Steve Cronin
University of Southern California
Electrical Engineering - Electrophysics





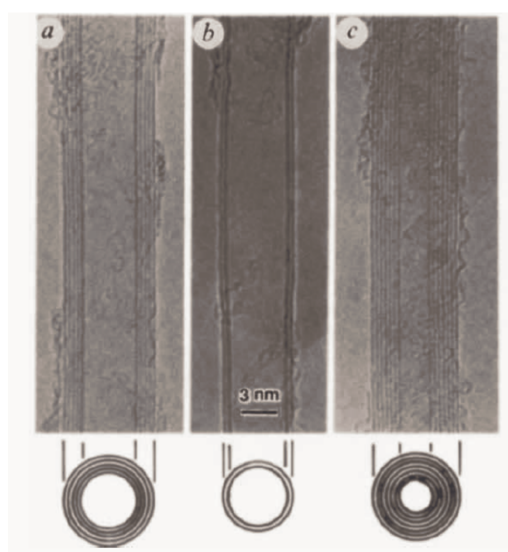
Iijima Discovers MWNTs - 1991

Sumio Iijima

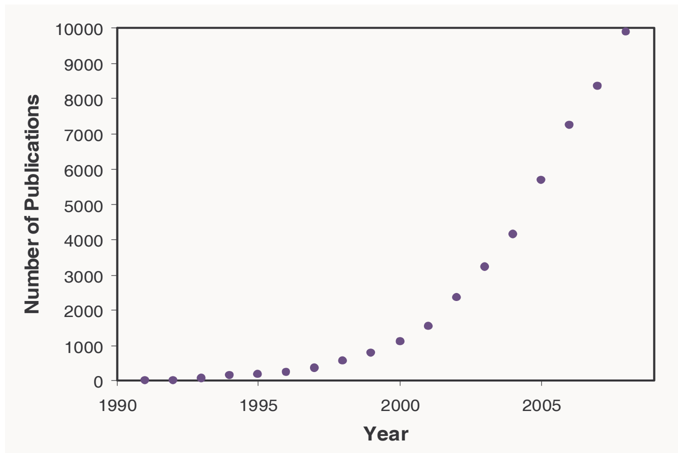
“HELICAL MICROTUBULES OF GRAPHITIC CARBON ”

NATURE 354 (6348): 56-58 1991

Times Cited: 5439



Carbon Nanotube Publications



Over 49,000 publications

Previous Discovery…?

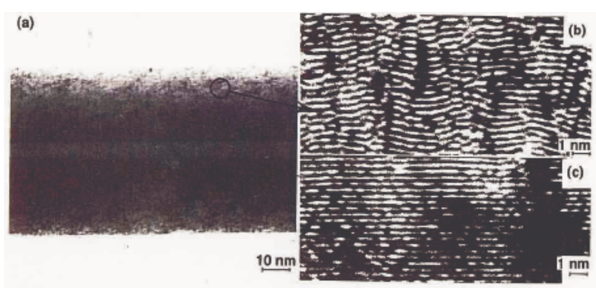


Figure 5. Hollow tube (a) and two different structures (b, c)

Morinobu Endo

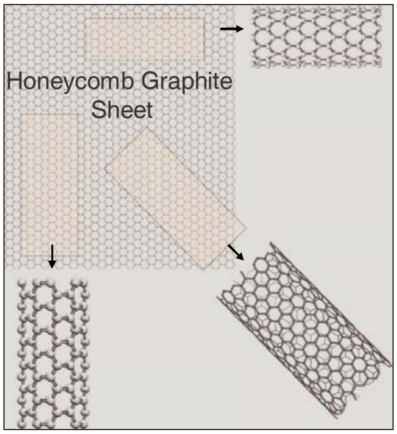
"Growth of carbon fibers in the vapor phase "

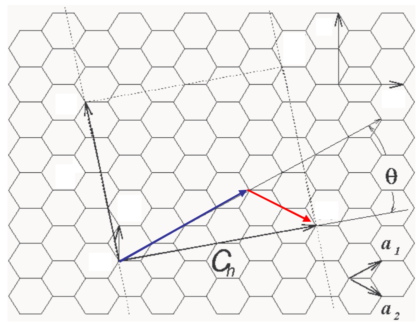
Had nanotubes, but wasn't looking for them.

M.Endo, CHEMTEC, 568-576, September 1988

What is a Carbon Nanotube?

Imagine rolling a sheet of graphite into a seamless cylindrical tube





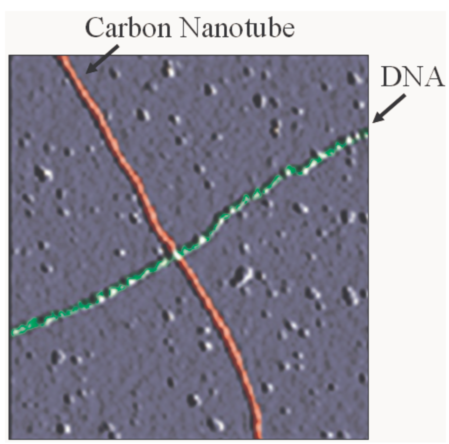
Chirality *(n,m)*:

$C_h = 4a_1 + 2a_2 = (4,2)$

- Two integers *(n,m)* determine all the properties of a carbon nanotube.
- Nanotubes can have metallic or semiconducting electronic structure, if *(n-m)*/3.

Scanning Tunneling Microscope (STM)

1nm

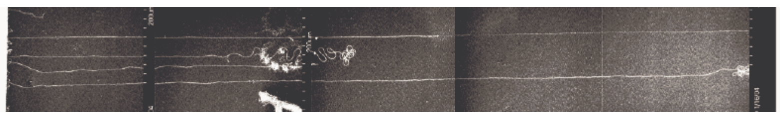


0.144nm

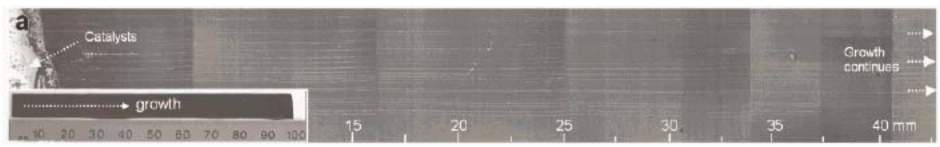
2nm

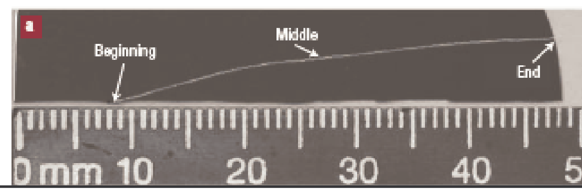
Advantages over Existing Materials

- 1nm diameter, up to 1cm in length, aspect ratio ~10^7



1.5mm

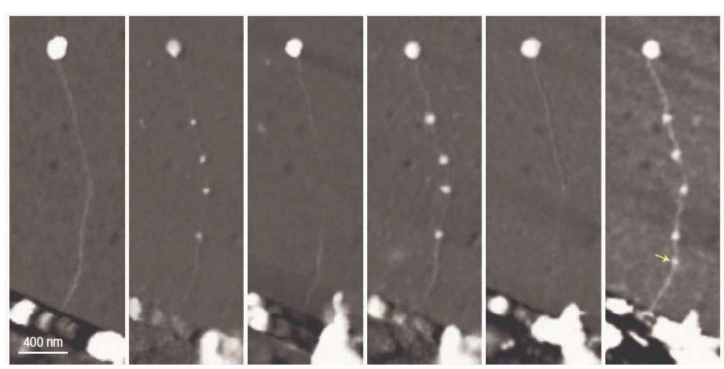




Burke, *et al*, Chem. Mat, **16**, 3414 (2004).
Hong, *et al*, JACS, **127**, 15336 (2005).
Liu, *et al*, Nat. Mat., **3**, 673 (2004).

Advantages over Existing Materials

- 1nm diameter, up to 1cm in length, aspect ratio ~10^7
- 1 defect in 10^6 C atoms => ballistic conduction

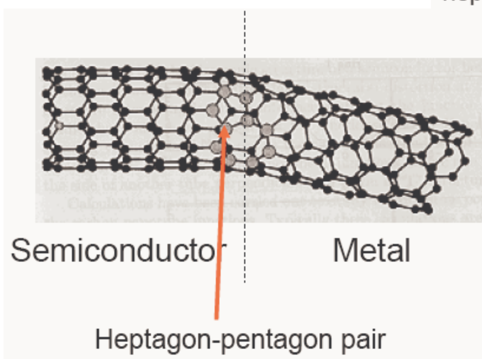


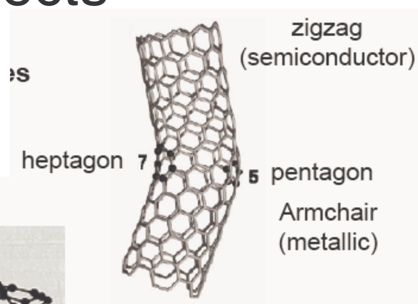
Selective nucleation on defect cites.

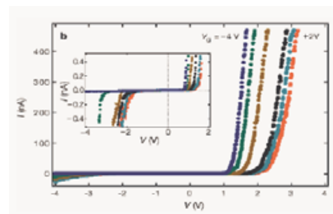
Collins, *et al*, Nat. Mat, **4**, 906 (2005).

Defects

- 5-7 defects







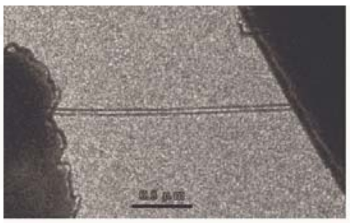
Chico et al., Z. Yao et al., “Carbon nanotube intramolecular junctions”, Nature, vol.402, Nov., p.274, 1999.

Advantages over Existing Materials?

- 1nm diameter, up to 1cm in length, aspect ratio ~10^7
- 1 defect in 10^6 C atoms => ballistic conduction
- High melting point ~3800^{o}C (surface of the sun 5500^{o}C)

Mechanical Strength

Young's Modulus = $\frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\sigma}{\varepsilon} = \frac{F/A_0}{\Delta L/L_0}$



E (TPa)	σ_T (TPa)	Method
0.81 (50%)		AFM-2 ends clamped [34]
1.28 (40%)		AFM-1 end clamped [22]
1.26 (20%)		TEM–thermally vibrating beam [23]
0.1–1 ($\sim 1/R$) (30%)		TEM–electrostatic deflection [15]
0.27–0.95	0.01–0.06	Dual AFM cantilevers [35]
0.91 (20%)	0.15 (30%)	TEM–direct tension (this work)

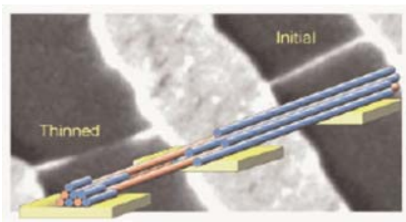
- High Young's modulus ~1TPa
- Uncertainty in diameter
- Steel = 0.2TPa
- 6-10% elastic limit

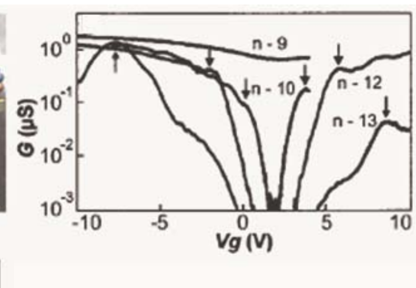
Zettl, *et al*, Materials science and Engineering, A334 (2002) p173-178.

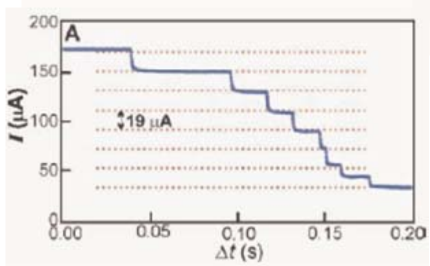
Advantages over Existing Materials?

- 1nm diameter, up to 1cm in length, aspect ratio ~10^7
- 1 defect in 10^6 C atoms => ballistic conduction
- High melting point ~3800^{o}C (surface of the sun)
- High young's modulus 1TPa (> diamond)
- High electronic current carrying capacity (10^9A/cm^2) ~10^3 times higher than that of the noble metals

High current carrying capacity







Threshold Current $= 10^9 A/cm^2$

Collins, *et al.*, Science (2001)

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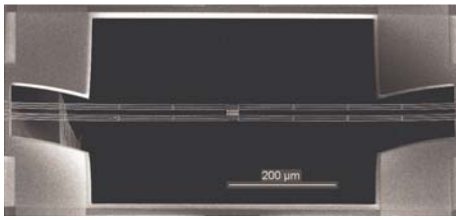
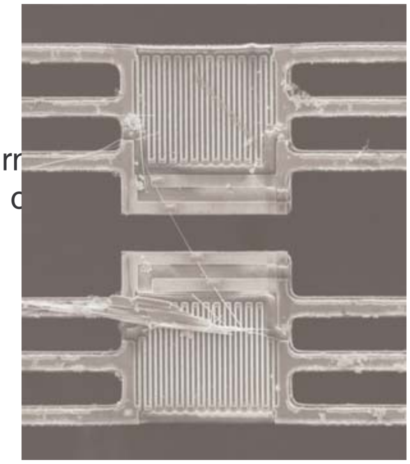
- Thermal conductivity 6600W/mK at room temperature is twice the maximum known bulk thermal conductor, isotropically pure diamond = 3320W/mK

Thermal Conductivity





- Two micro-devices which contain heaters and thermometers for measuring the heat flow through the nanotube
  - •One creates ΔT along nanotube
  - •The other measures the heat flow

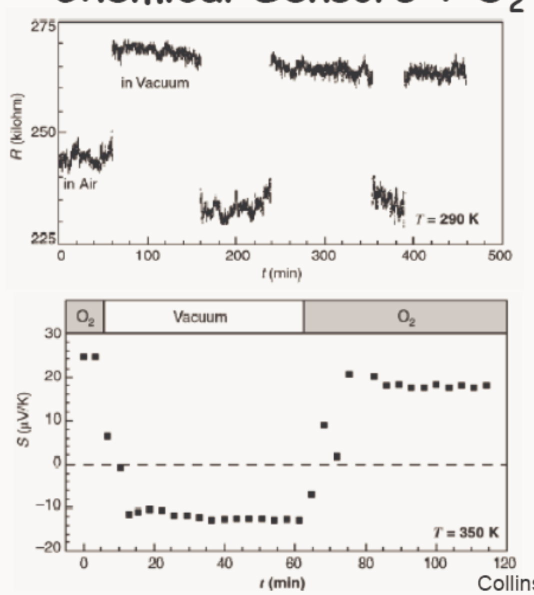
Phonon mean free path = 2.7μm
Ballistic thermal conduction

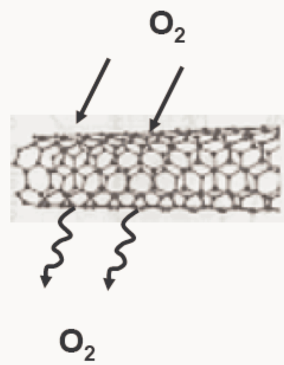
Shi, Majumdar, *et al*, Nano Letters, **5**, 1846 (2005)

Advantages over Existing Materials?

- 1nm diameter, up to 1cm in length, aspect ratio ~10^7
- 1 defect in 10^6 C atoms => ballistic conduction
- High melting point ~3800^{o}C (surface of the sun)
- High young's modulus 1TPa (> diamond)
- High electronic current carrying capacity (10^9A/cm^2) ~10^3 times higher than that of the noble metals
- Thermal conductivity 6600W/mK at room temperature is twice the maximum known bulk thermal conductor, isotropically pure diamond = 3320W/mK
- Surface to volume ratio 100%

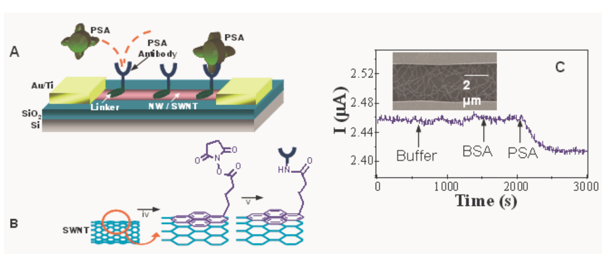
Chemical Sensors : O_2 Detection

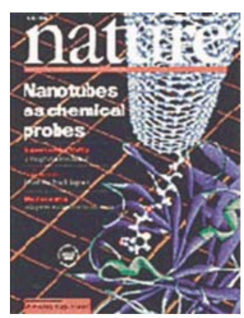




Collins et al., Science, **287**, 1801, 2000

Bio- and Chemical Sensors

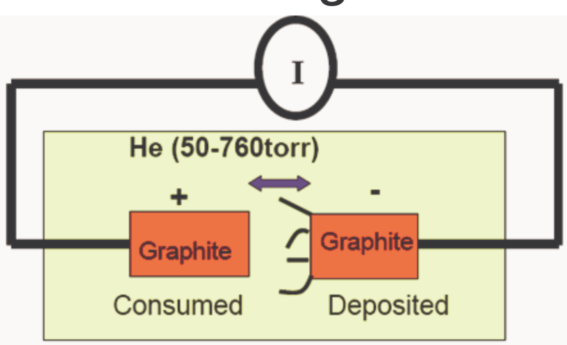




- 100% surface to volume ratio
- Profs. Zhou and Thomson

Nanotube Growth

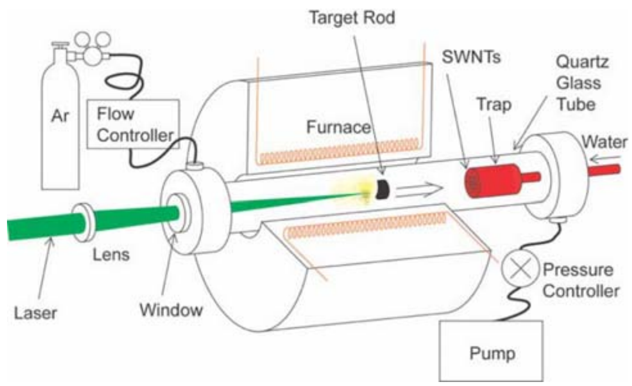
Arc Discharge Method



V : 10~30V, I : 50~300A

+ high crystallinity, yield
+ good quality
- unclean (α-Carbon and by-product)
(Removed by oxidation)

Laser Ablation



Laser Furnace:
•YAG or CO_2 laser aimed at carbon target containing catalytic metals
•SWNT diameter depends on furnace temperature and catalyst (Ni-Y large, Rh-Pd small)

Commercial Vendors

- tubes@rice
- CarboLex
- NanoLab

www.nano-lab.com

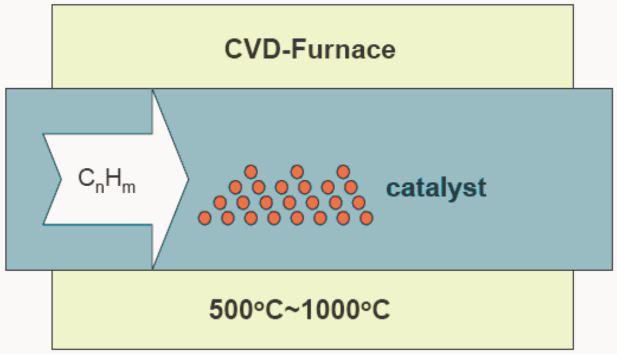
$500/gram!
$14,000/ounce

www.CarbonLex.com

The current price schedule for our AP-Grade, single-walled carbon nanotube (SWNT) material is:

Quantity	Price
More than 100 grams 50-100 grams Less than 50 grams	$60/g $80/g $100/g

Chemical Vapor Deposition (CVD)



+ SWNT, MWNT on any layer
+ well-ordered CNTs
-nanotube weaker, often uncapped

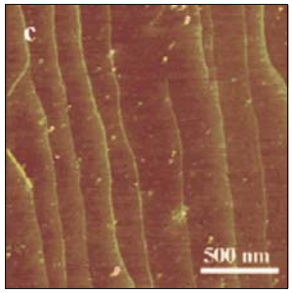
Chemical Vapor Deposition (CVD)

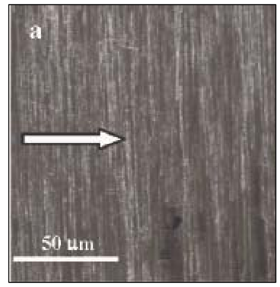
H_2, Ar, CH_4

Recipe:

- Dip chip in $Fe(NO_2)_3$ catalyst
- Nanotubes grow in methane at 900°C (CVD) 10 minutes

Aligned Growth of Carbon Nanotubes (Prof. Zhou at USC)

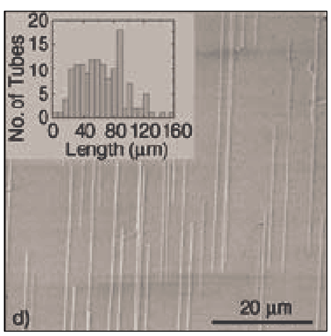




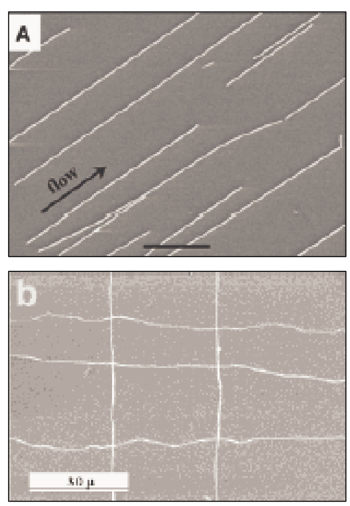
- Growth of aligned nanotubes using surface chemistry
- We can control the density up to 40 nanotubes/micron.

Han, *et. al.*, JACS, **127**, 5294 (2005)

Alternative Aligned Growth Techniques



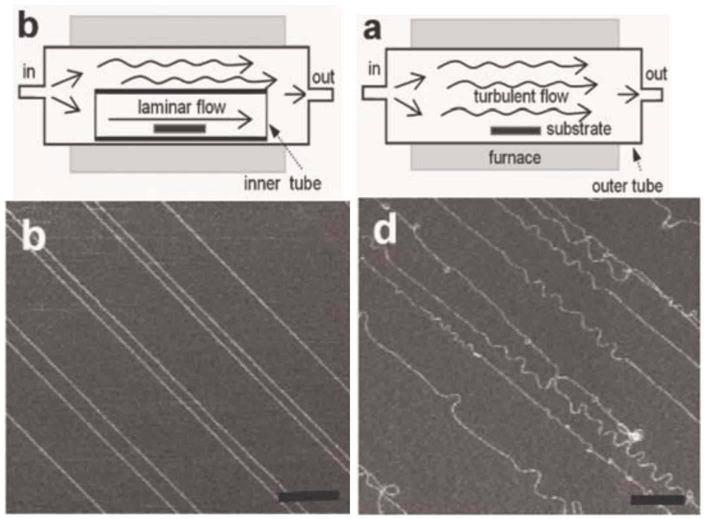
Aligned growth using electric field and high flow rates of methane gas



Sfier, *et al.*, Science (2004)

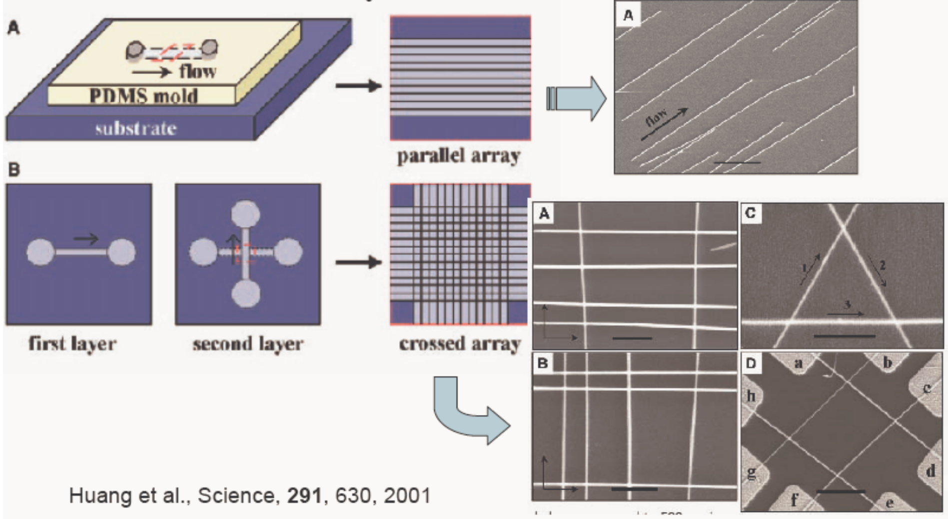
Huang, *et al.*, JACS (2003)

Growth of aligned nanotubes



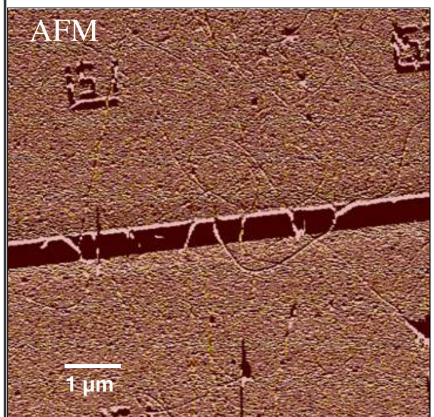
Hong, *et al*, JACS, **127**, 15336 (2005).

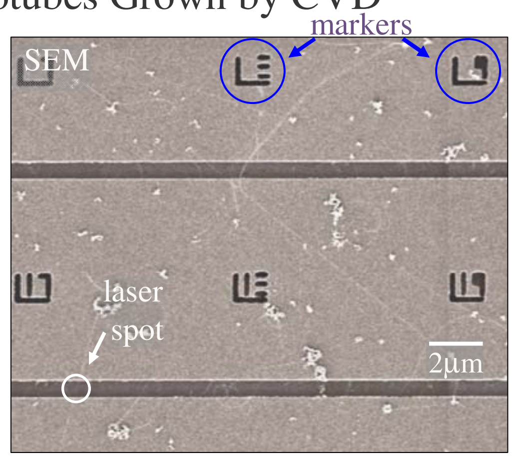
Aligned Assembly of CNT (by Fluidics)



Huang et al., Science, **291**, 630, 2001

Suspended Nanotubes Grown by CVD



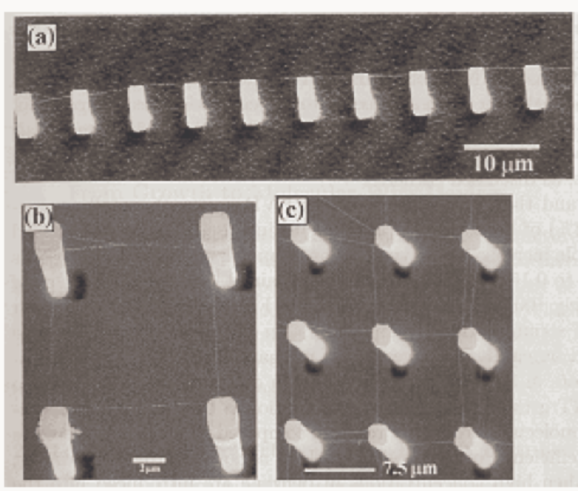


- Laser spot ~ 1µm
- Grid markers allow alignment of laser to a single isolated suspended nanotube

- Nanotubes are extremely sensitive to their environment (bundles, substrate)

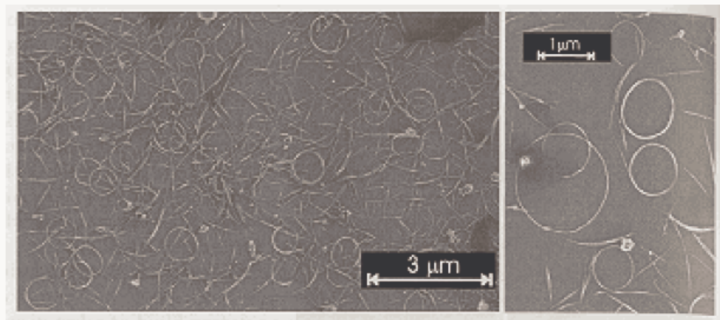
SEM and AFM Damages Nanotubes

Suspended SWNT



Franklin et al., Adv. Mater., **12**, 890, 2000.

Self-organization of CNT (Nano-rope, ring)



- MWNT is stabilized by van der Waals force.
- SWNT is stabilized via making coil due to van der Waals force.

Martel et al., J. Phys. Chem. B, **103**, 7751, (1999)

Synthesis of High-Quality & Very-Thin DWNTs

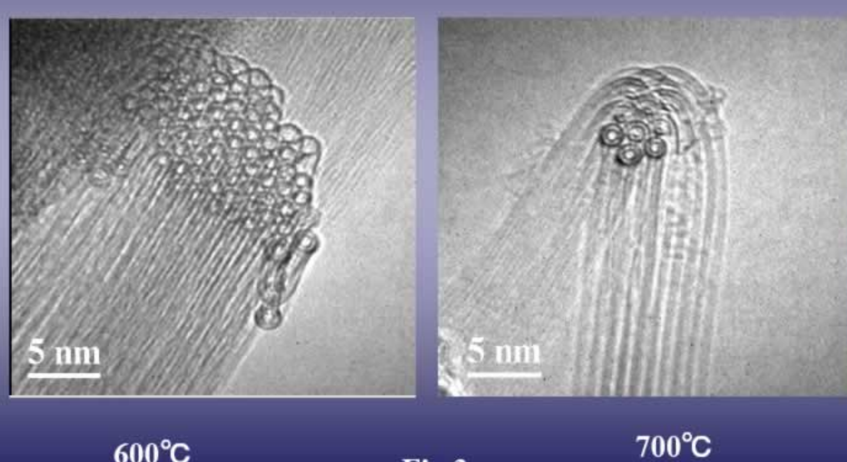
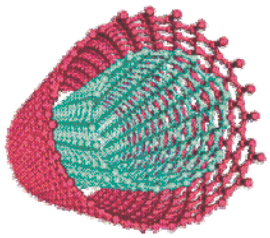
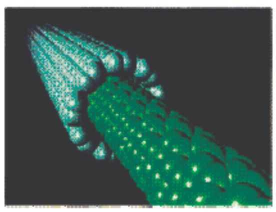
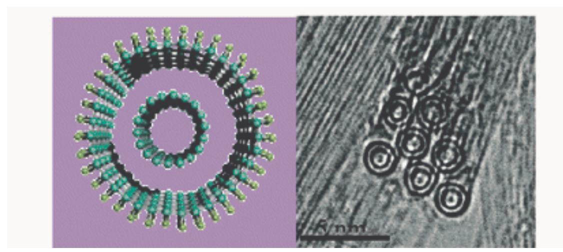


Fig.3

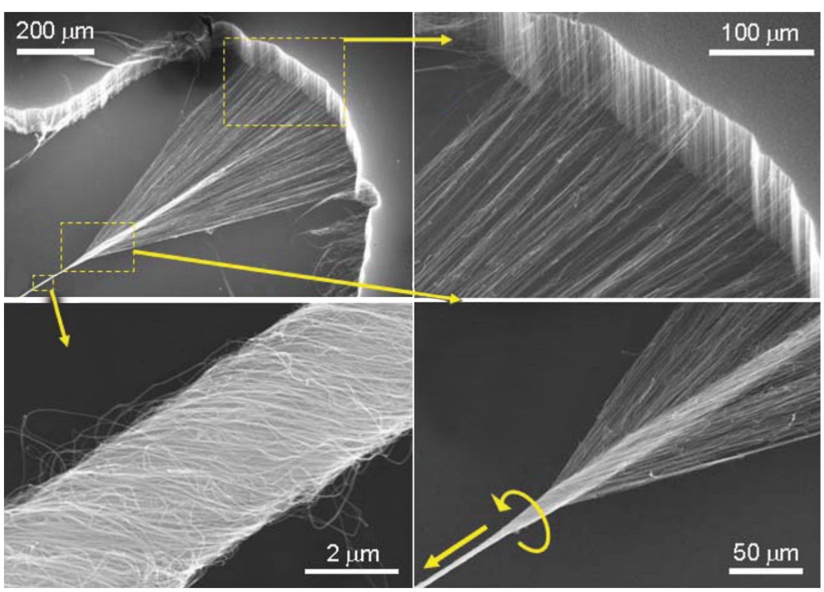
Double Walled Nanotubes





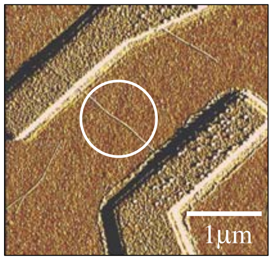


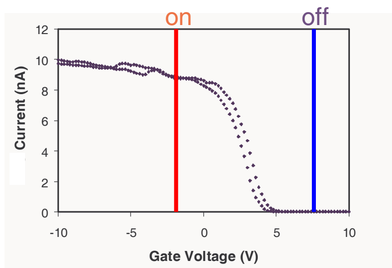
Spinning Carbon Nanotube Yarns

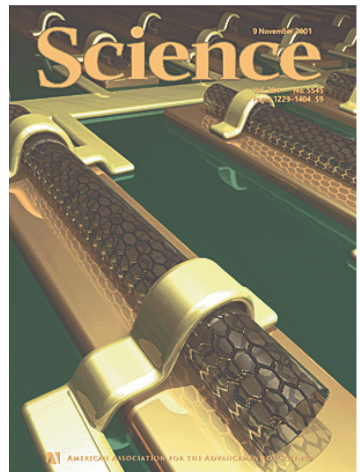


Mei Zhang, Ken R. Atkinson, and Ray H. Baughman, *Science*, 19 November 2004, 1358-1361.

Semiconducting NT-FET

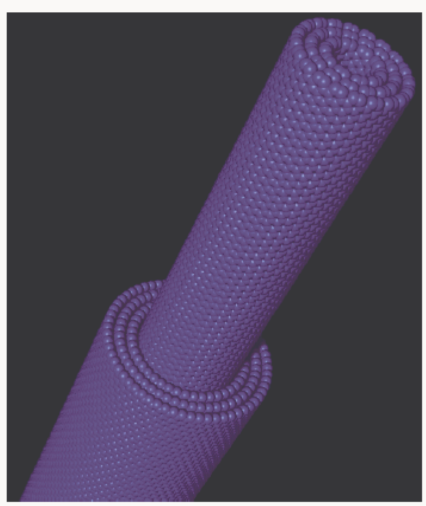






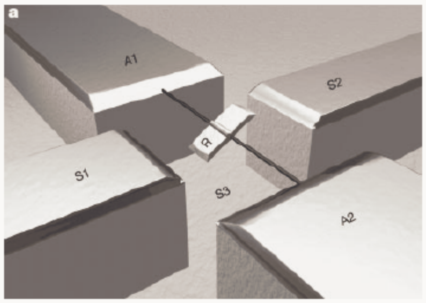
Cronin, *et al.*, APL, **84**, 2052 (2004).

Mechanical Rotor



Zettl (UC-Berkeley)

CNT Motors

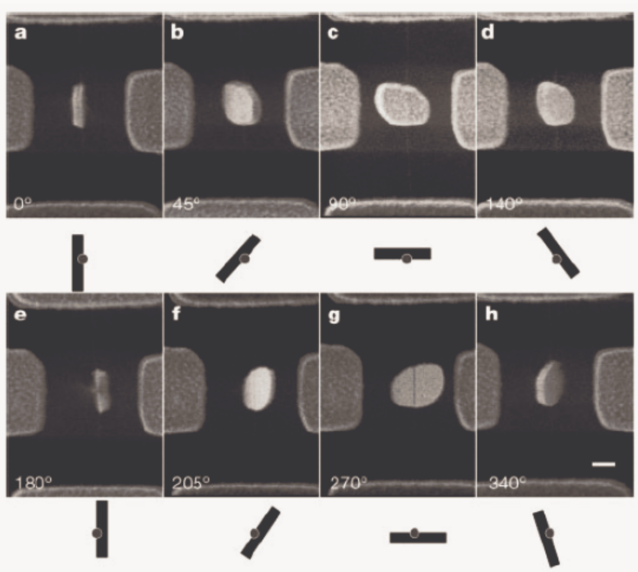


Breaking MWNTs shells :

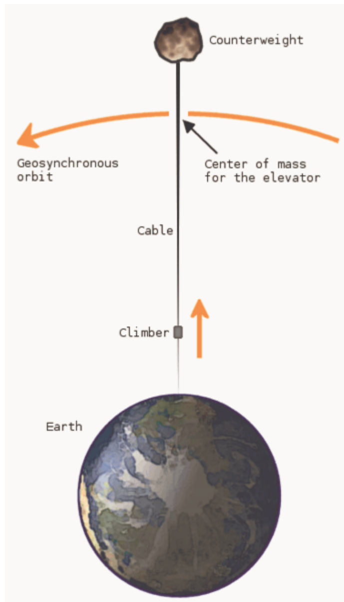
- **RIE etching**
- **Blow out by current**
- **Selective nanotube bond-damage induced by e-beam**

A.M. Fennimore et al., Nature, v.424, p.408, 2003

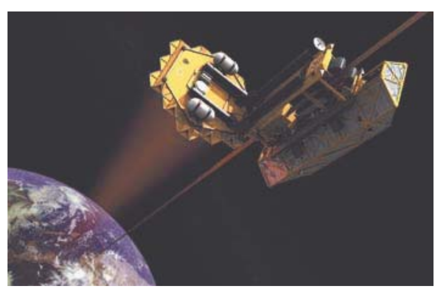
CNT Motors



Space Elevator

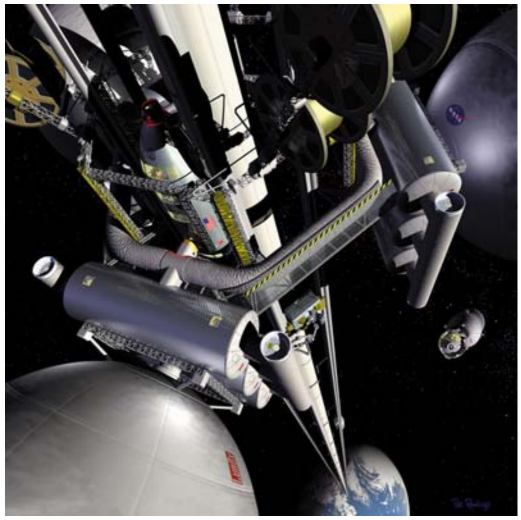


Space Elevator

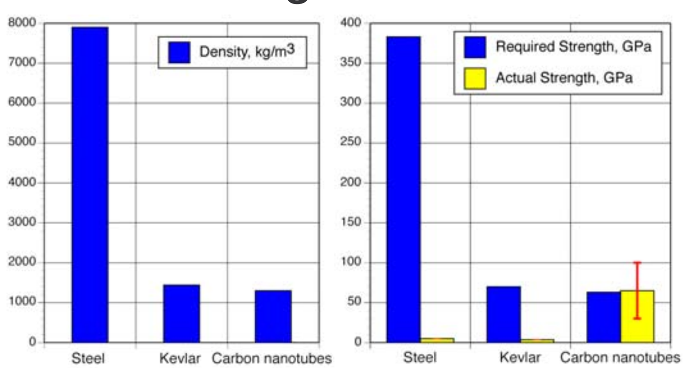


Mechanical Strength: High young's modulus 1TPa (> diamond)

Source: IEEE Spectrum, Aug 2005



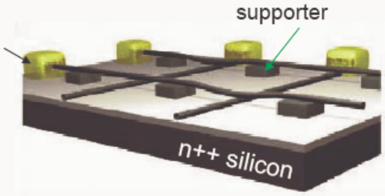
Space Elevator Not Possible with Existing Materials



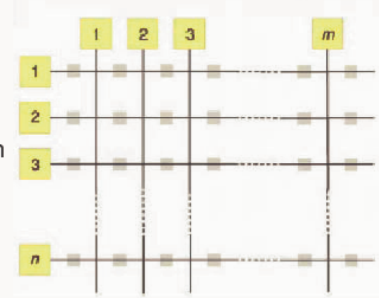
Need high strength, low density

- Longest carbon nanotube ~ 1 cm
- Geosynchronous orbit at 36,000 km
- Defects reduce strength
- Longer nanotubes have more defects
- Oxygen atoms and micrometeorites produce defects

Carbon Nanotube RAM



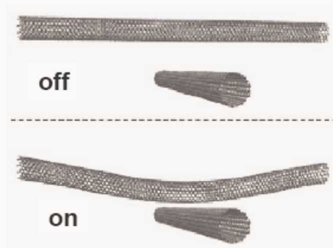
- Potential: 10^{12} elements/cm^2, 100 GHz
- NT array with suspended NT crossing a flat NT on a SiO2 layer with highly doped Si below
- Bistable at NT crossing
  - * Top NT suspended potential energy minimum
  - * Top NT contacting lower NT van der Waals attraction

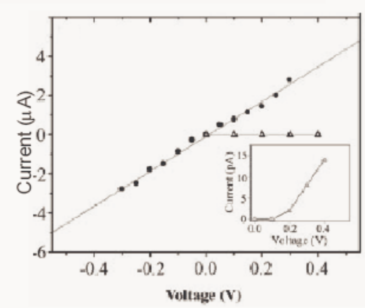


T. Ruekes et al., "Carbon Nanotube-Based Nonvolatile Random Access Memory for Molecular Computing, Science, vol. 289, p.94, Jul. 2000.

CNT RAM

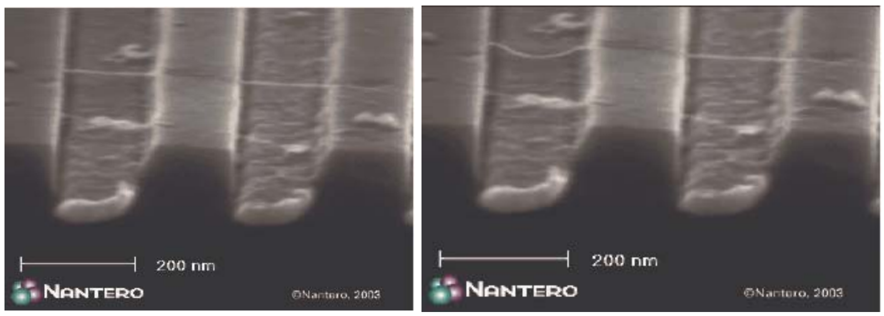
- RAM switch between on-off states with high voltage at electrodes.
- Experimental results show 10X higher resistance for off state.
- Bit value can be sensed by determining resistance with low voltage applied at electrodes.
- Aligning a large number NTs is still difficult, CVD growth may help.





But, NT VLSI Bottlenecks:
- Large scale placement, parallel fabrication techniques.
- Lithography still needed for source, drain, etc.

NanTero



Electro-mechanical random access memory (memory) device in the off (left) and on (right) states.

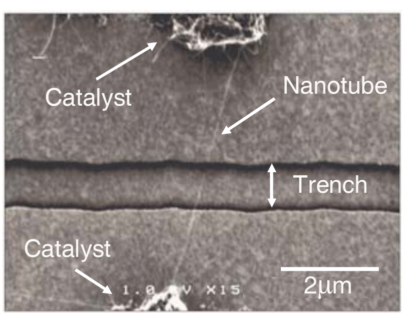
Why Study Carbon Nanotubes?

- 1nm in diameter, 1cm in length, aspect ratio ~10^7
- 100% surface-to-volume ratio
- 1 defect in 10^{12} C atoms => ballistic conduction
- High melting point ~3800^{o}C
- High Young's modulus 1TPa (> diamond)
- High electronic current carrying capacity (10^9A/cm^2) ~10^3 times higher than that of the noble metals
- Thermal conductivity 6600W/mK at room temperature is twice the maximum known bulk thermal conductor, isotropically pure diamond = 3320W/mK

Despite 49,000 publications, no large scale commercial applications of nanotubes

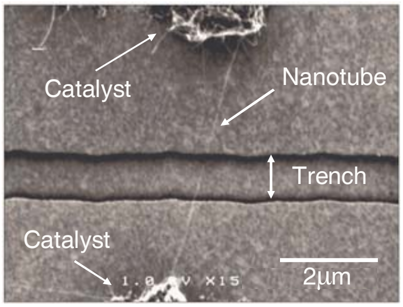
Our Measurements

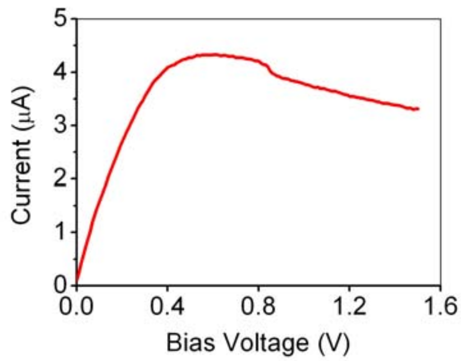
Sample Fabrication



- Pt electrodes deposited on top of trenches etched in Si/SiO_2.
- Catalyst patterned lithographically
- Nanotubes are growth in a mixture of ethanol and hydrogen over the wafer at 800°C.
- Measure the nanotubes, as-grown.

Negative Differential Conductance

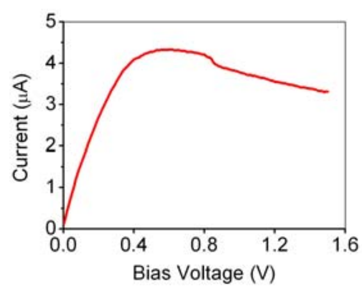




- Selected individual metallic nanotubes exhibiting NDC
- Pristine, highly crystalline, as-grown nanotubes
- Measure the intrinsic properties of nanotube

RF Applications

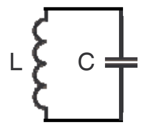
- High electron group velocity (840,000m/s).
- Transit time, $\tau_t = 10^{-13}$sec.
- Typical non-linear I-V is achieved in MOSFET with gate, which is limited by the gate capacitance charging time ~4GHz.
- NDC can be used to make an oscillator.

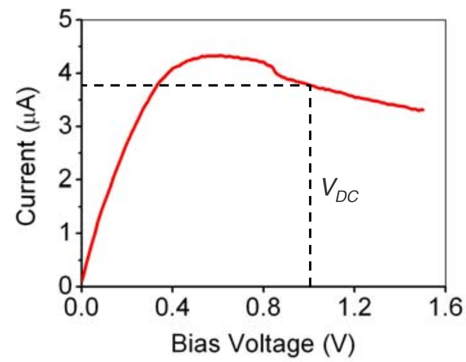


L=0.2µm

$\tau = L/v_g = 2\text{x}10^{-13}$sec => 4THz

Self-Sustaining RF Oscillator

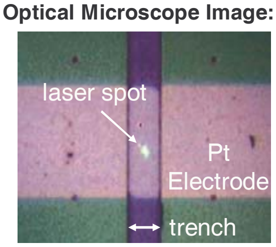




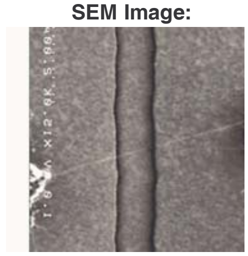
- We can use this device as an oscillator by biasing in the device in the NDR region and putting a high Q resonator across it.
- The "negative resistance" of the device "cancels" the loss of the resonator and a steady non-decreasing oscillation is sustained up to the THz range.

Experimental Setup

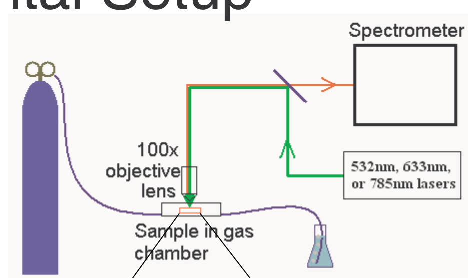
Optical Microscope Image:

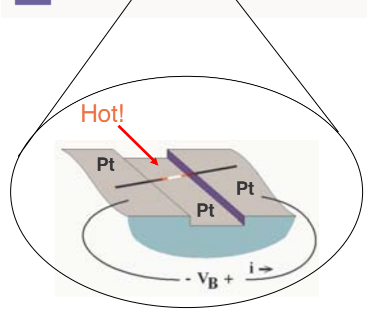


SEM Image:



Our device (example)

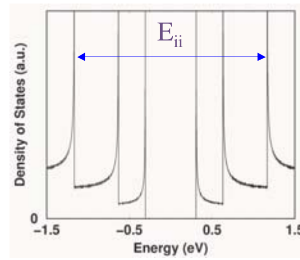


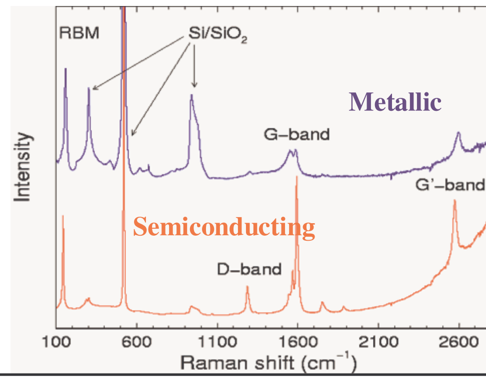


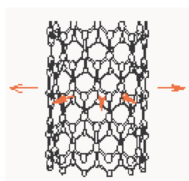
Single Nanotube Raman Spectroscopy

Despite the extremely small geometric cross-section the Raman signal from a single isolated nanotube can be observed.

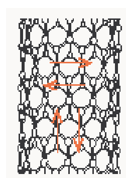
- 10^5 enhancement in scattering cross-section due to singularities in the DOS
- Resonance occurs when $E_{laser}=E_{ii}$
- Only observe nanotubes that are resonant with E_{laser}







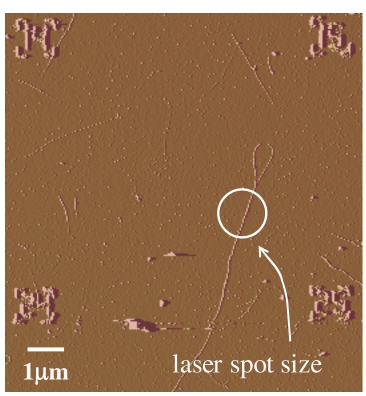
RBM



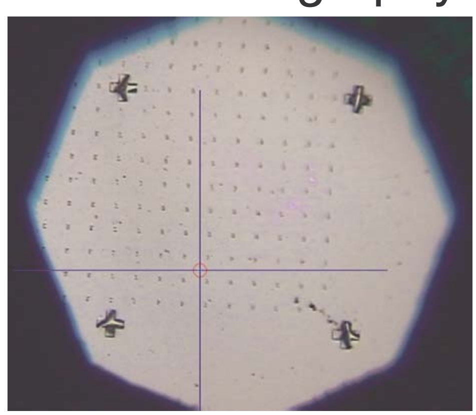
G-band

Jorio, *et al.*, PRL, **86**, 1118 (2001)

Nanotubes on a Substrate with Grid Patterned by *e*-Beam Lithography

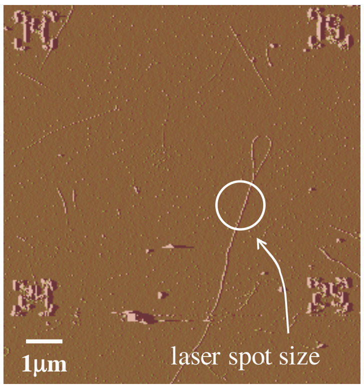


AFM Image

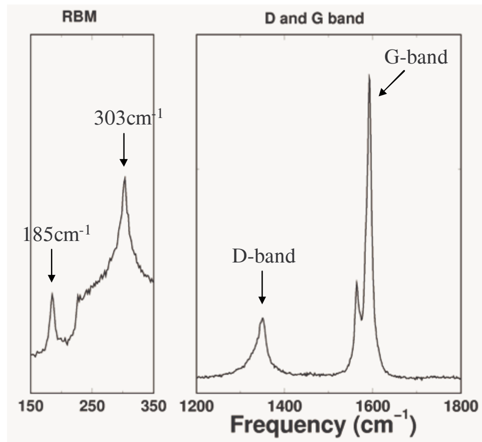


Optical Image

Raman Spectroscopy of Individual Nanotube on a Substrate with Grid



AFM Image



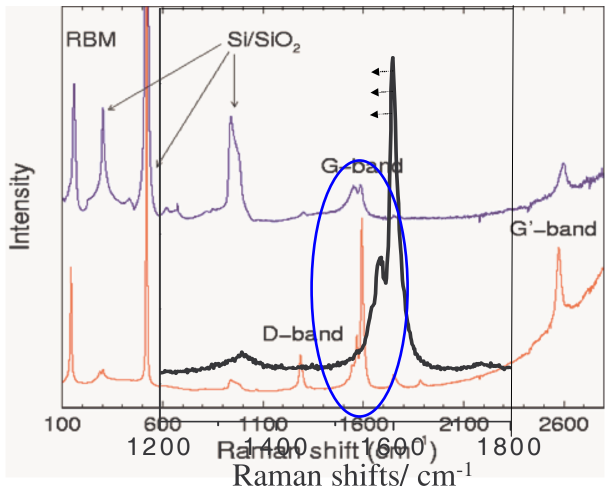
Raman Spectrum

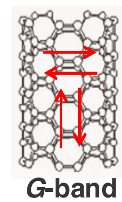
Raman tells us:

- Metal / Semiconducting nature → *G* Band lineshape
- Diameter (±5%) → Inverse to RBM
- Electronic transition energies (E_{ii}) → Laser Energy
- Rough chirality *(n,m)* → E_{ii} and ω_{RBM}
- Orientation of a nanotube → Polarized Raman Intensity
- Defect concentration → *D* Band Intensity
- Strain / Temperature effects → *G* band frequency shift
- Non-contact
- Non-destructive

Raman Spectra

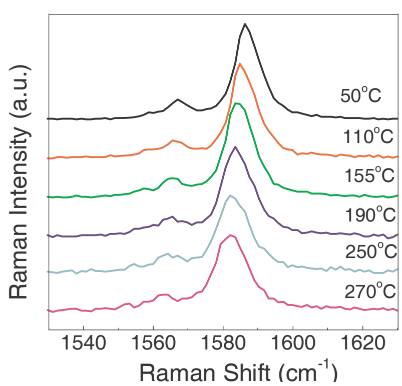
- Downshift of the *G*-band is caused by thermal expansion when the laser heats the nanotube and lengthens the interatomic C-C length.

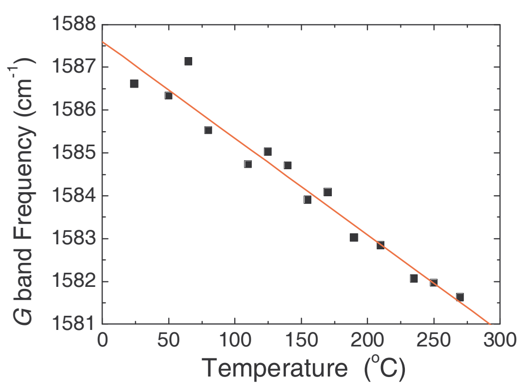




Jorio, *et al.*, PRL, **86**, 1118 (2001)

Temperature Coefficient of *G* band

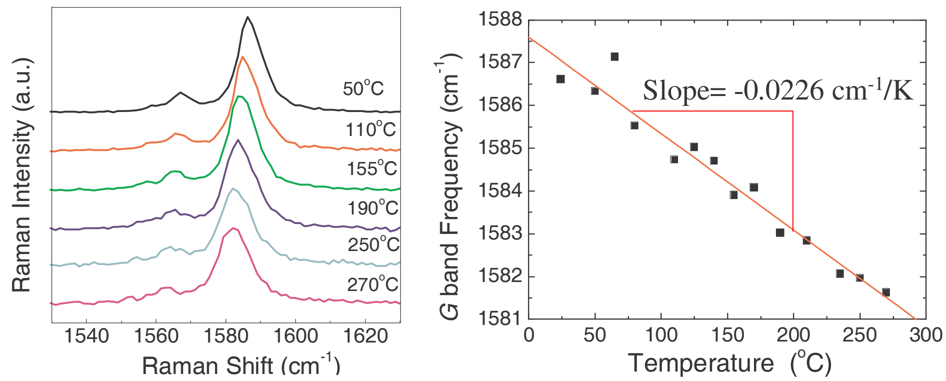




TOC= -0.044cm^{-1}/K, Atashbar, *et. al., App. Phys. Lett.* 86, 123112 (2005)
TOC= -0.042cm^{-1}/K, H. D. Li, *et. al., App. Phys.* 76, 2053 (2000)
TOC= -0.028cm^{-1}/K, Huang, *et. al., App. Phys.* 84, 4022 (1998)

I.K. Hsu, *et. al.,* App. Phys. Lett. 92, 063119 (2008)

Temperature Coefficient of *G* band

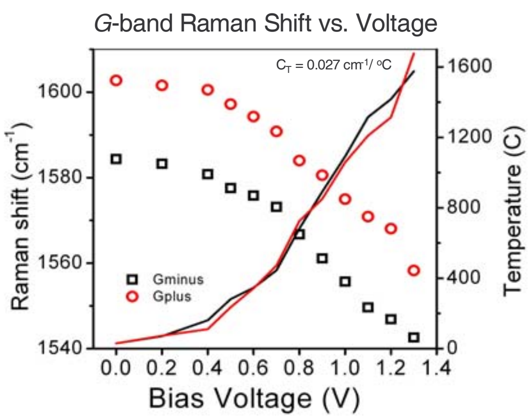


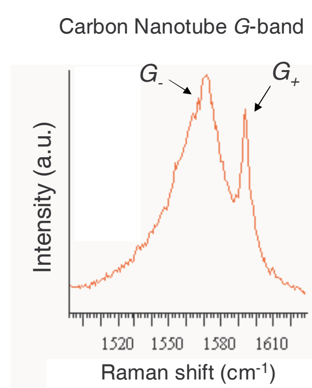
Temperature coefficient of *G* band shifts= -0.0226 cm^{-1}/K

TOC= -0.044cm^{-1}/K, Atashbar, *et. al., App. Phys. Lett.* 86, 123112 (2005)
TOC= -0.042cm^{-1}/K, H. D. Li, *et. al., App. Phys.* 76, 2053 (2000)
TOC= -0.028cm^{-1}/K, Huang, *et. al., App. Phys.* 84, 4022 (1998)

I.K. Hsu, *et. al.,* App. Phys. Lett. 92, 063119 (2008)

Electrical Heating



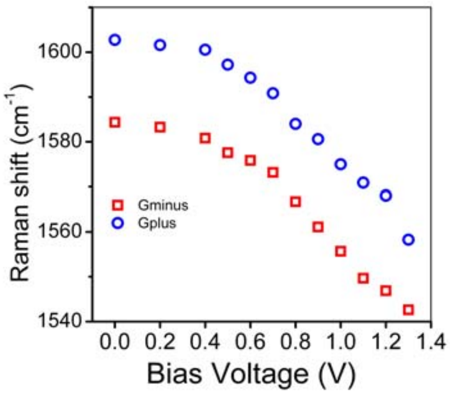


Nanotube reaches 1600°C at high voltage bias

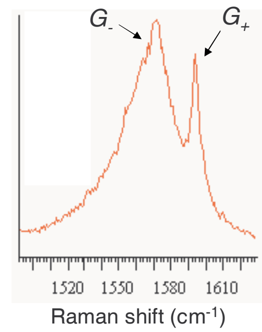
Bushmaker *et al.* Nano Lett. **7,** 3618 (2007)

Electrical Heating

G-band Raman Shift vs. Voltage



Carbon Nanotube *G*-band



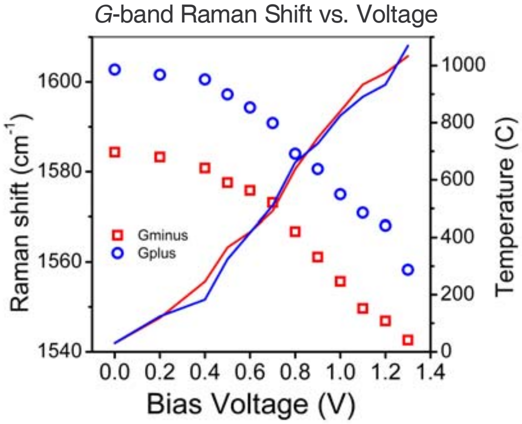
Nanotube reaches 1000°C at high voltage bias, with quadratic fit.

Chiashi, et al, Jpn. J. Appl. Phys., **47**, 2010 (2008).

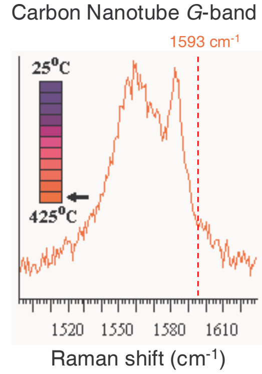
Bushmaker *et al.* Nano Lett. **7,** 3618 (2007)

Electrical Heating

G-band Raman Shift vs. Voltage



Carbon Nanotube *G*-band



Nanotube reaches 1000°C at high voltage bias, with quadratic fit.

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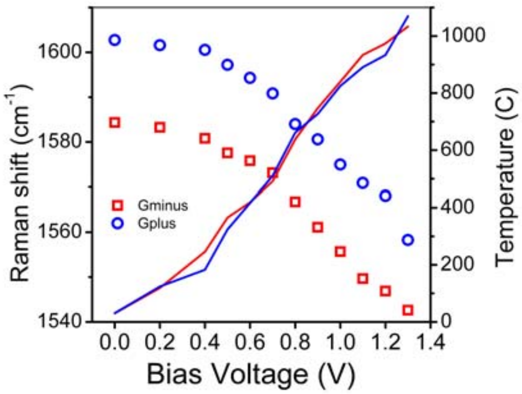
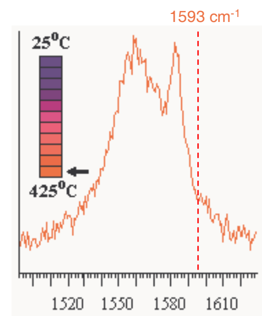
Bushmaker *et al.* Nano Lett. **7,** 3618 (2007)

Electrical Heating

G-band Raman Shift vs. Voltage



Carbon Nanotube *G*-band



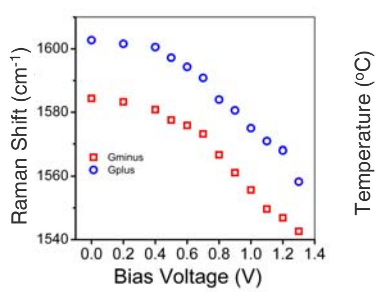
Raman shift (cm^{-1})

Nanotube reaches 1000°C at high voltage bias, with quadratic fit.

Chiashi, et al, Jpn. J. Appl. Phys., **47**, 2010 (2008).

Bushmaker *et al.* Nano Lett. **7,** 3618 (2007)

G_+ (TO) Preferential Heating

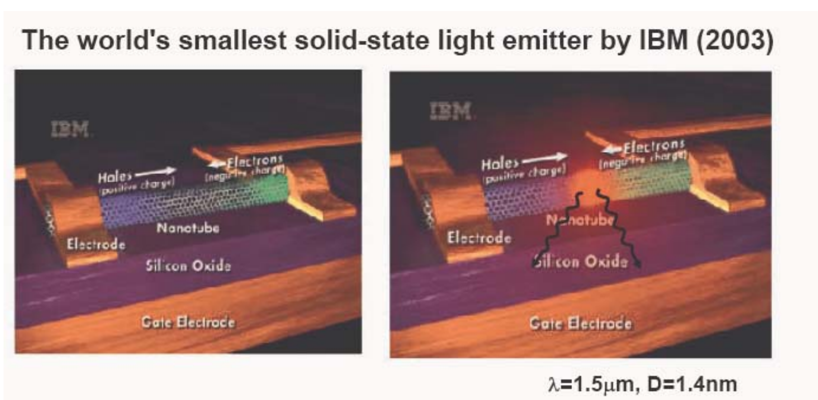


- Preferential shift indicates large non-equilibrium phonon populations
  - G_+ @ 1000°C
  - G_- @ 40°C
- An extreme state of thermal non-equilibrium

Bushmaker *et al.* Nano Lett. **7** 3618 (2007)

Potential Applications

Infrared Emission and Detection



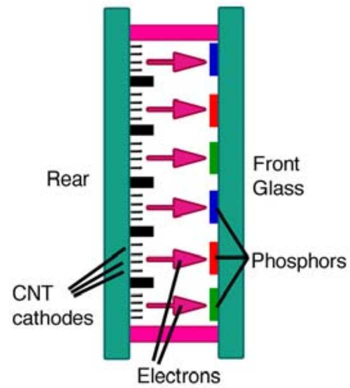
Emission: Electron-hole recombination produces light.
Detection: Incident light produces an el-ho pair.

M. Freitag, Y. Martin, J. A. Misewich, R. Martel, and Ph. Avouris, *Photoconductivity of Single Carbon Nanotubes*, Nano Lett., **3**, 1076 (2003).

J. A. Misewich, R. Martel, Ph. Avouris, J. C. Tsang, S. Heinze, J. Tersoff, *Electrically Induced Optical Emission from a Carbon Nanotube FET*, Science, **300**, 783, (2003).

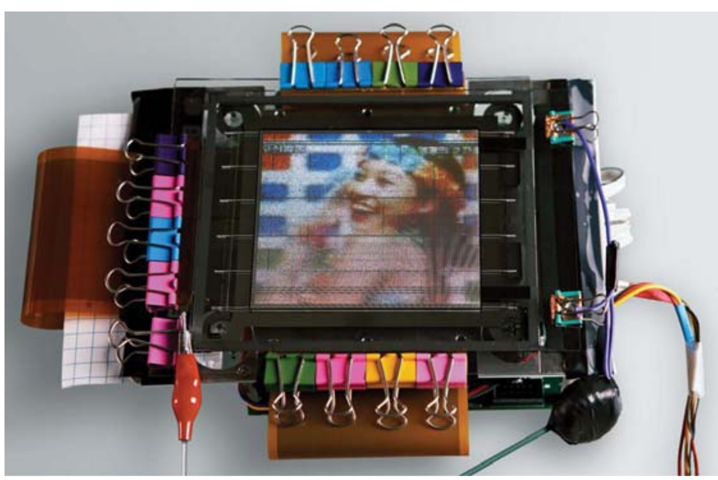
Field Emission

A cathode ray tube (CRT).



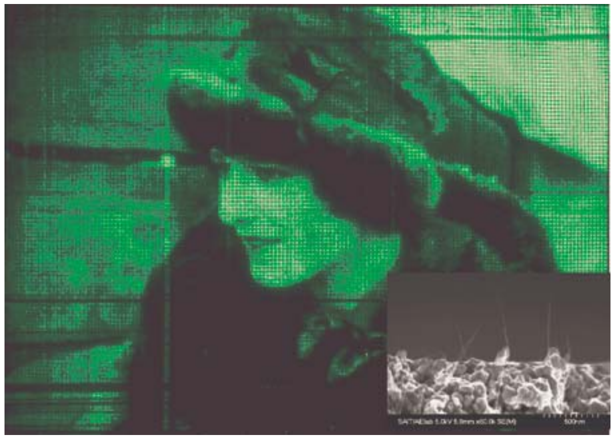
A field effect display (FED).

Field Emission



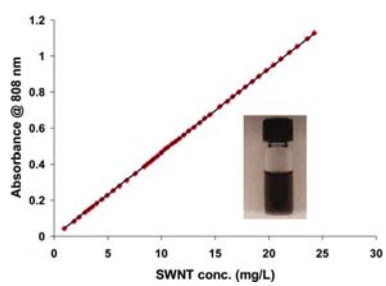
Samsung prototype field emission display using carbon nanotubes.
Technology Review, November 2004, May 2005

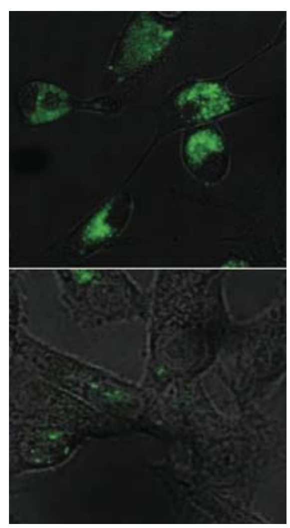
Field Emission Display



Carbon Nanotubes-based Field Emission Display (6 inches) from CEA/LETI technologies (courtesy of Jean Dijon)

Drug Delivery

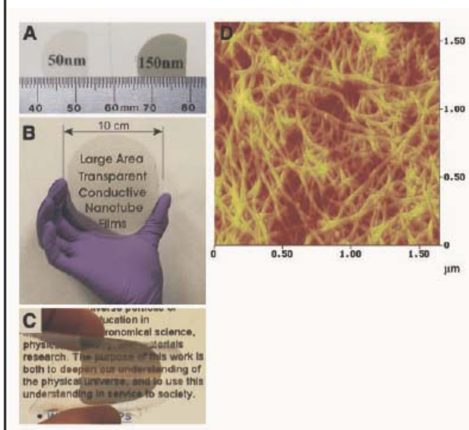


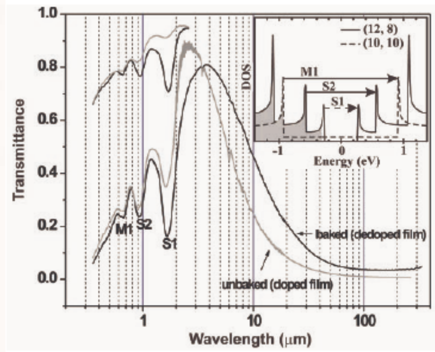


Functionalized carbon nanotubes (green) taken up by cancer cells with folate receptors (top) and normal cells (bottom).

N. W. S.Kam, M. O'Connell, J. A. Wisdom, and H. Dai, "Carbon nanotubes as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction," PNAS, 102, 11600-11605, (2005) and Discover Magazine, Nov. 2005.

Transparent Conducting Electrodes

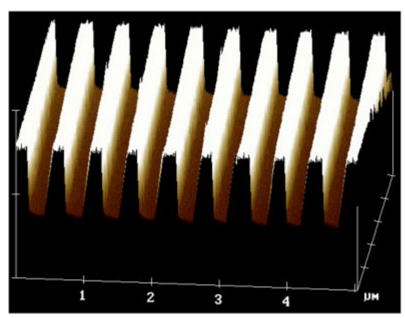




Mei Zhang,Shaoli Fang, Anvar A. Zakhidov, Sergey B. Lee, Ali E. Aliev, Christopher D. Williams, Ken R. Atkinson, Ray H. Baughman, "Strong, Transparent, Multifunctional, Carbon Nanotube Sheets," *Science,* 19 August 2005, 1215-1219.

AFM Imaging *with* Nanotubes

AFM Probe Tip



600 nm deep trenches;
250 nm wide

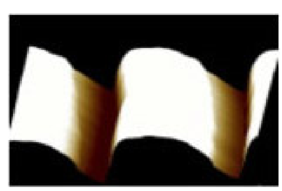
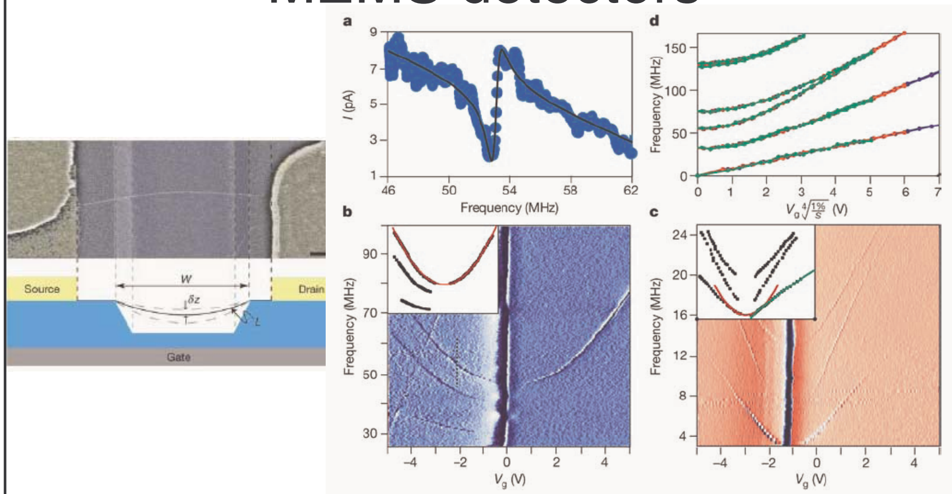


Image using conventional tip

MEMS detectors



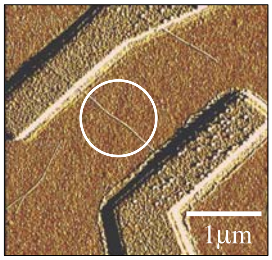
- 1μm segment of nanotube contains ~160,000 carbon atoms and weighs ~3x10^{-18}grams
- detecting attogram (10^{-18}g) masses
- $\Delta R/R$ at resonance ~ 10^{-9}

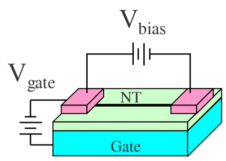
] V. Sazonova, Y. Yaish, H. Ustunel, D. Roundy, T. A. Arias and P. L. McEuen, *A tunable carbon nanotube electromechanical oscillator*, Nature, **431**, 284 (2004).

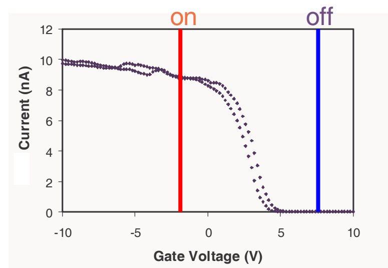
Technological Hurtles

- Random growth
- Controlled growth or separation methods:
  - metallic from semiconducting
  - by diameter
  - by chirality
- Short (microns in length)
- Defect concentration
- …

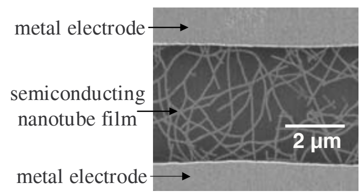
NT-FET





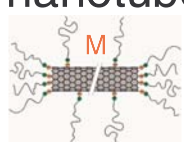


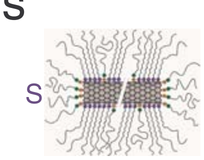
- Build transistor arrays from semiconducting NT films.
- Metallic nanotubes short-circuit the behavior of the semiconducting nanotubes
- Can we selectively burn out resonant metallic nanotubes?



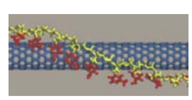
Current Limitation: Can't separate semiconducting nanotubes

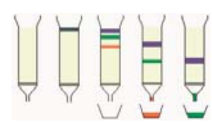
- Precipitation of SWNTs non-covalently functionalized with ODA
  D. Chattopadhyay *et al.*, JACS **125**, 3370 (2003)



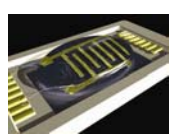


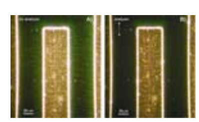
- Ion-exchange liquid chromatography of ssDNA wrapped SWNTs
  M. Zheng *et al.*, Nature Materials **2**, 338 (2003)





- Alternating current dielectrophoresis in an aqueous SWNT suspension
  R. Krupke *et al.*, Science **301**, 344 (2003)



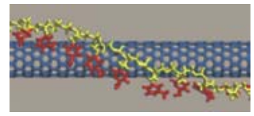


- Selective functionalization with diazonium salts
  M. S. Strano *et al.*, Science **301**, 1519 (2003)
- Centrifugation after addition of diluted bromine
  Z. Chen *et al.*, Nanoletters **3**, 1245 (2003)

What is the best way to analyze what these processes actually do?

ATTENTION —
many of these processes separate SWNTs by diameter in addition to metallicity, yielding deceptive results

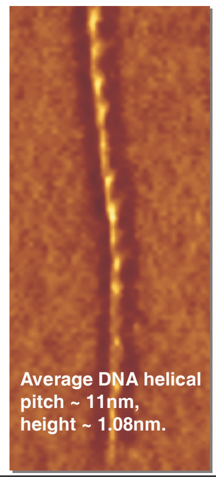
DNA– an Alternative CNT Isolation Method to SDS Dispersion



DNA Wrapping:
→ Aromatic interaction
→ Partial coverage, different perturbation

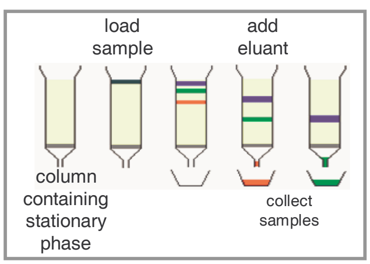
Chromatography and Fractionation:
→ DNA strands selects smaller d_t CNTs
→ IEC separation by charge
→ Fractionated sample enriched in a single (n,m) specie

Interesting Science:
→ Environment effects on optical processes.
→ Phonon-assisted processes



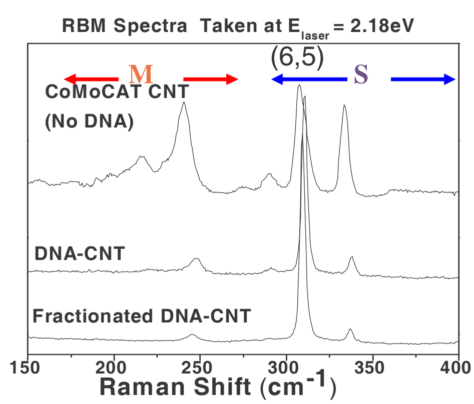
DNA-Assisted SEPARATION

M. Zheng *et al.*, *Science*, **302**,1546 (2003).



Ion-exchange chromatography (IEC)

Hybrid DNA-SWNTs:
• M-SWNT different surface charge density, higher polarizability, elute before S-CNTs



Separation mechanisms

•Small d_t SWNTs elute before large d_t SWNTs