Introduction to Nanotechnology and Nanoscience – Class#10

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Outline

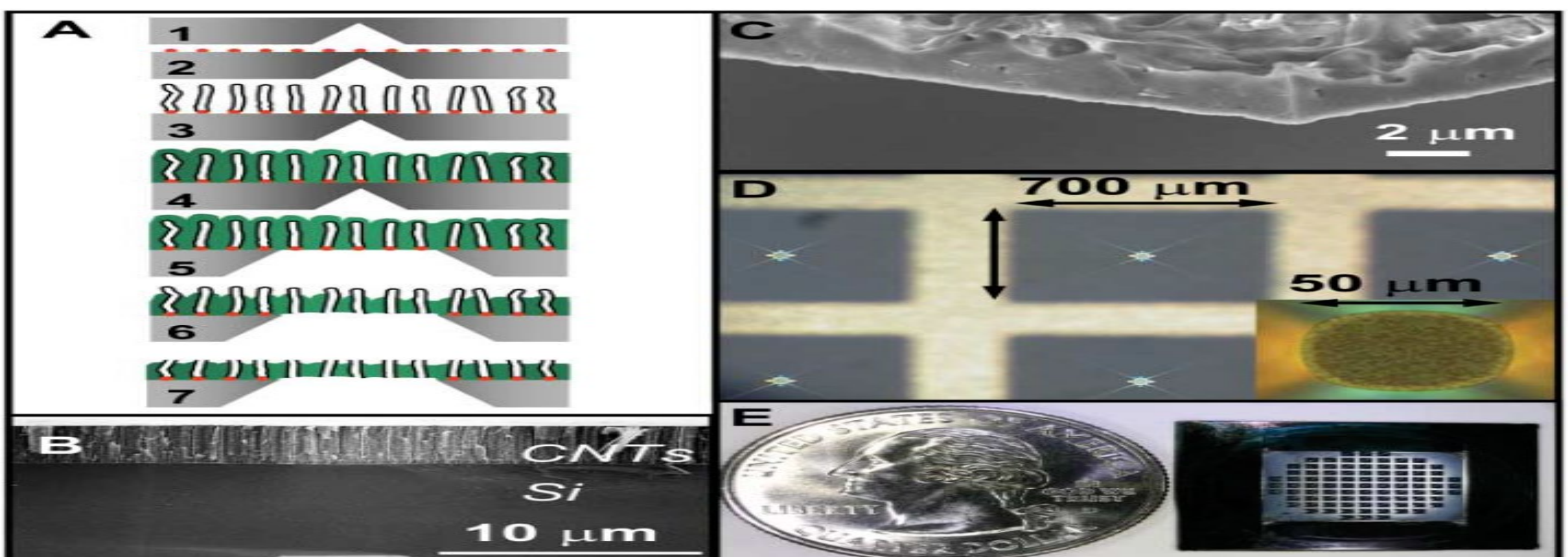
- ☐ Recap
- ☐ HW #3, Problem #2
- ☐ Band Structure and Fermi Level
- ☐ Graphene & Lab #1
- ☐ Paper 3

CNT Membrane

Fast Mass Transport Through Sub–2-Nanometer Carbon Nanotubes

Jason K. Holt,[1*] Hyung Gyu Park,[1,2*] Yinmin Wang,[1] Michael Stadermann,[1] Alexander B. Artyukhin,[1] Costas P. Grigoropoulos,[2] Aleksandr Noy,[1] Olgica Bakajin[1]†

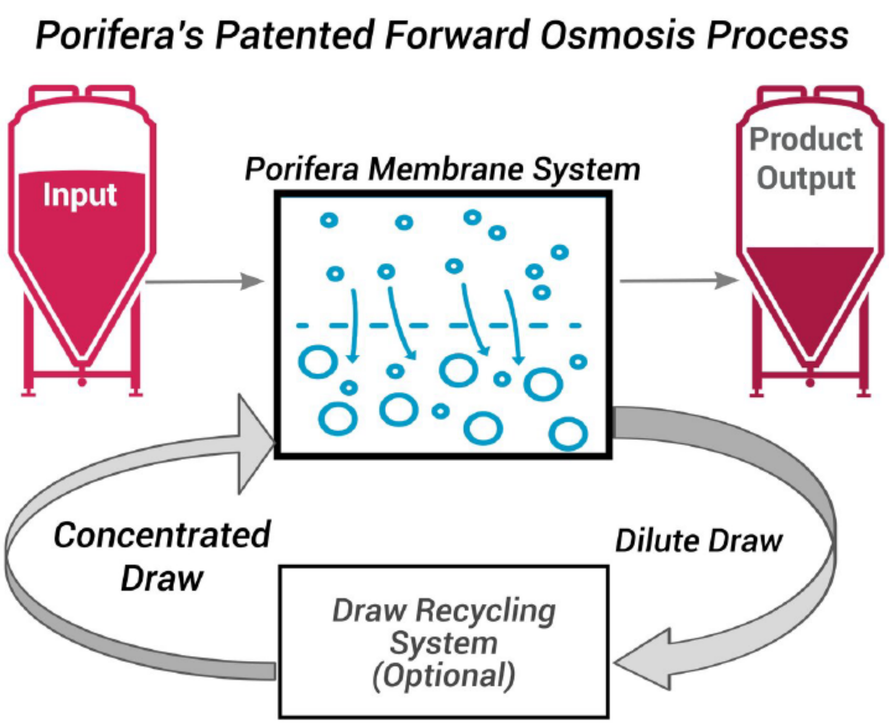
19 MAY 2006 VOL 312 SCIENCE www.sciencemag.org



Start-up Company

Porifera®

Technology



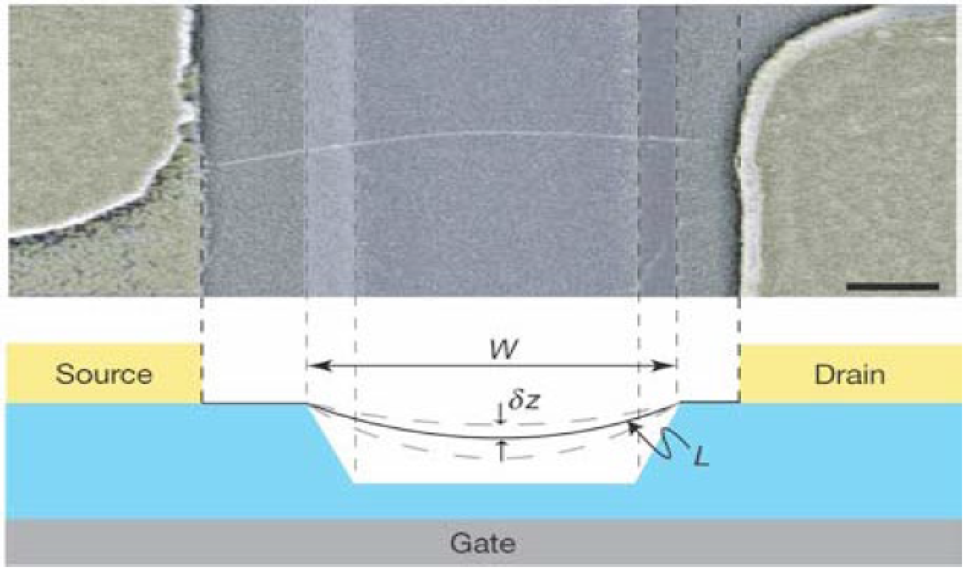
A powerful pairing of Forward Osmosis and unique draw regeneration solutions for optimal concentration and purification.

Porifera was established in 2009 in response to a Department of Defense DARPA challenge to develop a low-energy, easily transportable water purification system. Our team of PhDs created a membrane with better selectivity and 3x more throughput than any other product on the market.

HW#3, Problem 2

Problem 2 (CNT Resonator)

A carbon nanotube is suspended between two contacts as shown below (W in the figure is 1.0 μm. Figure is from Sazonova et al., *Nature* **431**, 284 - 287 2004)



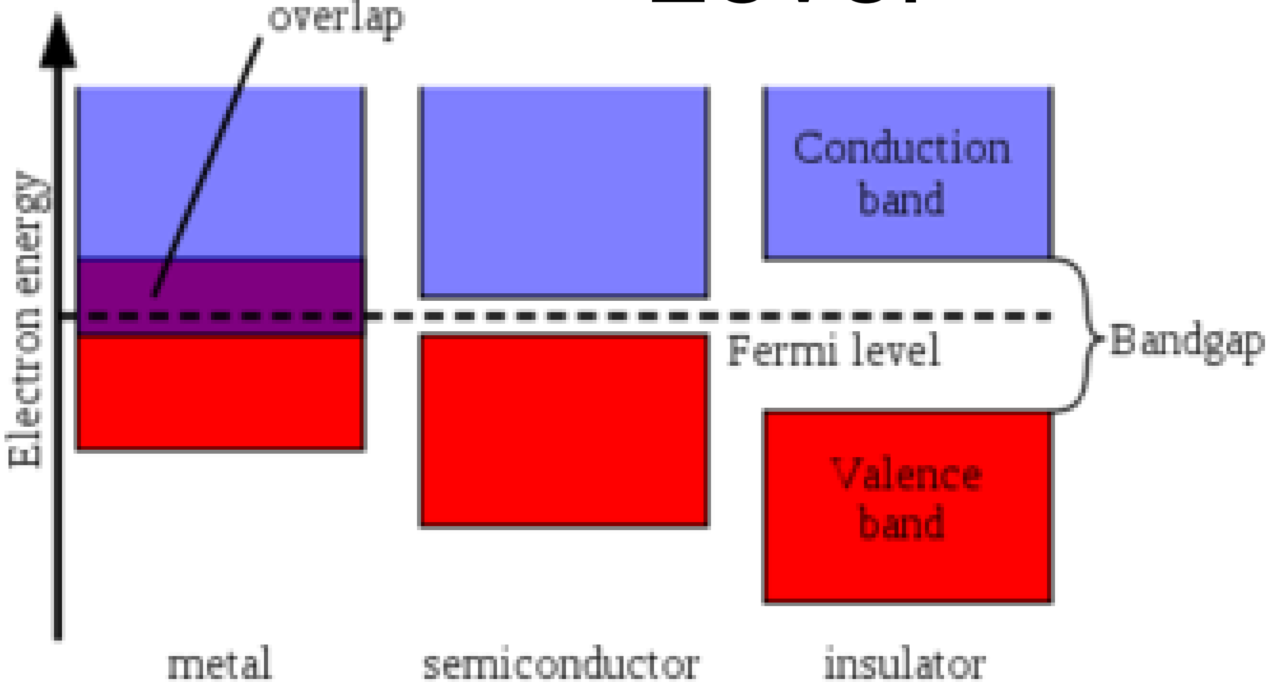
(a) design a process flow to make this set up (you can either come up your own process or take a look at the original paper to see how they did it)

(b) What is the mechanical resonance frequency of the nanotube? Consider that the diameter, D, of the carbon nanotube is 1.3 nm, the density is 1300 kg/m^3, the length is 1μm, and the Young's Modulus, E, is 1.2 TPa. You will need to know that the moment of the cross-sectional area of the carbon nanotube about the neutral axis is $I = (\pi d^4/64)$

(c) Compare this resonance frequency with that of one suspended single-crystal silicon beam that is 7.7μm in length, 330nm in width, and 800nm in height.

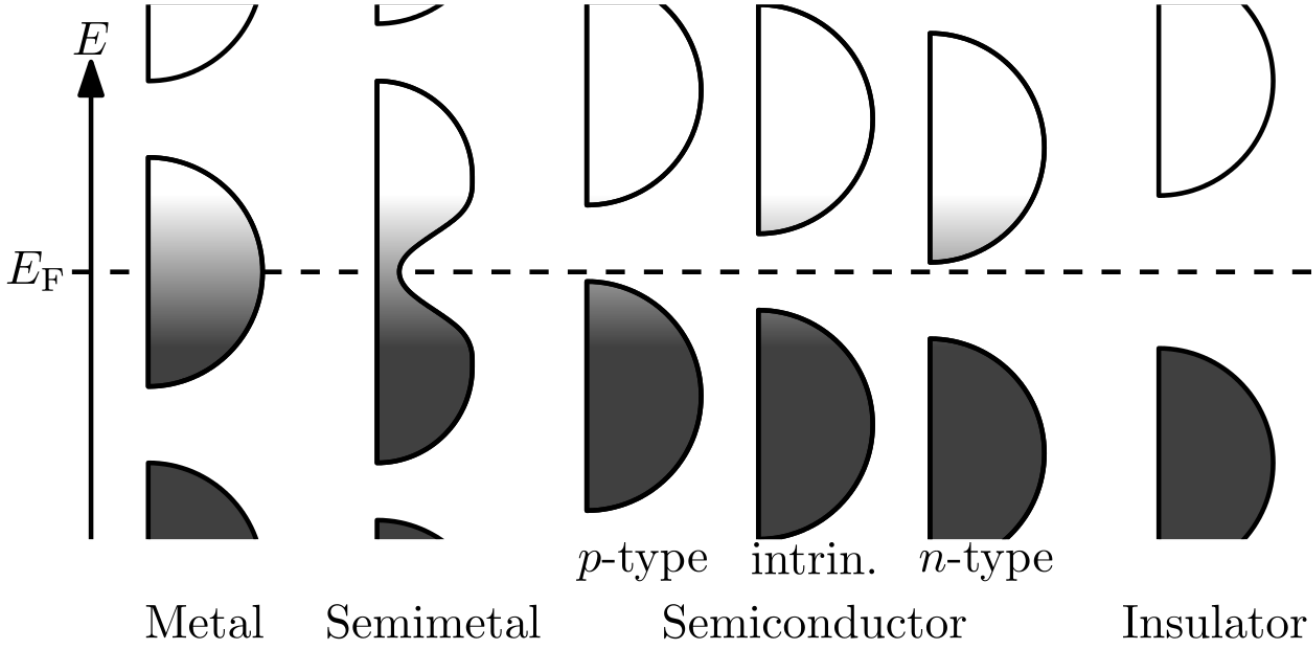
(d) What do the first four resonance modes of the suspended carbon nanotube look like? Sketch a drawing of these modes.

Band Structure and Fermi Level



Electrons settle into the lowest available energy states at absolute zero temperature and build a "Fermi sea" of electron energy states. The Fermi Level (with Fermi energy E_f) is the "surface" of this sea where electrons will not have enough energy to rise above the surface. It is the energy level which is occupied by the highest electron orbital at 0 Kelvin (absolute zero temperature)

Fermi Level

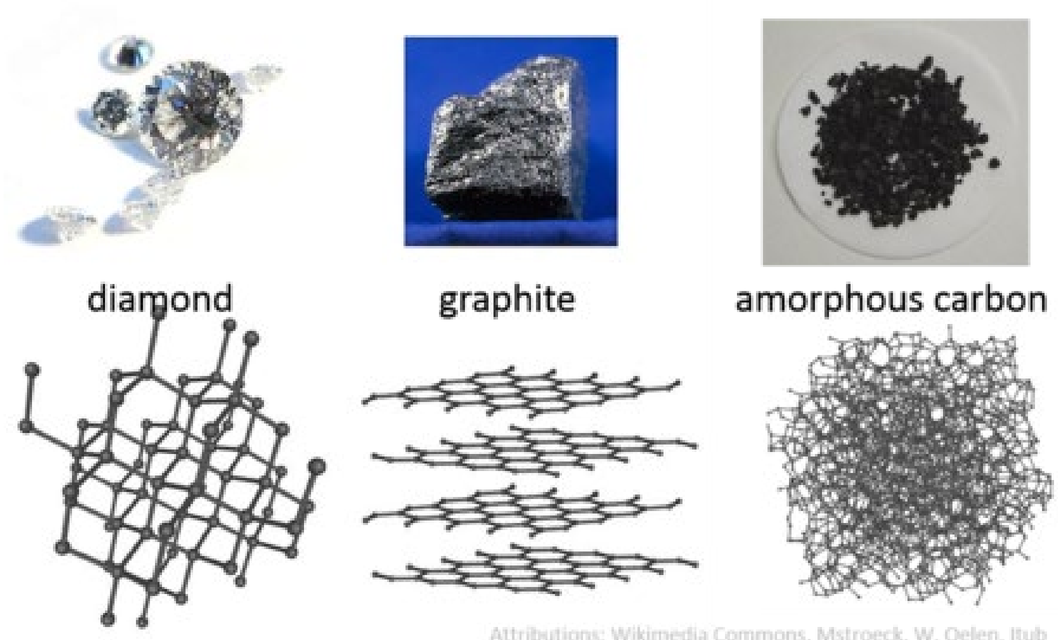


Here, **height is energy while width is the <u>density of available states</u>** for a certain energy in the material listed. The shade follows the **<u>Fermi–Dirac distribution</u>** (*black*: all states filled, *white*: no state filled).

In **<u>metals</u>** and **<u>semimetals</u>** the Fermi level E_F lies inside at least one band.

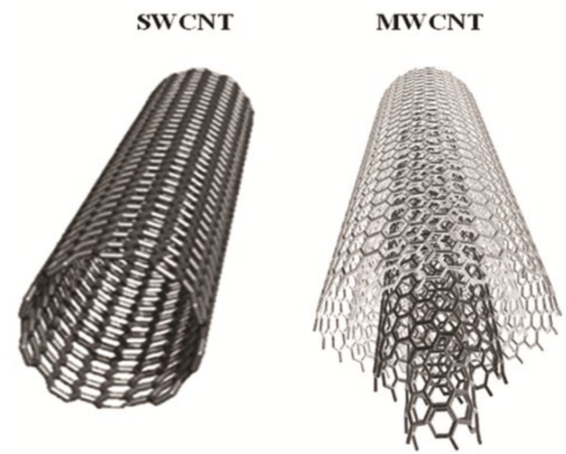
In **<u>insulators</u>** and **<u>semiconductors</u>** the Fermi level is inside a **<u>band gap</u>**; however, in semiconductors the bands are near enough to the Fermi level to be **<u>thermally populated</u>** with electrons or **<u>holes</u>**.

Graphene

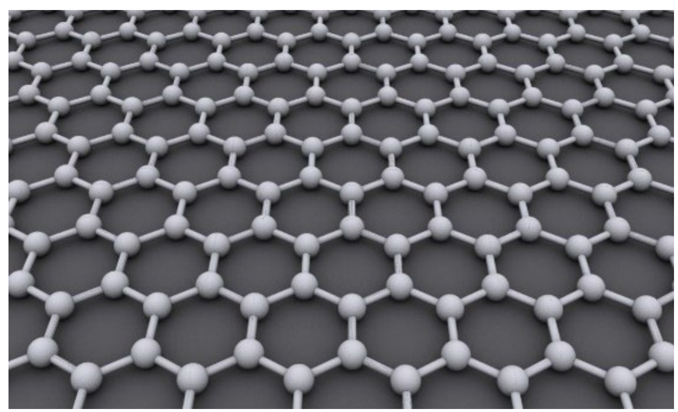


http://wiki.seg.org/wiki/Carbon

Carbon nanotubes

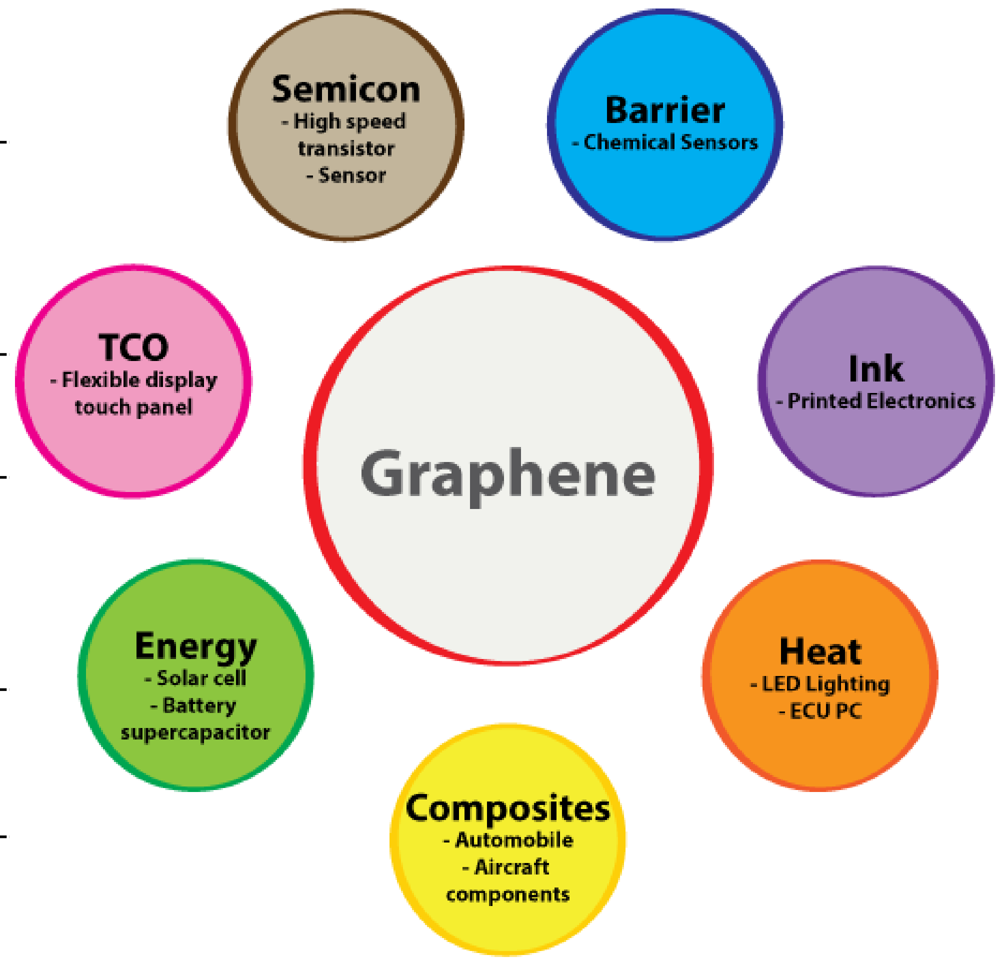


Graphene



Graphene Properties

Charge carrier mobility	~200,000 $cm^2/V\ s$
Thermal conductivity	~5000 W/m K
Transparency	~97.4%
Specific surface area	~2630 m^2/g
Young's modulus	~1 TPa
Tensile strength	~1100 GPa

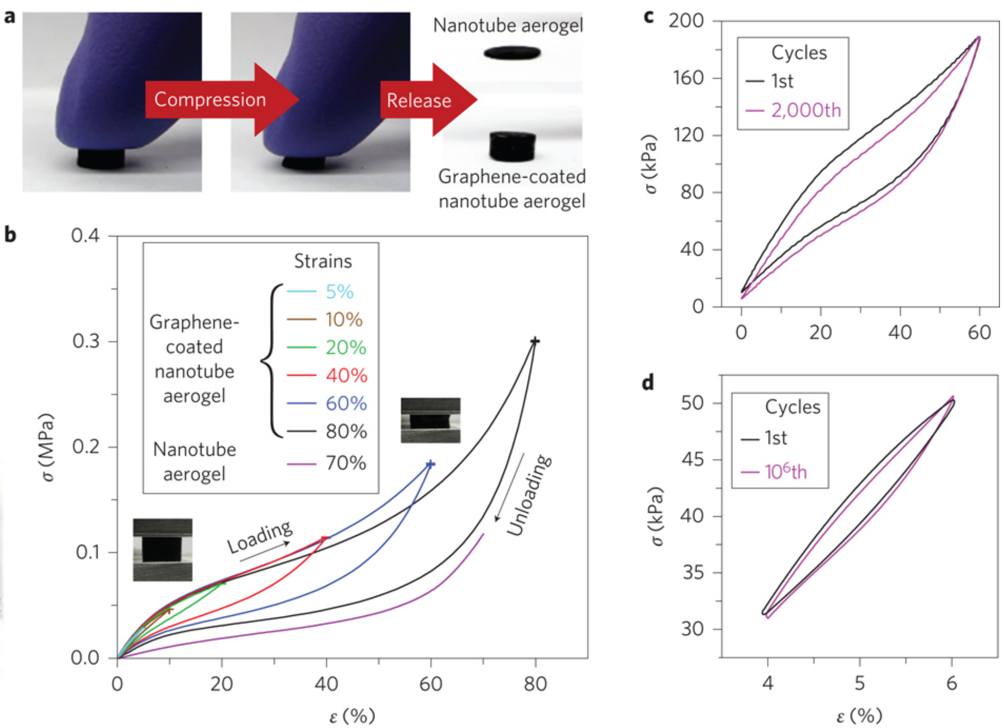


Properties of CNT and Graphene

Properties of CNT, graphene, diamond, silicon and steel.

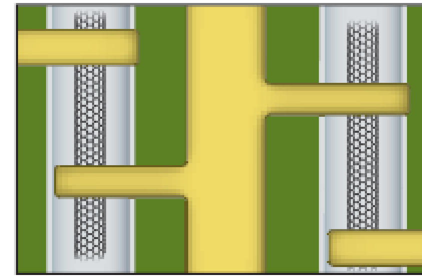
	Young's modulus (GPa)	Tensile strength (GPa)	Bandgap (eV)	Carrier mobility ($cm^2 V^{-1} s^{-1}$)
Graphene	2000 ± 400 [16]	130 ± 10 [17]	0 [28]	~2 × 10^5 [24]
MWNT	270–950 [25]	11 [29]–150 [30]	~0	–
SWNT	~1000 [31]	13–53 [32]	0–2 [26]	0.79–1.2 × 10^5 [33]
Diamond	1220 [34]	1.2 [34]	5.5 [35]	~156 [36]
Silicon	130–169 [18]	7 [37]	1.12 [38]	~1000 [39]
Steel	~200 [40]	0.25 [41]	–	–

http://www.extremetech.com/wp-content/uploads/2013/02/elephant.jpg

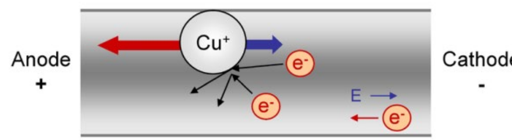


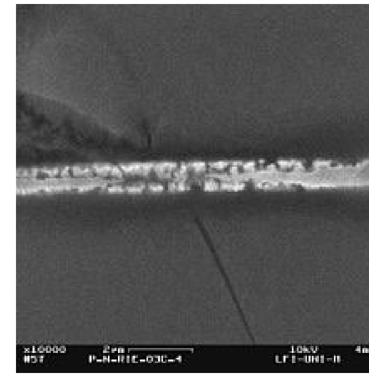
Nature Nanotechnology **7**,562–566 (2012)

Nanotubes For Wiring

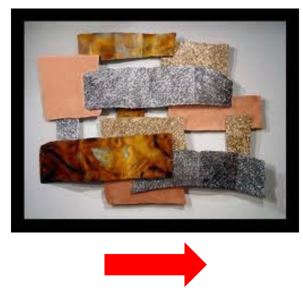


- **Electromigration** is a problem for metal wires at small sizes
  - Covalent structure of CNT prevents similar breakdown

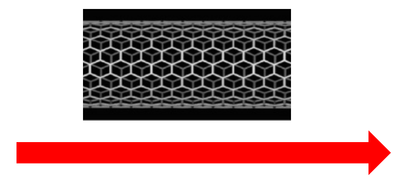




- Nanotube current density is enormous



J ~ 10^5 A/cm²



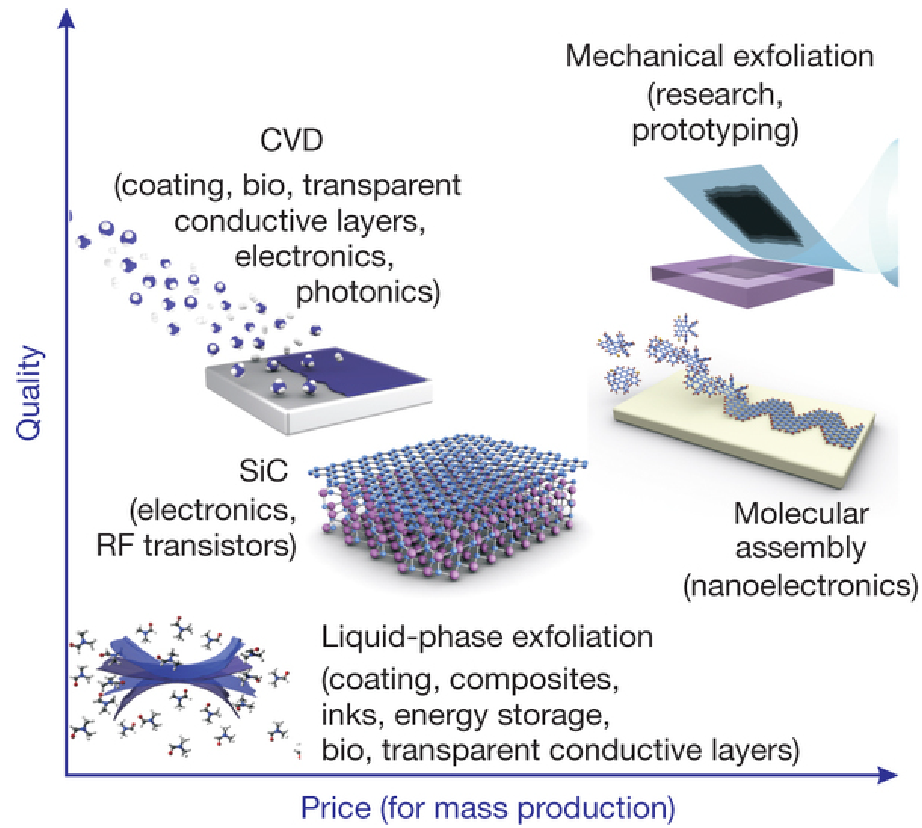
J ~ 10^9 A/cm²

- Contact resistance is necessarily large with this fabrication

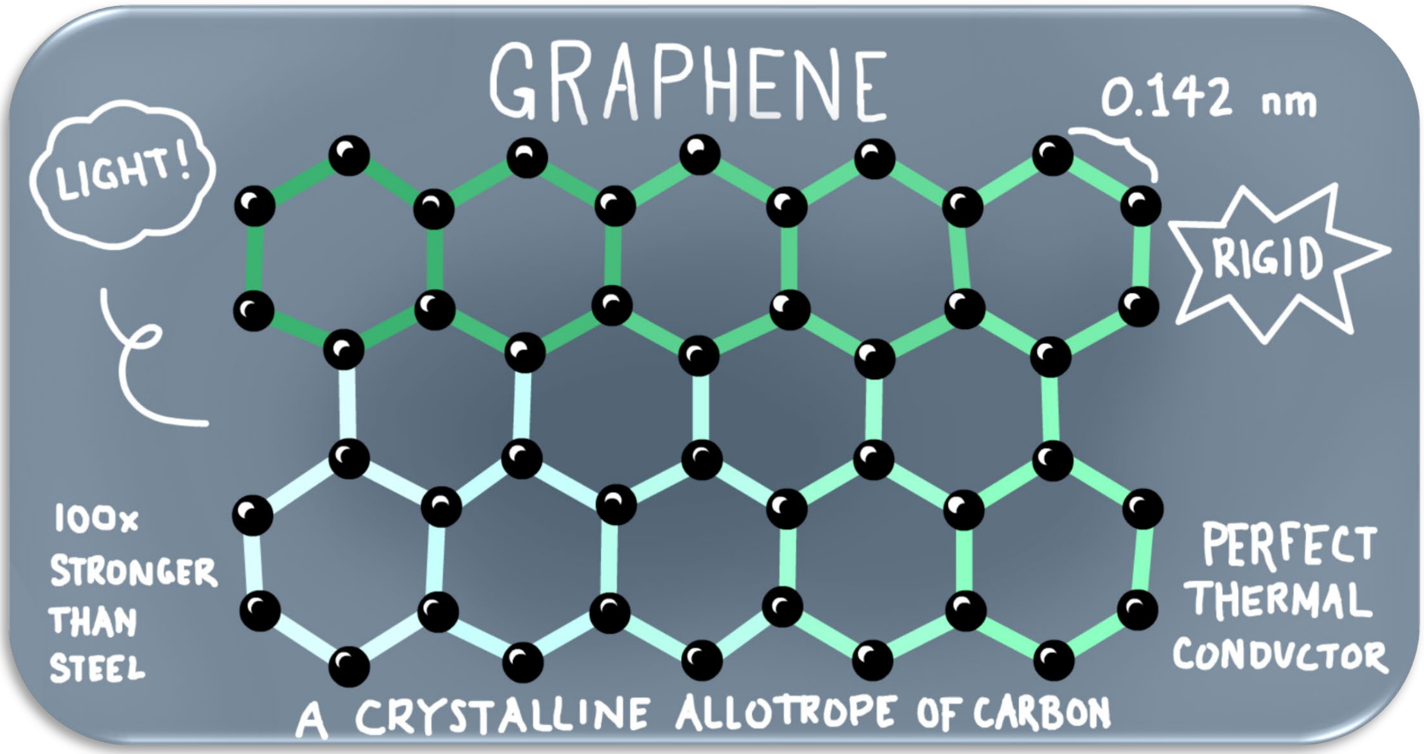
$$\frac{h}{4e^2} \simeq 6.5\, k\Omega$$

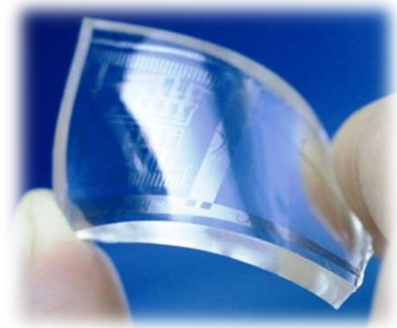
Graphene Production

- Mechanical exfoliation from graphite
- Chemical vapor deposition
- Reduction from graphite oxide
- …



Paper #2





Prior synthesis method requires high temp and multistep chemical synthesis [Ref:2-7]

- e.g. Chemical vapor deposition (1000 degree C)
- Less “scalable” (limited size, hard to mass produce)

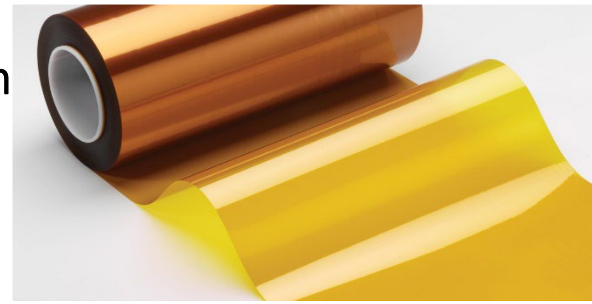
This paper introduce an inherently scalable, and cost-effective means to produce graphene

https://upload.wikimedia.org/wikipedia/commons/thumb/3/3f/Argonne's_Tribology_Lab_Plasma-Assisted_Chemical-Vapor_Deposition.jpg/220px-Argonne's_Tribology_Lab_Plasma-Assisted_Chemical-Vapor_Deposition.jpg
http://graphenewholesale.com/wp-content/uploads/2015/05/unnamed.png
http://compositesmanufacturingmagazine.com/wp-content/uploads/2015/01/Graphene-for-blog-750x400.jpg

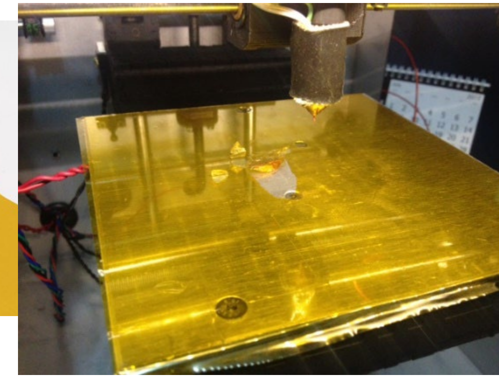
Overview

Material/Substrate:

- Commercial Polyimide (PI) film
  - E.g. Kapton tape



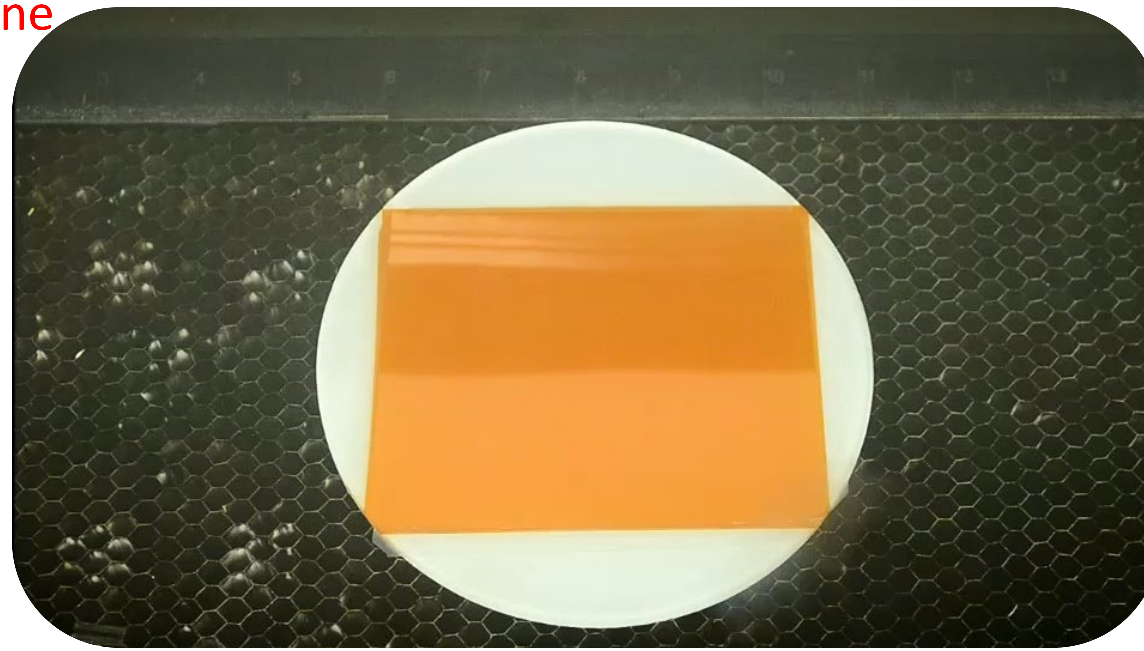
http://www.dupont.com/content/en_us/home/products-and-services/membranes-films/polyimide-films/brands/kapton-polyimide-film/_jcr_content/thumbnail.img.jpg/1478183057044.jpg



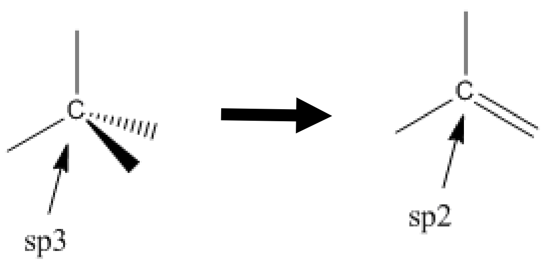
https://solidoodletips.files.wordpress.com/2012/07/rje-torn-kapton.jpg

Method:

- Infrared CO_2 laser irradiation
- Computer controlled laser scribing
- Polyimide → Porous Graphene

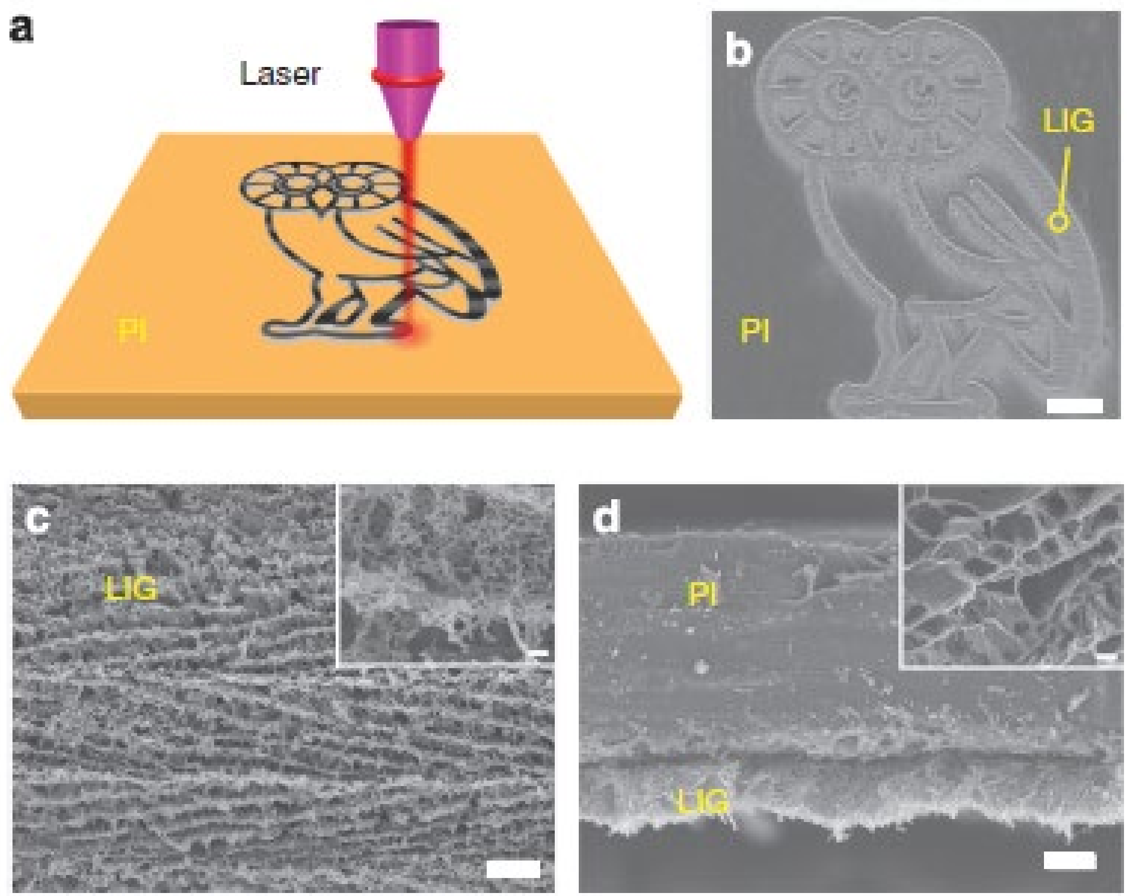


Laser-induced graphene (LIG)



Lab #1

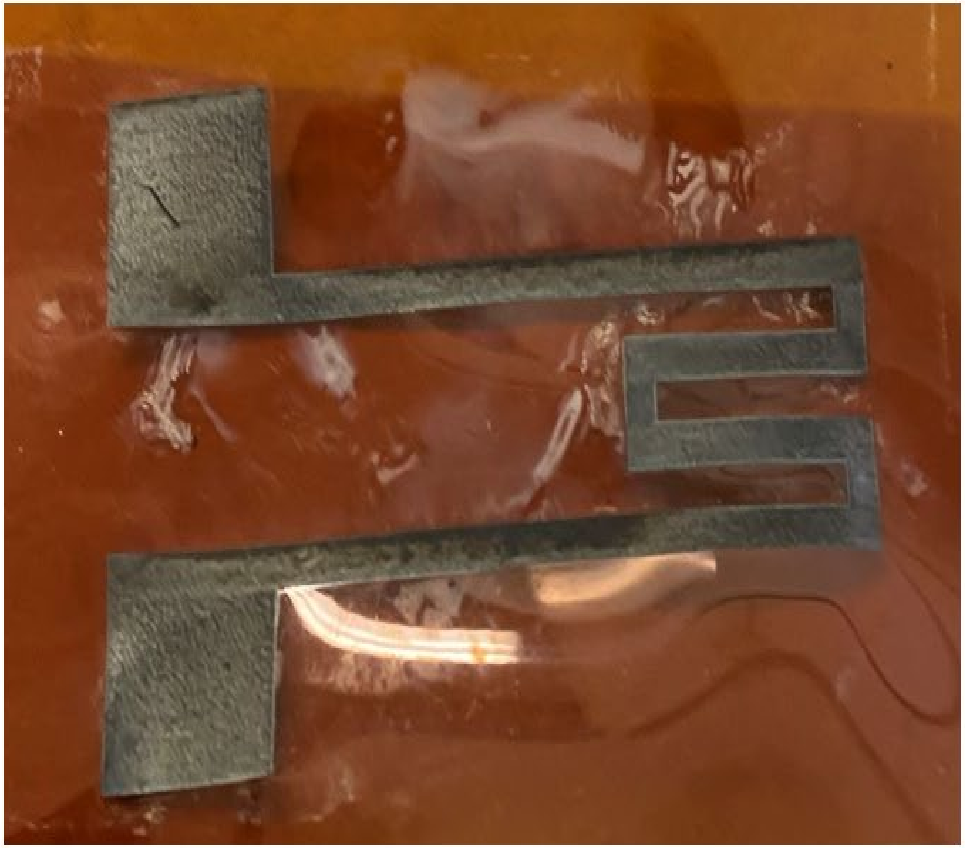
- ☐ Laser conversion of graphene from polymer substrate
- ☐ 1113 Etcheverry
- ☐ Sign up your time on bCourses to be announced soon



NATURE COMMUNICATIONS | 5:5714 | DOI: 10.1038/ncomms6714

Review – Lab#1

Lab 1 – LIG on PI



Dimensions: 50x70x0.1 mm

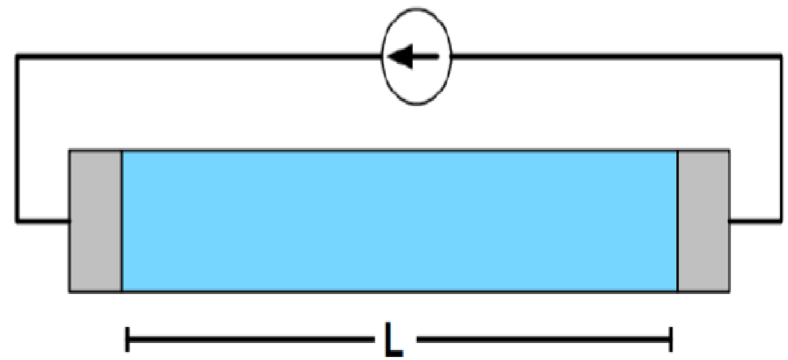
R=1.661kΩ

Contact Resistance

Source: http://tuttle.merc.iastate.edu/ee432

Contact Resistance

In measuring resistance with the four-point-probe, we used 4 contacts (2 for current, 2 for voltage) to determine the sheet resistance of a layer while minimizing effects of contact resistance. However, in transistors and other electronic devices, the contacts are a necessary part of the device, and it is useful to determine the contact resistance so that we can have some idea of how it might affect device performance.



The two contacts are located at the ends of the bar and each has a contact area of AC.

$$R_T = 2R_m + 2R_C + R$$

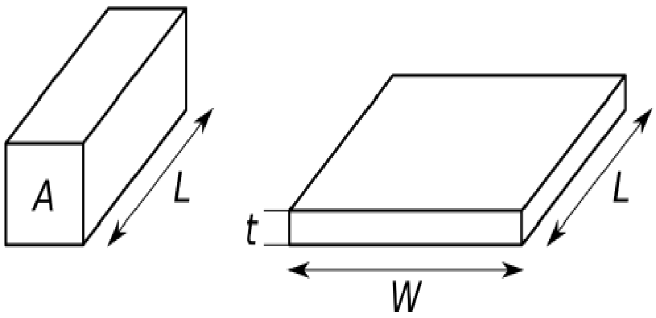
Metal resistance is very small compared to others, then

$$R_T = 2R_C + R$$

Sheet Resistance

Sheet Resistance

- Sheet resistance is measure of resistivity averaged over the surface.
- It is used to characterize the resistance in thin films.
- It can be used to compare the electrical properties of devices that are significantly different in size.
- Since L/W has no units, sheet resistance should have units of Ω, but it is not the sample resistance.
- To distinguish it from the general resistance, the unit is Ω/square.



$$R = R_{sh}\frac{L}{W}, [\Omega]$$

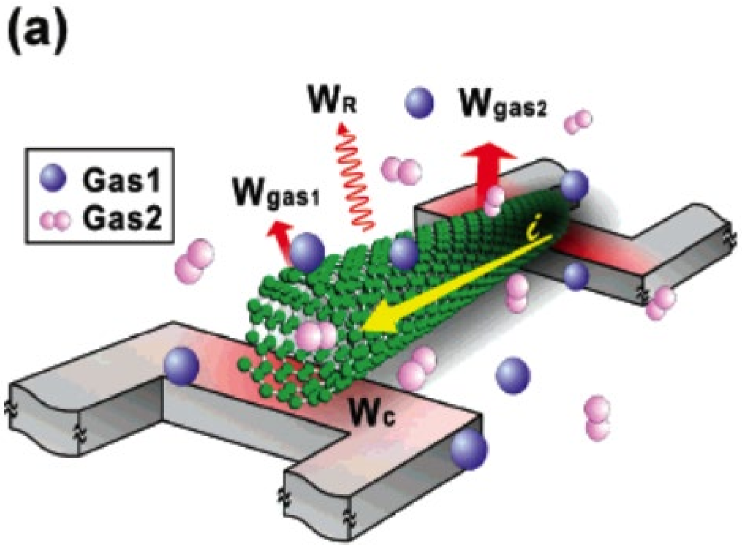
$$R = \rho\frac{L}{A} = \rho\frac{L}{Wt} = \frac{\rho}{t}\frac{L}{W}$$

$$R_{sh} = \frac{\rho}{t}, [\Omega / sq]$$

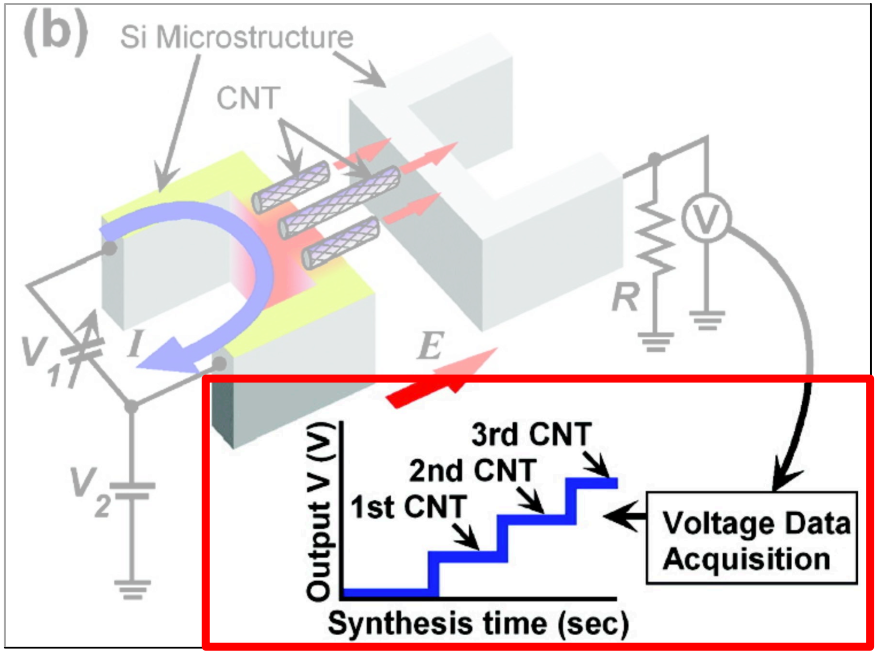
An Electrothermal Carbon Nanotube Gas Sensor

Electrothermal Gas Sensing Mechanism

- An MWCNT is suspended between silicon structures.
- An electric current is passed through the MWCNT.
- "Energy conservation calls for total heat generation equal to the summation of heat conduction to the two microstructures (W_C), gases (W_G, shown in the figure as Wgas1 and Wgas2 representing the case of two types of gases of different thermal conductivity values), and heat radiation (W_R)"
- Change in resistance identifies the gas.



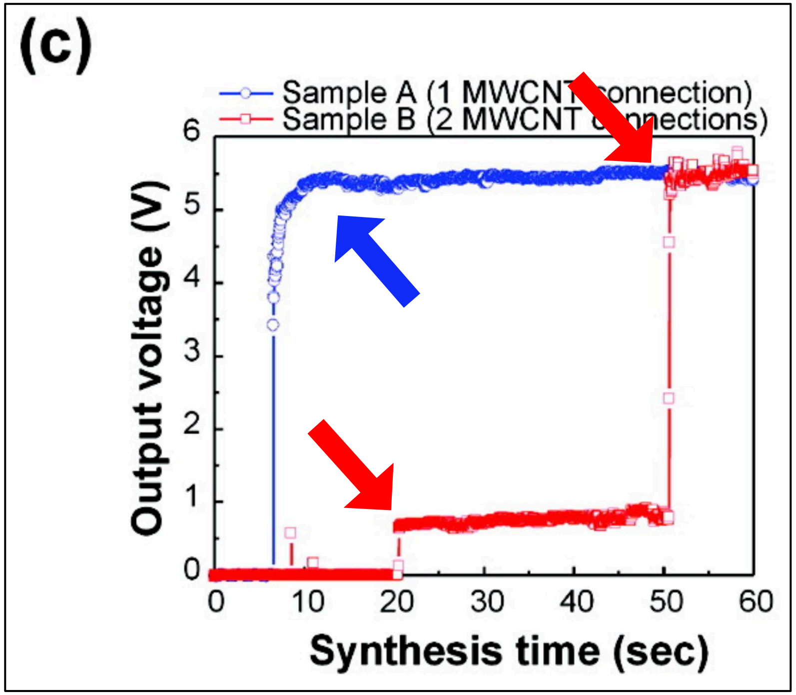
Carbon Nanotube Synthesis

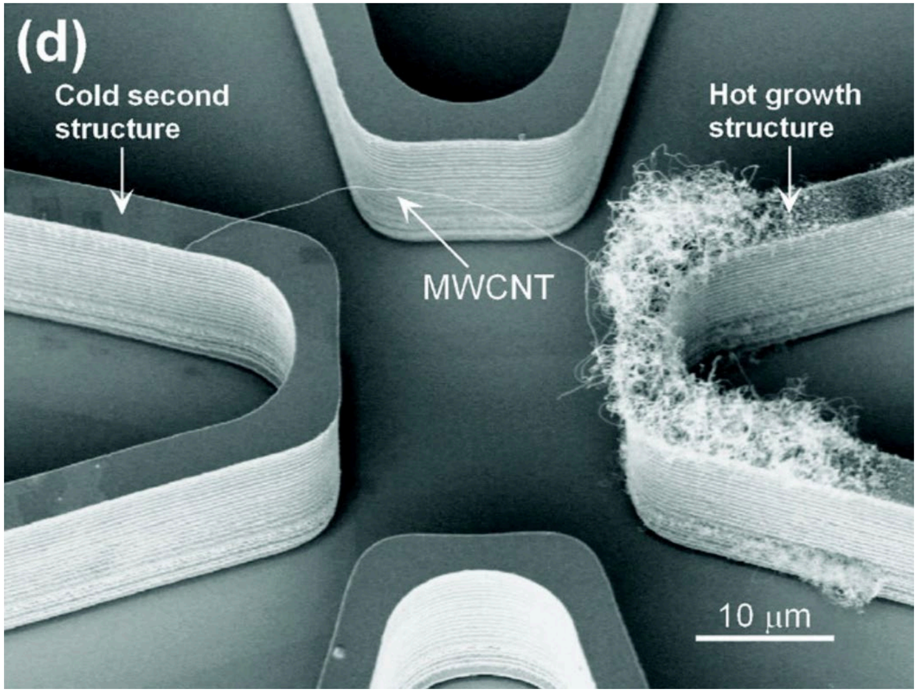


- Circuit provides electrical feedback control
- Each carbon nanotube connection = spike in output voltage
- Enables careful control of the # of CNT connections

Kawano, Takeshi et. al., Nano Letters (2007)

Carbon Nanotube Synthesis

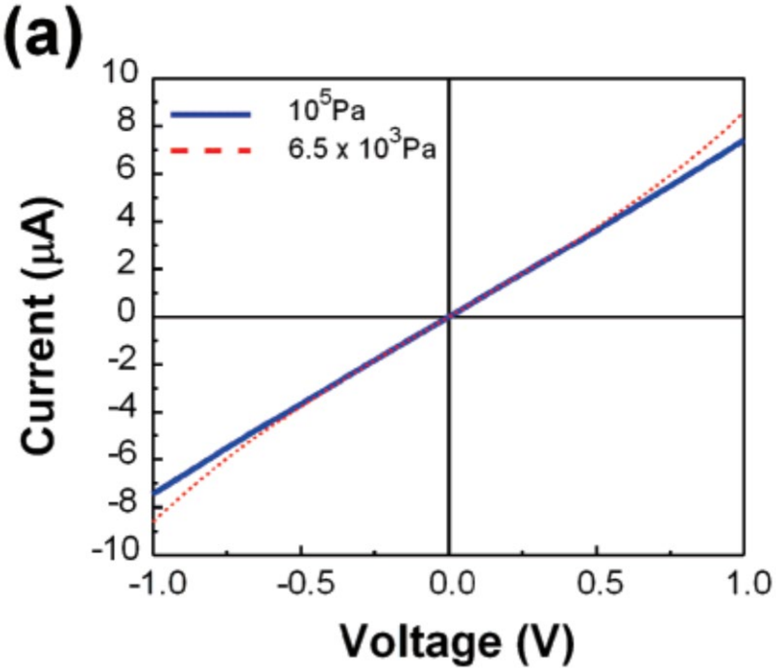




Kawano, Takeshi et. al., Nano Letters (2007)

Electrothermal Traits of the MWCNT

- Current vs Voltage curves plotted in 10e5 and 6.5 × 10e3 Pa argon states
- Gas thermal conductivity induce resistance change
- Linear behavior shows ohmic contact under low power
- Under high power similar to Pirani gauge model



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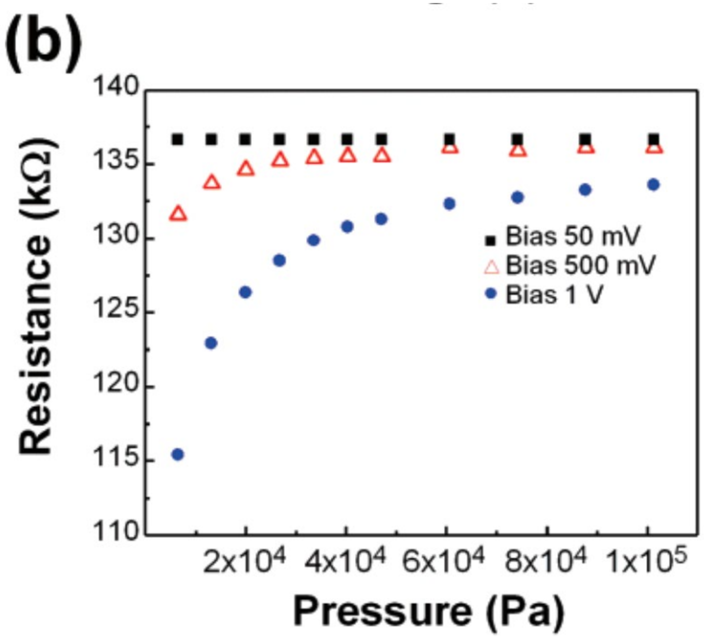
Electrothermal Traits of the MWCNT (cont.)

- Resistance vs Pressure curves plotted under 1, 0.5, 0.005 V
- Higher sensitivity under higher bias voltage
- Temperature coefficient reveals linear behavior at -0.137% K-1
- Gas density is low, no collisions



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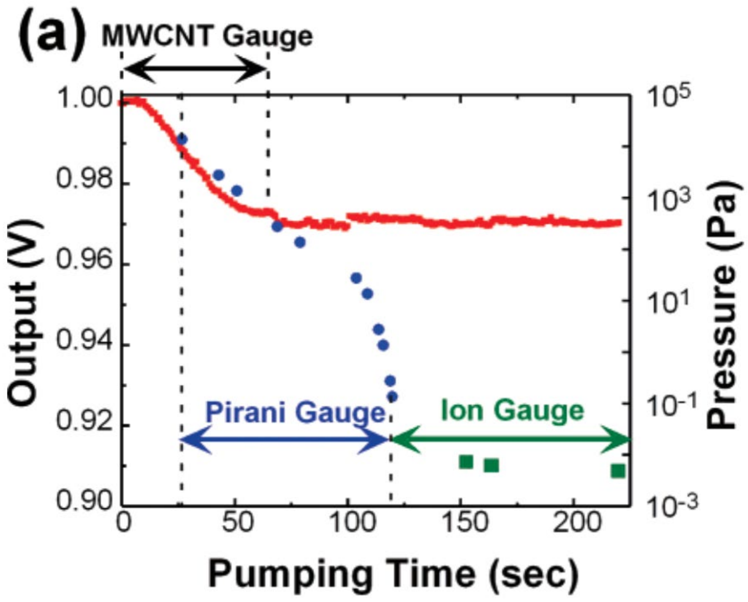
Single-stage Amplifier: Voltage Outputs

- Voltage output vs Time includes pressure readouts of gauges
- Consistent readings between 10e2 and 10e5
- Repeated using alternating nitrogen and air states
- Pirani: 10e4 to 10e-1
- Ion: <10e-1
- MWCNT: 10e2 to 10e5



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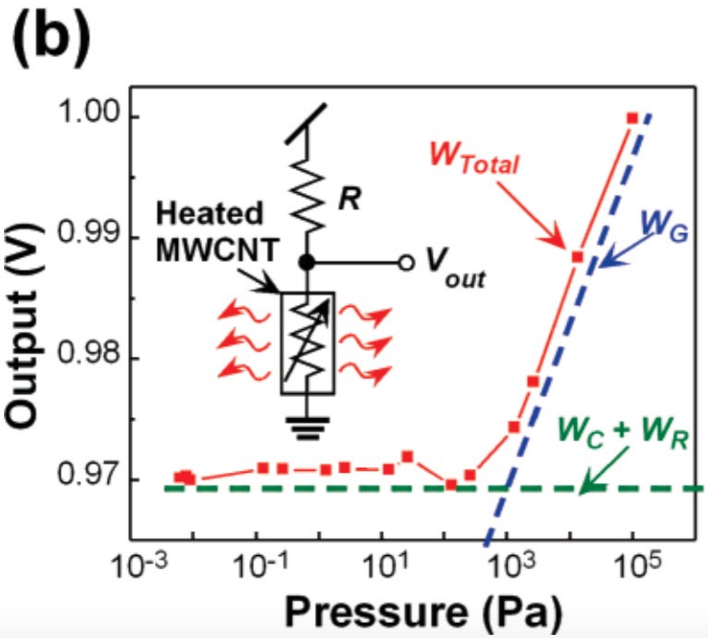
Single-stage Amplifier: Voltage Outputs (cont.)

- Indicates detections and limit of MWCNT
- Low pressure detection by heat conduction
- Contacts (Wc) and radiation (Wr)
- Small contact area + low thermal conductivity = more pressure sensing capability



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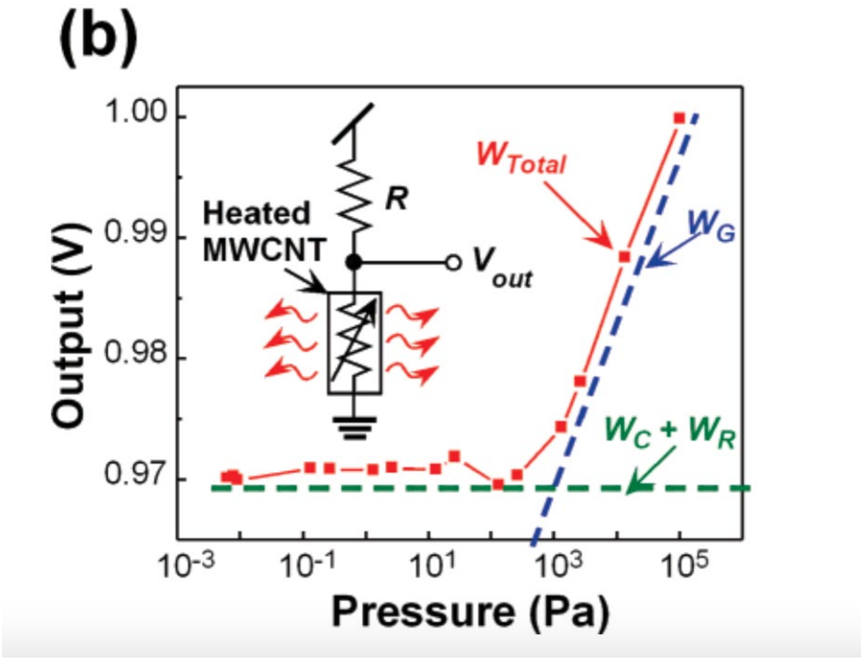
Single-stage Amplifier: Energy Transfer

- Low pressure (Wc + Wr = Wt) reveals energy loss of MWCNT
- Wc, Wr, and Wt can be found at baseline pressures
- Radiation energy loss:

$$W_R = \epsilon\sigma(T_{CNT}^4 - T_0^4)A$$

- Wr < 20nW
- Wc ~= 7.5 uW



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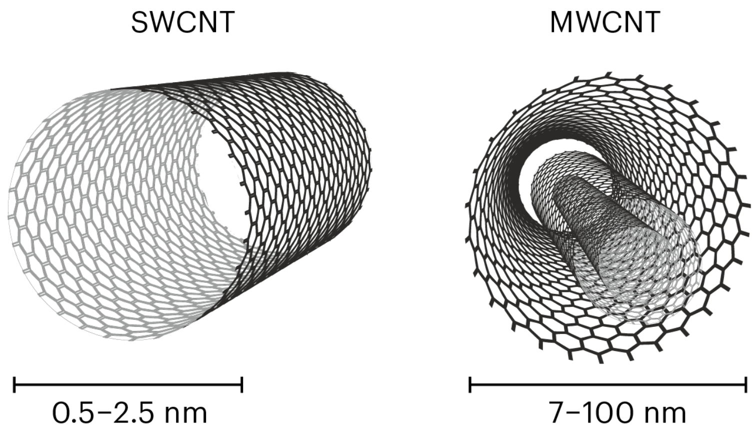
Temperature Profile Simulation

- Temperature profile calculated from energy balance (Resistive Heating Energy vs. WC,WR, and WG)
- Temperature profile gives accurate representation of sensor response based on environments
- Allows for calculation of Thermal Conductivity Value (kCNT)



Comparison of SWCNT and MWCNT structures

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Thermal Conductivity Value

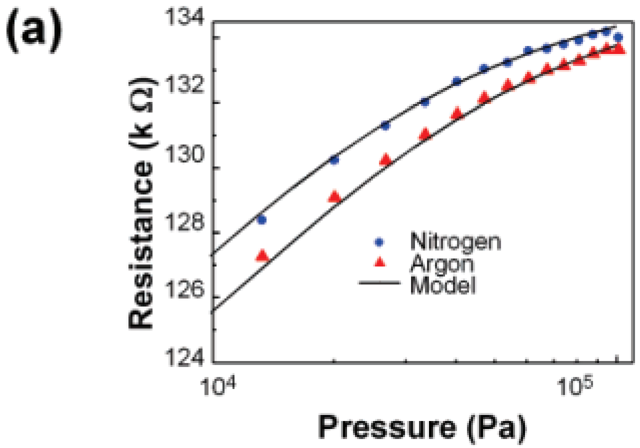
- kCNT value is extracted via Wc and heat conduction equation
- Value found to be 300 W/mK
- Theoretical / experimental range 6600-25 W/mK
- Defects in growth process may cause smaller kCNT
- Smaller kCNT value means more sensitive device

$$\frac{1}{2}W_{\mathrm{C}} = k_{\mathrm{CNT}}A\frac{\mathrm{d}T_{\mathrm{CNT}}}{\mathrm{d}l}|_{l=0}$$

Heat Conduction Equation

Differentiation of Argon and Nitrogen

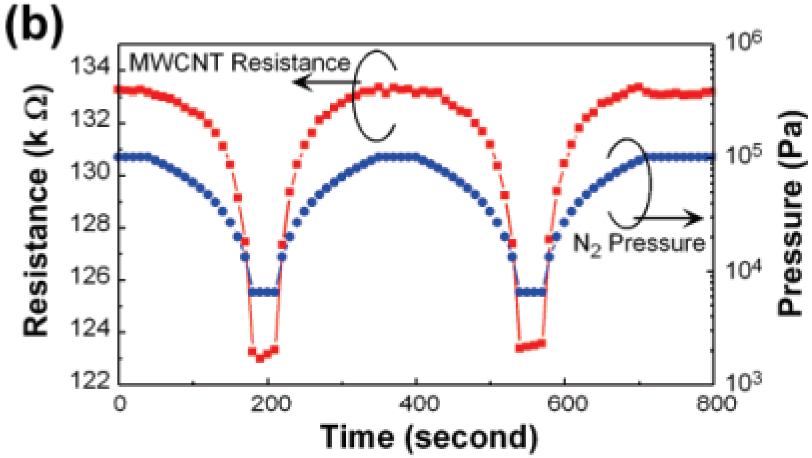
- MWCNT sample capable of differentiating Argon and Nitrogen at various pressures
- Able to do so because of different thermal conductivity values of the gasses
- SWCNT able to differentiate via relaxing hot optical phonons



Resistance change vs pressure for nitrogen and argon gasses compared to analytical model

Advantages

- Fast response and reversible
- Compact
- Energy Efficient
- Stable continuous operation



Continuous resistance change versus time with a pressure control of every 10s in a nitrogen environment

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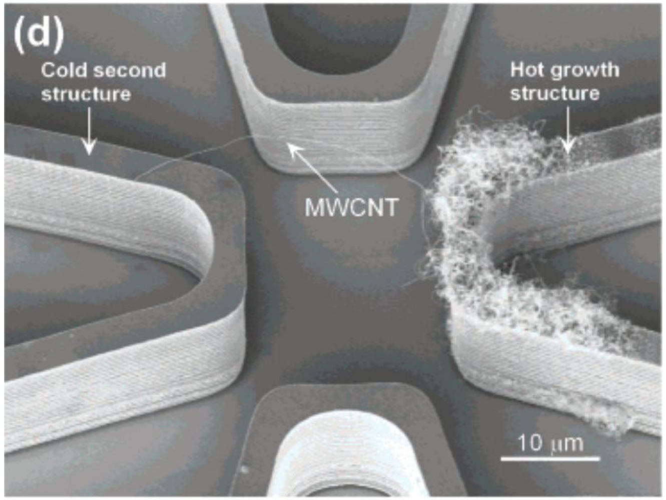
Future Improvements

- Reduce contact area
- Increase CNT length
- Lower kCNT
- Improved external circuit design



SEM image of a single MWCNT electrothermal gas sensor