# Introduction to Nanotechnology and Nanoscience – Class#11

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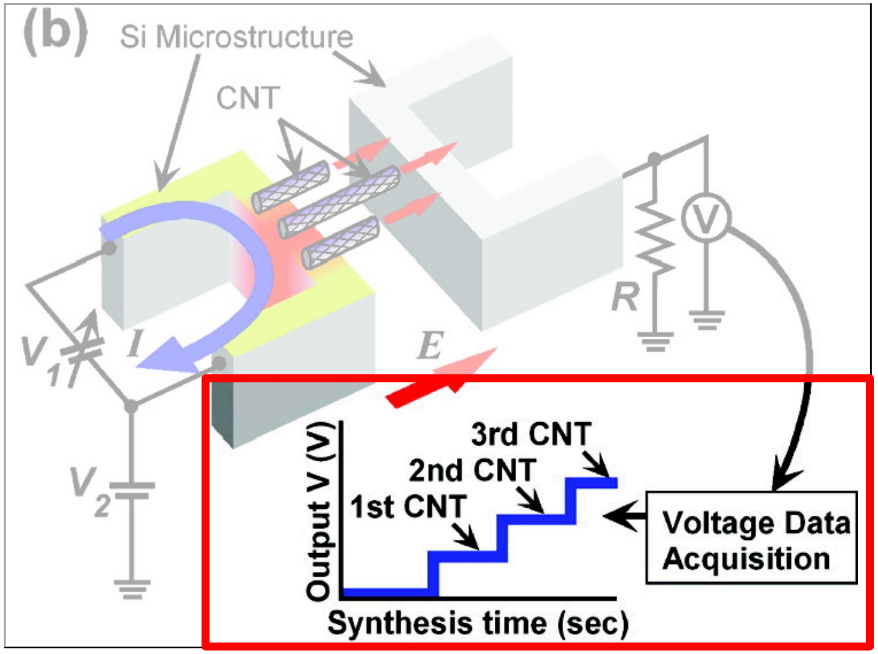
# Outline

- Quiz I – 2/27/2024
- Paper 3 last part
- Paper 4

# Quiz I

- 2/27/2024 during the class time
- 10% of the course grade
- Close book, open one-page (double-sided) cheating sheet
- Up to today’s lecture
- HWs up to HW3
- Papers up to paper 4

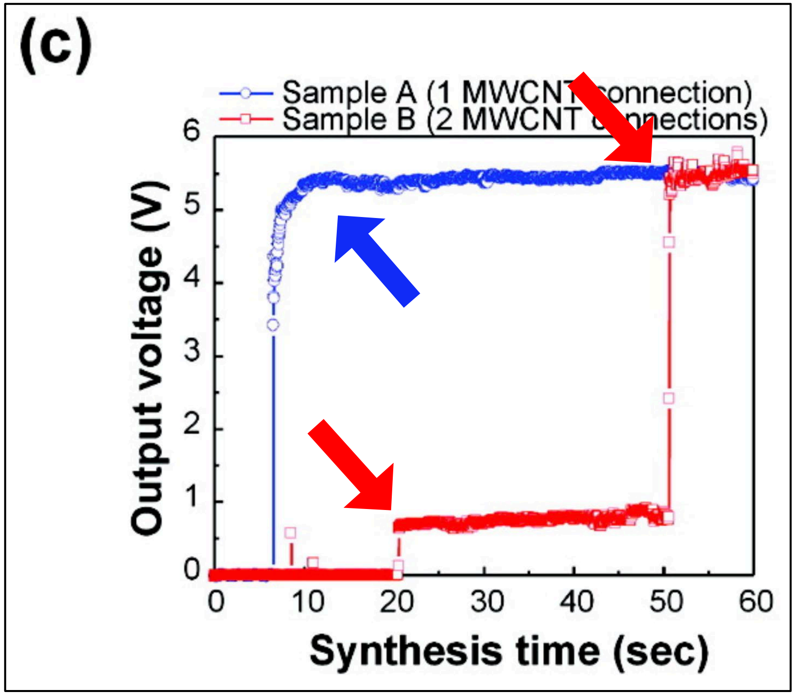
# Carbon Nanotube Synthesis

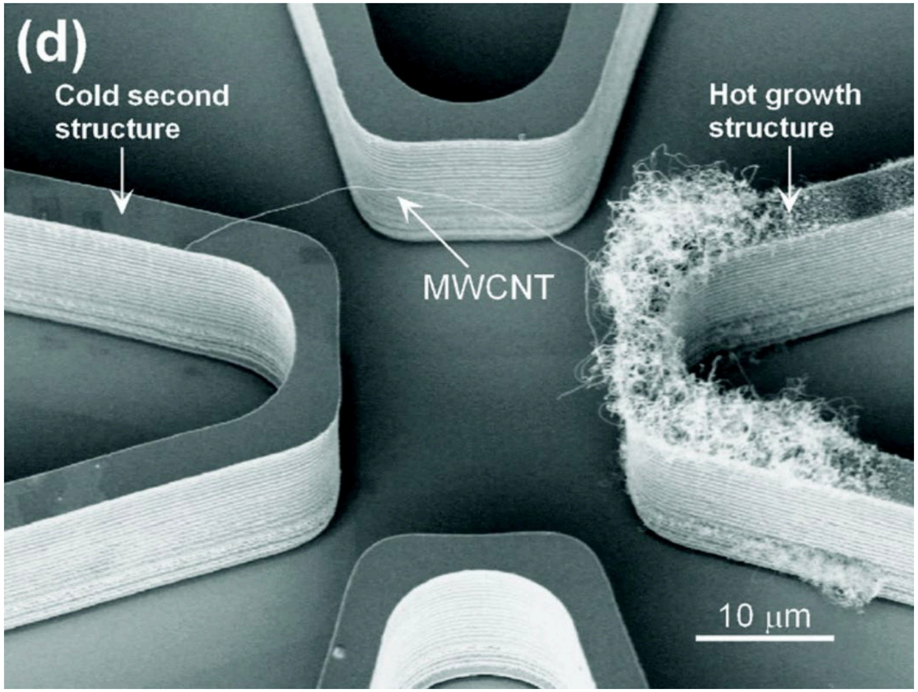


- **Circuit provides electrical feedback control**
- **Each carbon nanotube connection = spike in output voltage**
- **Enables careful control of the # of CNT connections**

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

# Carbon Nanotube Synthesis

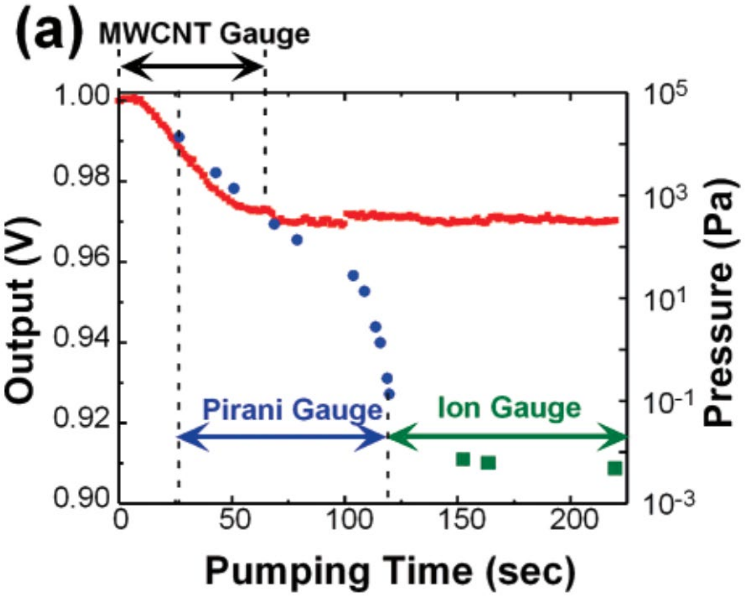




Kawano, Takeshi et. al., Nano Letters (2007)

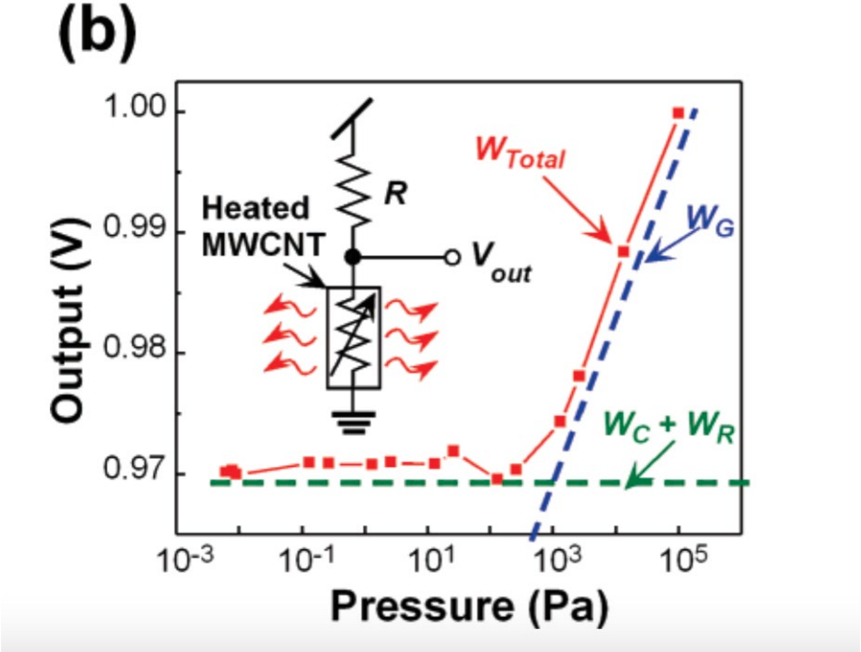
# Single-stage Amplifier: Voltage Outputs

- 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



# 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



# Thermal Conductivity Value

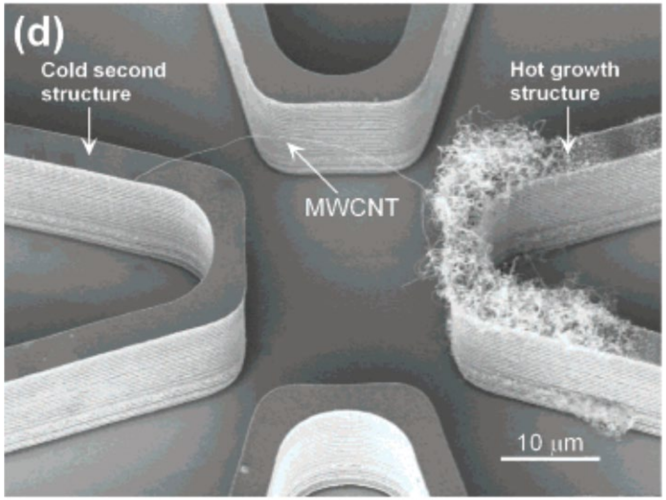
- kCNT value is extracted via Wc and heat conduction equation
- Value found to be 300 W/mK
- Theoretical / experimental range 6600-25 W/mK
- Defects in growth process may cause smaller kCNT
- Smaller kCNT value means more sensitive device

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

*Heat Conduction Equation*

# Future Improvements

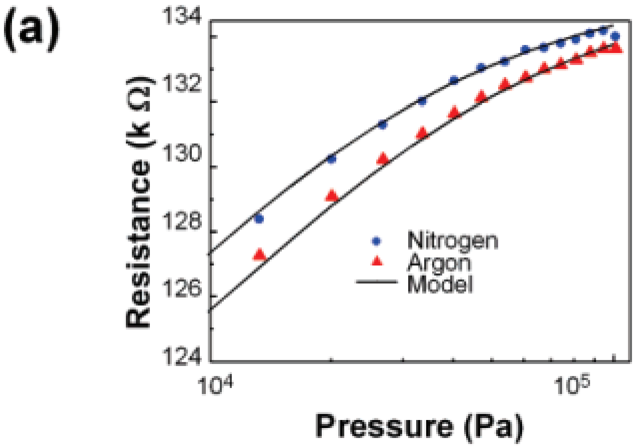
- Reduce contact area
- Increase CNT length
- Lower kCNT
- Improved external circuit design



*SEM image of a single MWCNT electrothermal gas sensor*

# 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

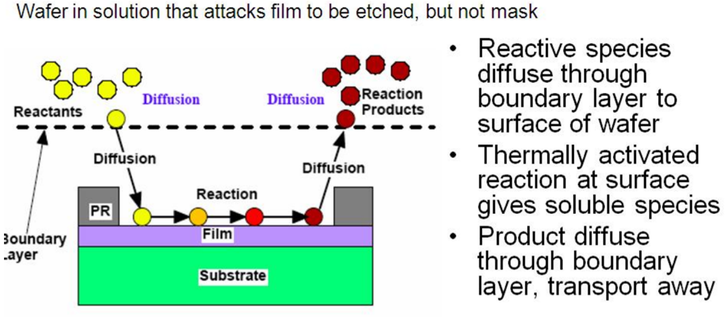


*Resistance change vs pressure for nitrogen and argon gasses compared to analytical model*

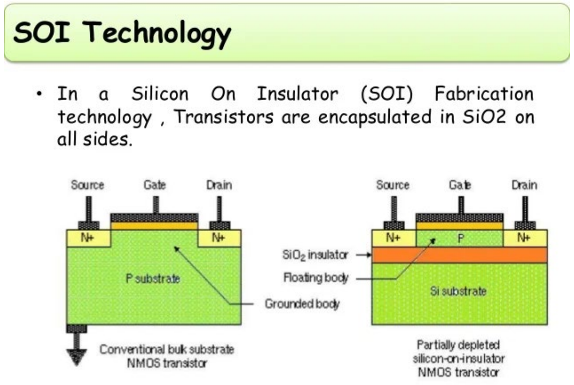
# Silicon Microstructure Preparation

- Silicon microstructures are prepared using a **silicon-on-insulator** (SOI) process with one mask
- **Wet chemical etching** is used to release the free-standing silicon microstructures
- The silicon microstructure is **highly doped p-type** single crystalline silicon
- A mixture of Ni-Fe (80%-20% by wt.) is evaporated to serve as the catalyst for synthesis of MWCNT

## Wet Chemical Etching


Wafer in solution that attacks film to be etched, but not mask

- Reactive species diffuse through boundary layer to surface of wafer
- Thermally activated reaction at surface gives soluble species
- Product diffuse through boundary layer, transport away


**SOI Technology**

- In a Silicon On Insulator (SOI) Fabrication technology , Transistors are encapsulated in SiO2 on all sides.

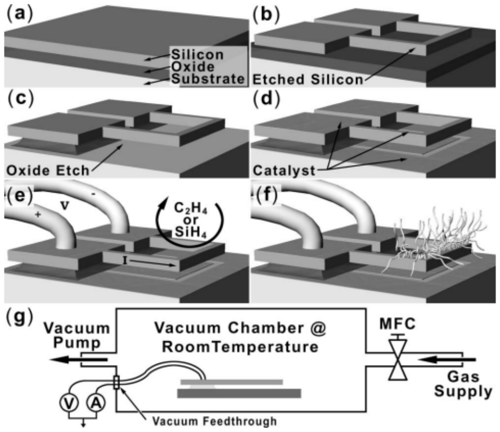


FIG. 1. Series depicting the fabrication of microbridges, growth of nanostructures and experimental setup and process. (a) Initial three-layer wafer. (b) Microstructure layer patterning and etching. (c) Timed etch of the sacrificial oxide layer. (d) Maskless catalyst evaporation. (e) Wirebonds and electrical actuation in the desired gaseous ambient. (f) Resulting nanostructures. (g) Schematic of the experimental setup in a room-temperature chamber.

# MWCNT Synthesis

- **Synthesis of MWCNT** is conducted at room temp in vacuum chamber of **30 kPa** with an **acetylene-argon gas mixture** once the growth structure has been heated
- **Process outlined** in reference (6) Englander, O.; Christensen, D.; Lin, L. *Appl. Phys. Lett.*2003, *82*, 4797.
- **CNT growth requires higher temperatures than silicon nanotubes**

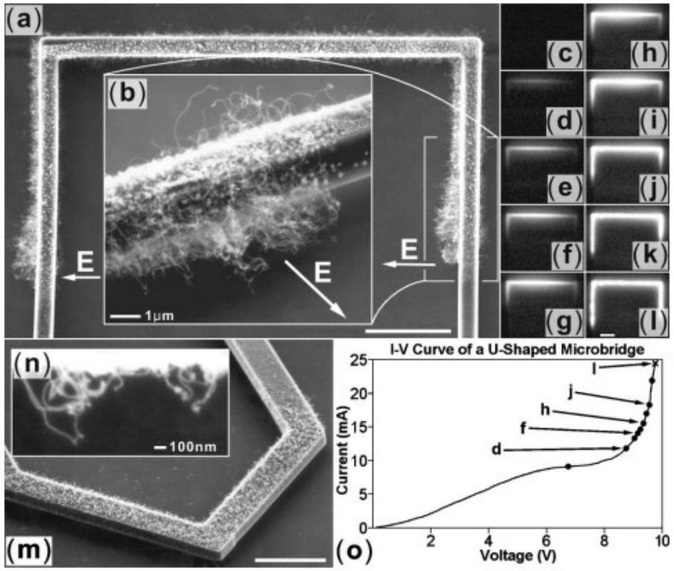
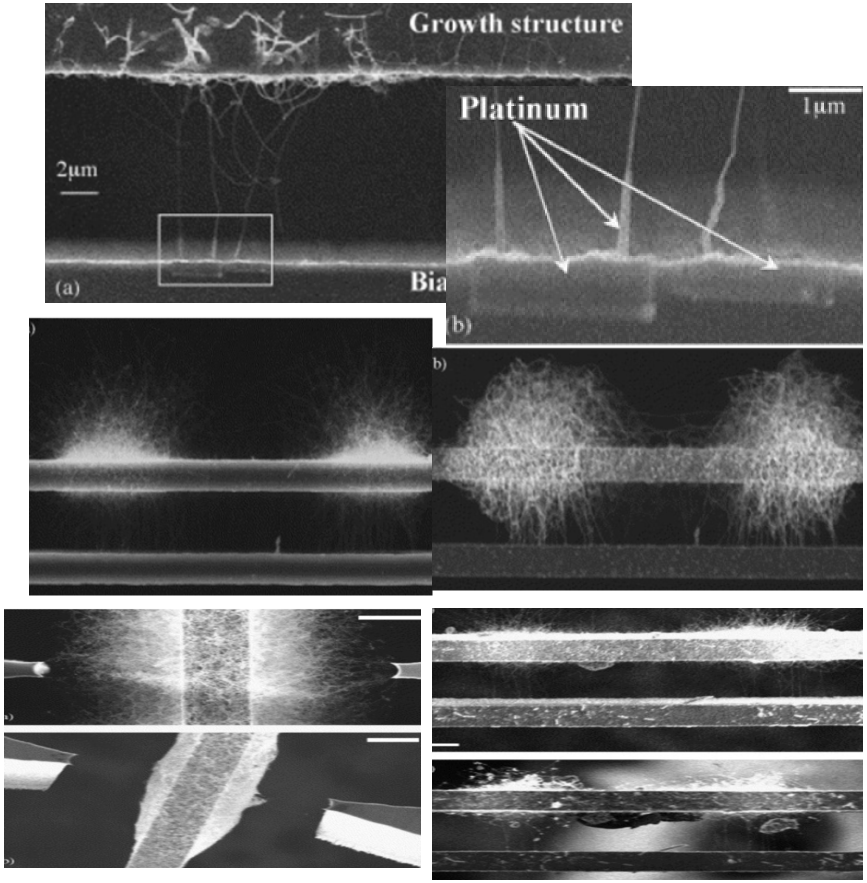


FIG. 3. Nanotube synthesis. (a) Synthesis localized to microbridge legs. Growth occurs largely in the direction of the local *E* field. (b) High-resolution SEM of the right microbridge section (oblique view). Note how the CNT curves and follows the *E* field. (c)–(l) Series of optical photographs of microbridge heating. Maximum growth occurs where glow is barely visible, and this corresponds to 850–1000 °C. (m) CNT growth (5 min) localized in the center of a pointed microbridge. (n) High-resolution SEM of a CNT with diameter of ~40 nm. (o) Experimental $I-V$ data from microbridge heating. Data points correspond to (c)–(l). The growth shown in (a) corresponds to the actuation region between point (h) and point (j). All scale bars are 10 $\mu$m in length, unless otherwise marked.

# **Post-processing techniques for locally self-assembled silicon nanowires** - reference (7)

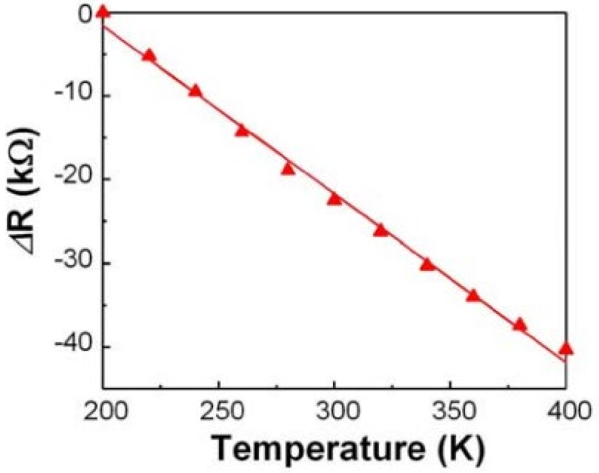
Inherent issues in micro-to-nano tech, such as unreliable contacts and high resistances, make it difficult to develop reliable NEMS.

1. **Local contact metallization**
    - Ends of nanotube are plated with metal, such as platinum; resistance reduced 20%
    - Quick, accurate, no lithography
2. **Global metallization**
    - Maskless thermal evaporation of palladium onto as assembled system; requires additional vigilance not to introduce crosstalk or shorts
    - Increases nanowire diameter approx. 40nm
3. **Aqueous treatment**
    - NEMS covered with low surface tension liquid, IPA, followed by accelerated drying in oven at 90 Celsius, followed by critical point drying (CPD); eliminates surface tension effects;



# TCR Characterization

- The **temperature coefficient of resistance (TCR)** of one MWCNT was used in all experiments
- TCR is measured with an **input current < 0.5 uA** in a temperature controlled chamber
- **Approximated as a linear response** in the temperature region of 200K - 400K and the resistance region of -40kΩ to 0; i.e. TCR = slope of line



# Electrothermal Model

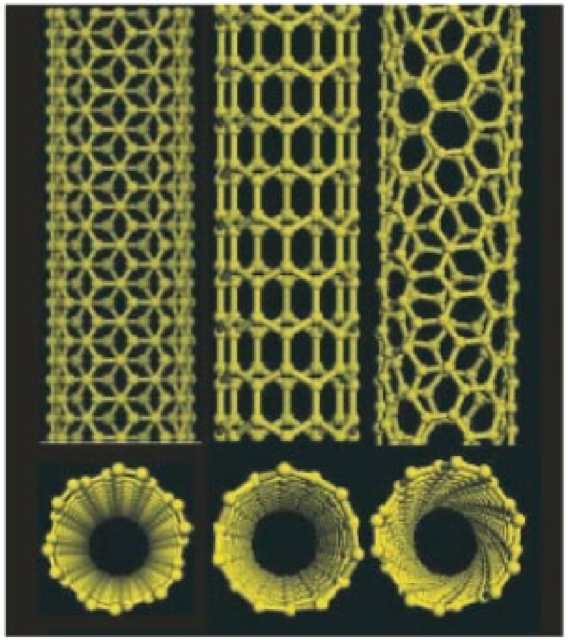
- A **1-D electrothermal model** can be **derived** the principle of energy conservation using *dx* on the MWCNT
- ***Kg*** = heat transfer coefficient via gas, ***Dcnt*** = diameter of MWCNT, ***J*** = current density, **ρ** = resistivity at T
- The bottom equation is solved with boundary conditions of the temperature profile
- **Resistance of the MWCNT** is calculated based on this profile and the TCR
- The **value of k and thermal conductivity of the gases** can be found via curve fitting

$$k_{CNT} A \frac{\partial T_{CNT}}{\partial x}\Big|_{x+dx} - k_{CNT} A \frac{\partial T_{CNT}}{\partial x}\Big|_{x} - K_g (T_{CNT} - T_0)\pi D_{CNT}\, dx + J^2 \rho_0 [1 + TCR(T_{CNT} - T_0)] A dx = 0$$

$$k_g \equiv \frac{K_g \pi D_{CNT}}{Ap}$$

$$k_{CNT} \frac{\partial^2 T}{\partial x^2} - k_g (T_{CNT} - T_0) p + J^2 \rho_0 [1 + TCR(T_{CNT} - T_0)] = 0$$

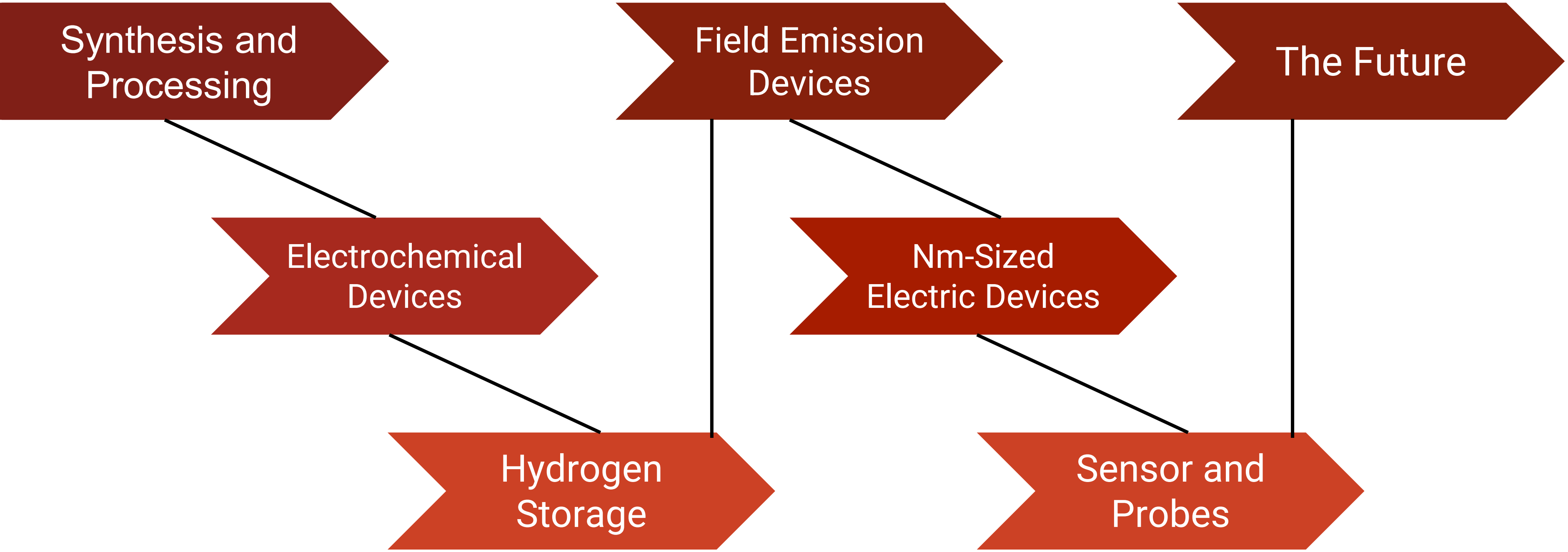
# Carbon Nanotubes- The Route Toward Applications



Ray H. Baughman, A. Zakhidov, W. Heer *Science* 297, 787 (**2002**).

By Adilman Flores, Rushil Ganguli, Luke Goldade, Ke Hu, Franco Huemura, and Joe Huff

# The Route To Applications



Synthesis and Processing

Field Emission Devices

The Future

Electrochemical Devices

Nm-Sized Electric Devices

Hydrogen Storage

Sensor and Probes

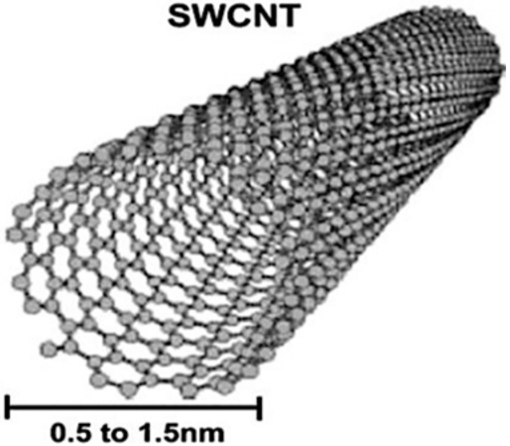
# Two Main Types of Carbon Nanotubes

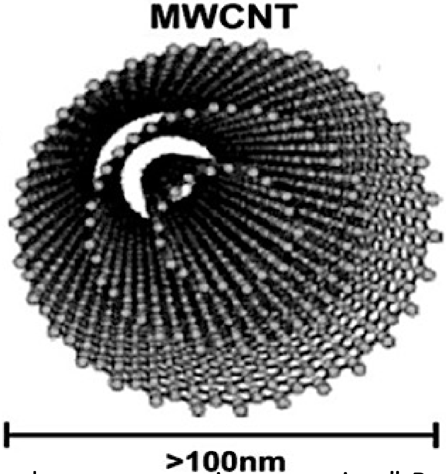
Single-Walled Nanotubes (SWNTs)

- Metallic if in Armchair configuration
- Band gap decreases with increasing diameter

Multi-Walled Nanotubes (MWNTs)

- Can either metallic or Semiconducting

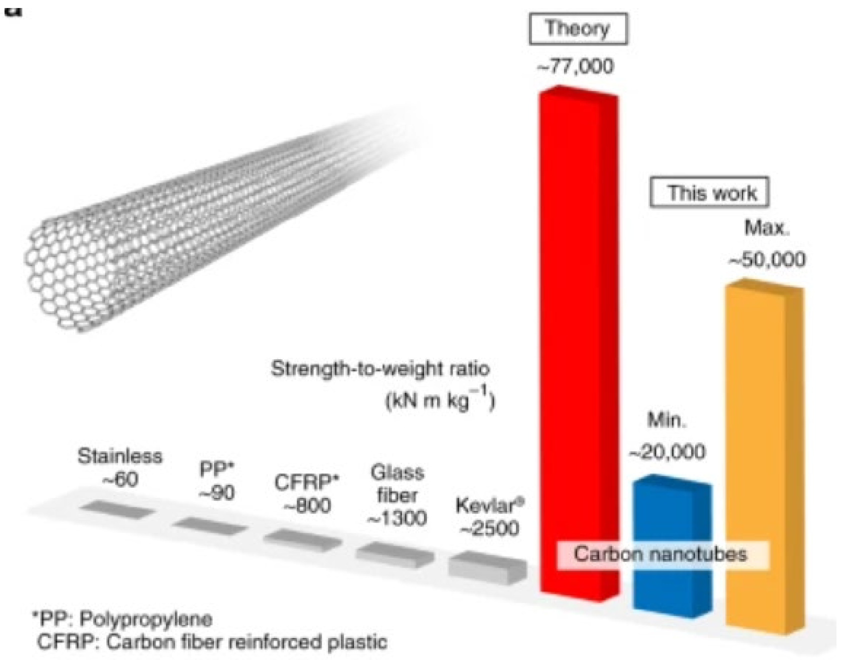




B. Ribeiro, E. Botelho, M. Costa, C. Bandeira. “Carbon nanotube buckypaper reinforced polymer composites; a review” *Polimeros*, (**2017**)

# Diverse properties of Carbon Nanotubes

- Electronic properties of CNT allow them to carry high current with essentially no heat
- Phonons propagate easily allowing great thermal conductivity
- SWNTs are stiff and remarkably strong, with high Young’s modulus and tensile strength

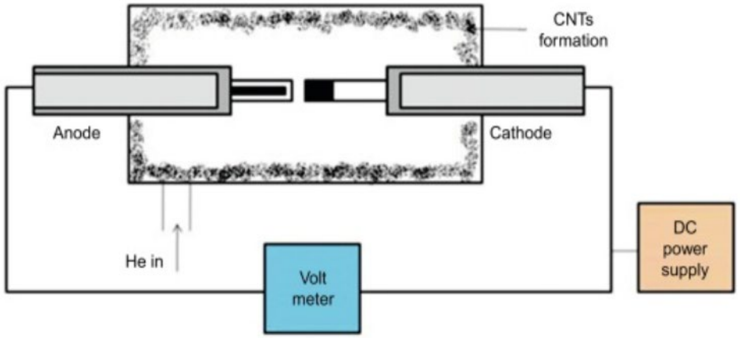


*PP: Polypropylene
CFRP: Carbon fiber reinforced plastic

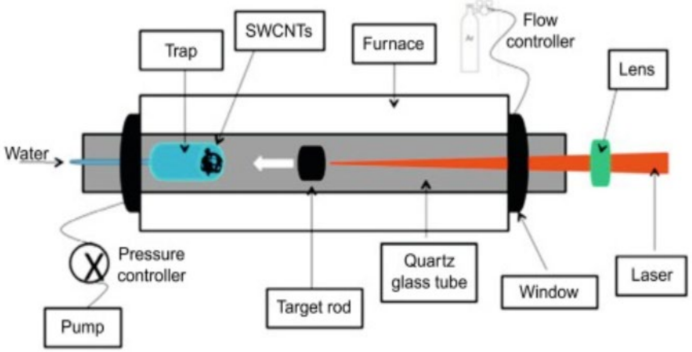
A Takakura, K. Beppu, T. Nishihara, A. Fukui , et all. “Strength of carbon nanotubes depends on their chemical structures” *Nature Communications, 3040,* ***2019.***

# Overview of Main Types of Synthesis

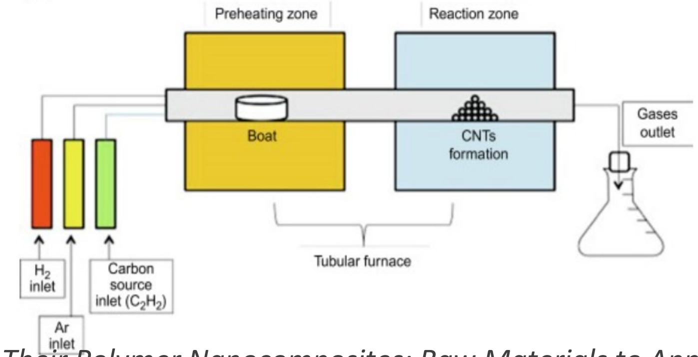
## Carbon-Arc Discharge



## Laser Ablation of Carbon



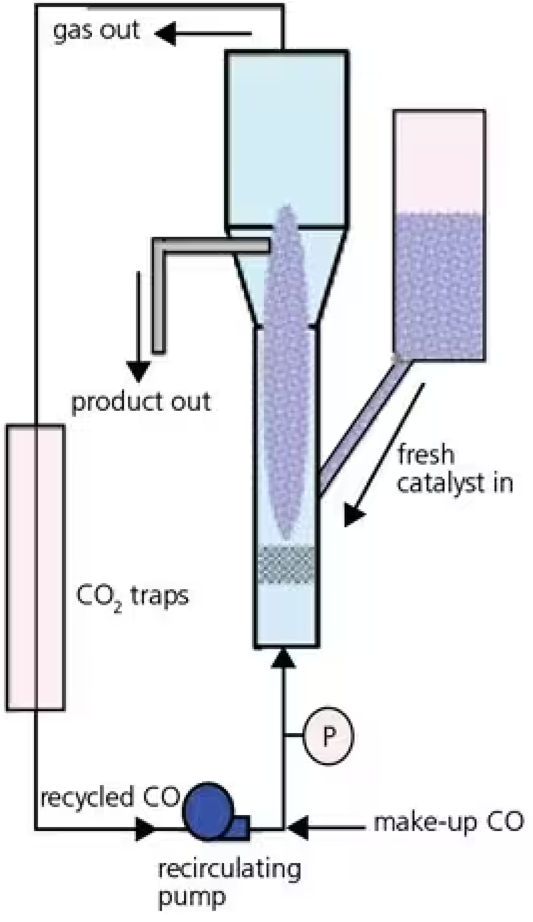
## Chemical Vapor Deposition (CVD)



J. C. Moses, et al. *Carbon Nanotubes and Their Polymer Nanocomposites: Raw Materials to Applications.* Elsevier, **2019**

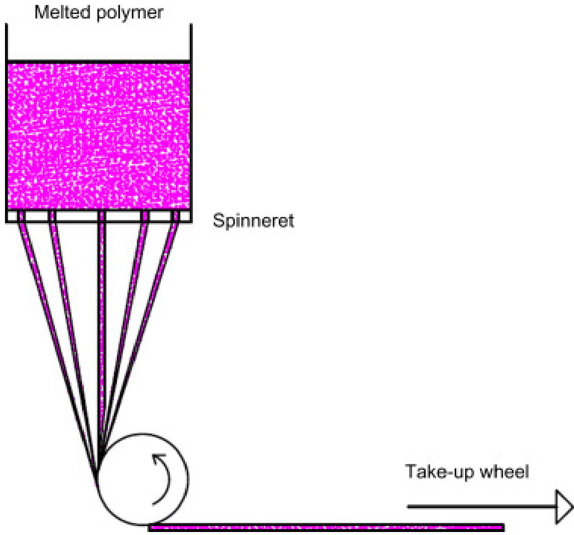
# SWNT synthesis

- Chemical Vapor Deposition is the most scalable manufacturing method (figure to the right shows the CoMoCAT process) for SWNT’s
- CVD process includes preparing a substrate which is made up of carbon activated powder, metal catalyst, and metal salt solution.
- After thorough mixing the substrate will be put into a CVD reactor (shown in the figure) and produce CNTs through decomposition.
- The cost even 22 years after the publication of the original paper still resides at 1000$/g for high purity SWNT (90%+) and around 30$ for low purity SWNT



Scalable Process

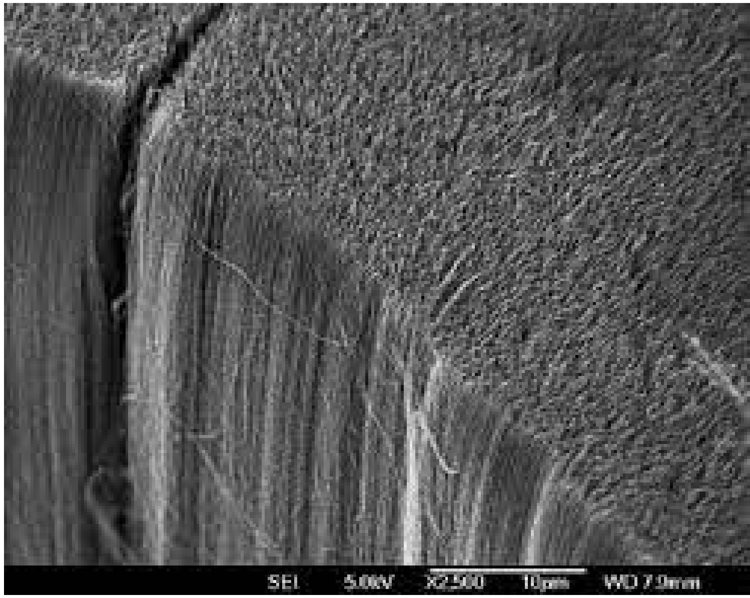
# Issues with SWNT Synthesis



- SWNT’s are incredibly expensive making them hard to use in commercial fields.
- SWNT synthesis result in major concentrations of impurities.
- Theses impurities are mostly other forms of carbon that are not nanotubes and the only the common way to rid these impurities is through acid treatment.
- Acid treatment tends to create more impurities and can degrade nanotube length and perfection adding more to the cost of production.
- SWNT’s also form in bundles due to Van der Waals forces between the tubes, this makes the viscosity in resins and thermoplastics with SWNT’s in it very high if too many bundles are present ( above10% ). This limits the amount of SWNT’s present in the polymers decreasing material strength.

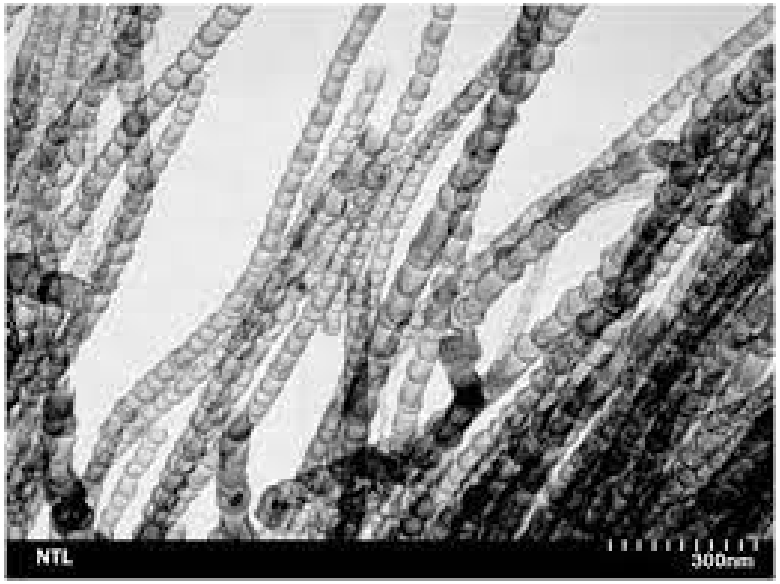
# MWNT Synthesis

- CVD is also the preferred production of MWNTs at larger scales
- The differences between the CVD synthesis for SWNT and MWNT are the conditions of temperature range, hydrocarbon source for the reactor, and the catalyst being less controlled for MWNT synthesis.
- This is due to MWNT’s not having the limitation of single layering which in turn make MWNT’s material properties less impressive than SWNT’s.
- MWNT’s are grown in forest-like formations as shown in the right figure.



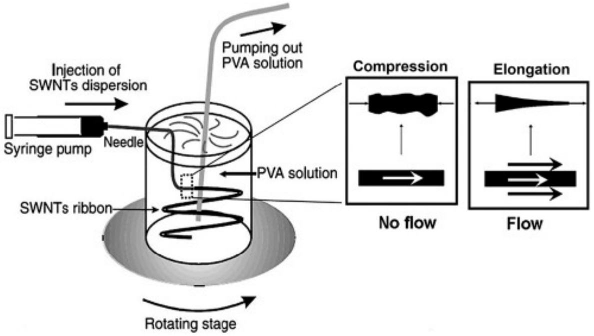
# Issues with MWNT Synthesis

- During the 1990’s research on MWNT’s was limited due to the purchaser agreement set by Hyperion to restrict the pursuit of independent patents by customers.
- However, this patent coverage by Hyperion on their MWNT’s expired in 2004 so other large scale producers were able to emerge using the technology they pioneered.
- MWNT’s made through the pyrolysis method end up with high densities of defects within the forest of MWNT’s produced.

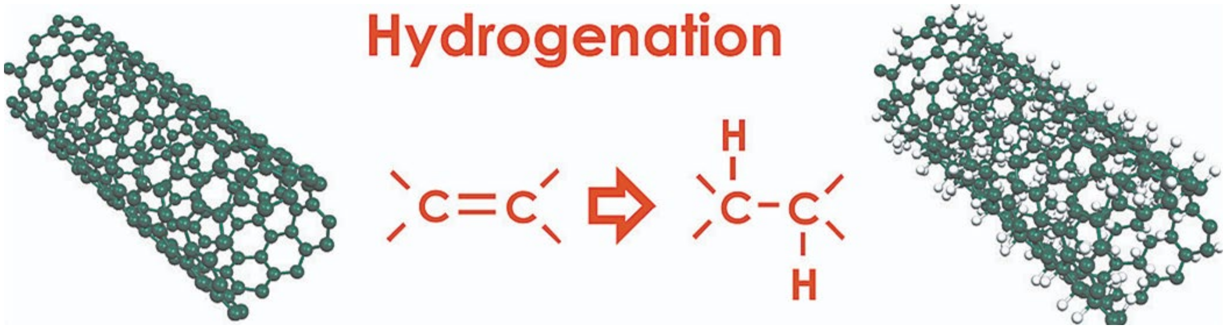


# Advancing Technologies for CNT’s

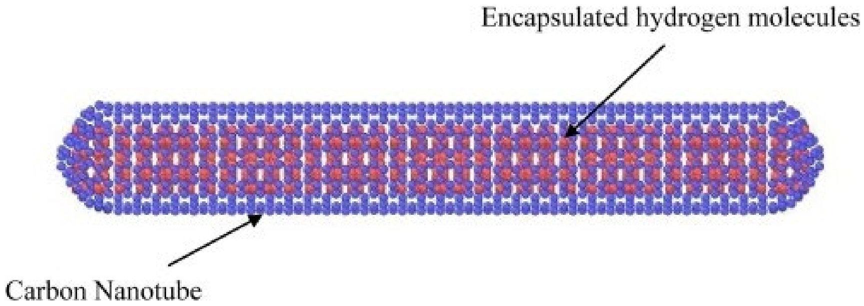
- A coagulation-based process created by Brigitte Vigolo allowed the continuous spinning of fibers containing SWNT’s.
- This process includes coating the nanotubes in polyvinyl alcohol, this causes the tubes to bind more effectively than the Van der Waals binding that is more commonly seen.
- The coating is then removed by pyrolysis.
- Currently this process has low draw rate front he coagulation bath and the nanotubes are usually not well aligned after inspection.
- The pyrolysis of the coating to remove it causes the Young’s Modulus to decrease from 50 GPa to 15GPa which is a significant loss in strength.
- As for MWNT’s, the patterned deposition of MWNT forests that are vertically aligned is an advancing technology due its importance in electronic devices.



# Hydrogen Storage using CNT (Mechanism)



Formation of Stable C-H bond

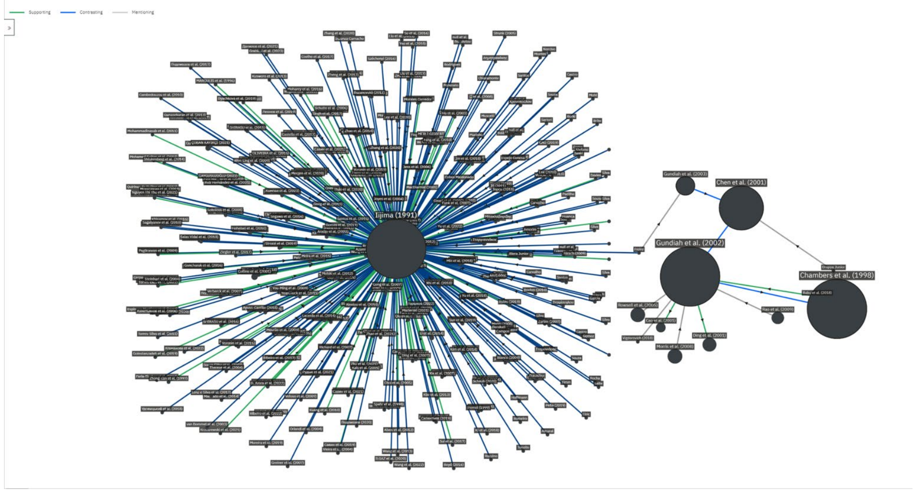


V. Vijayaraghavan, Jacob F.N. Dethan, A. Garg **Nanomechanics and modelling of hydrogen stored carbon nanotubes under compression for PEM fuel cell applications**, Computational Materials Science, Volume 146, 2018, Pages 176-183, ISSN 0927-0256

Anton Nikitin, et al. **Hydrogen Storage in Carbon Nanotubes through the Formation of Stable C–H Bonds**, Nano Letters 2008 8 (1), 162-167, DOI: 10.1021/nl072325k

# Hydrogen Storage using CNT (Problems)

1. Experimental reports of high storage capacities are so controversial that it is impossible to assess the applications potential.
2. Numerous claims of high hydrogen storage levels have been shown to be incorrect.
3. Other reports of room temperature capacities above 6.5 weight % (a U.S. Department of Energy benchmark) await confirmation.



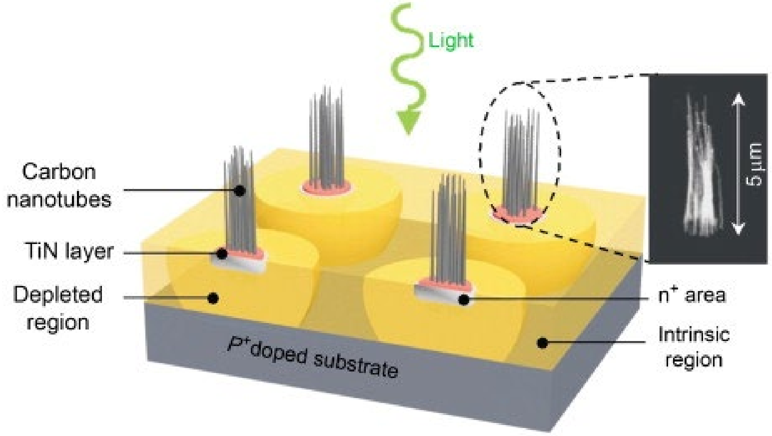
**HOT & DEBATABLE Topic**

# Field Emission Device (Mechanism)

1. “A potential applied between a carbon nanotube–coated surface and an anode produces high local fields, as a result of the small radius of the nanofiber tip and the length of the nanofiber.”

1. “These local fields cause electrons to tunnel from the nanotube tip into the vacuum.”

1. “Electric fields direct the field-emitted electrons toward the anode, where a phosphor produces light for the flat panel display application.”



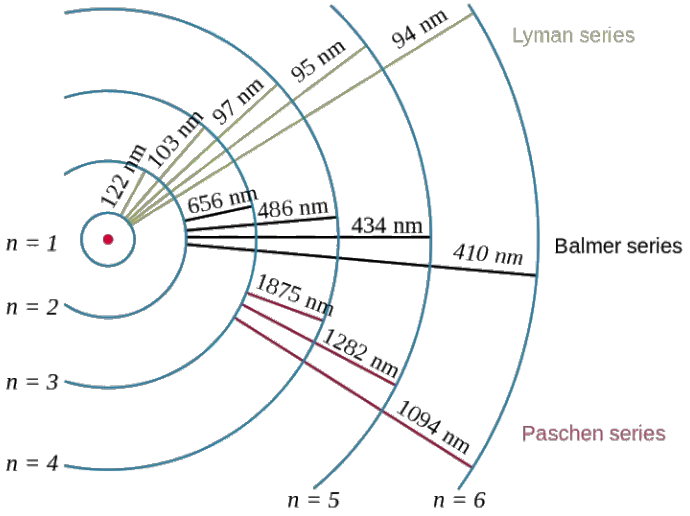
Matthew T. Cole, Mark Mann, Kenneth B.K. Teo, William I. Milne, Chapter 5 - **Engineered carbon nanotube field emission devices**, Editor(s): Waqar Ahmed, Mark J. Jackson, In Micro and Nano Technologies, Emerging Nanotechnologies for Manufacturing (Second Edition), William Andrew Publishing, 2015, Pages 125-186, ISBN 9780323289900,

# Field Emission Device (Benefits & Problems)

1. Stable emissions
2. Long lifetime
3. Low emission threshold potential

VS.

1. Nanotube tip electron emission arises from discrete energy states, rather than continuous electronic bands.
2. Emission behavior depends critically on the nanotube tip structure.
3. Not easy to be mass-manufactured.



# Field Emission Device (Current Development)

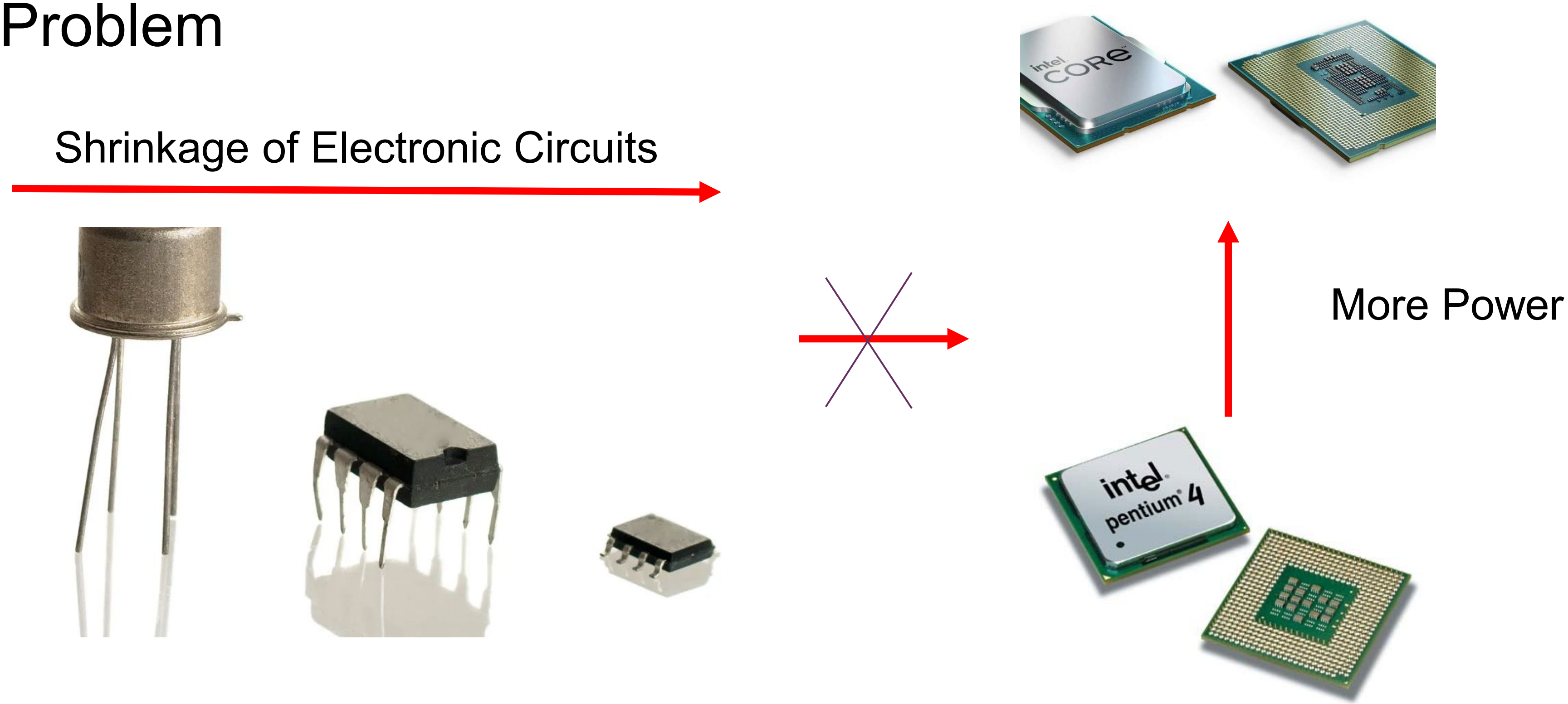
- “Current densities as high as 4 A/cm2 have been obtained, compared with the 10 mA/cm2 needed for flat panel field emission displays and the 0.5 A/cm2 required for microwave power amplifier tubes.”

- “Samsung has produced several generations of prototypes, including a 9-inch red-blue-green color display that can reproduce moving images.”

- “It is not certain when or whether the flat panel nanotube displays will be commercially available, considering concurrent improvements in relatively low-cost flat panel liquid crystal displays and the emerging organic and polymeric light-emitting diode displays. “

# Nanometer-Sized Electronic Devices

## Problem

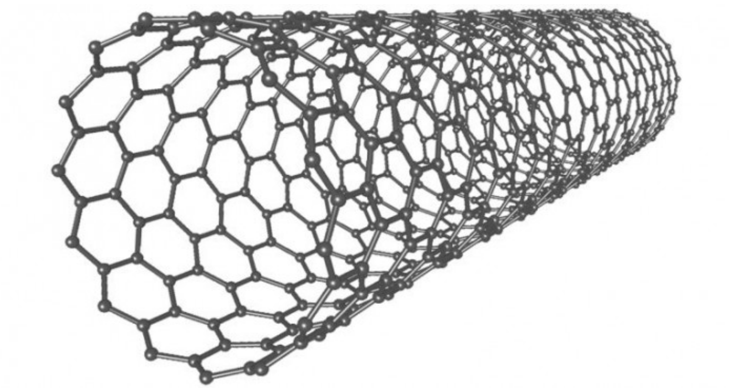


Shrinkage of Electronic Circuits

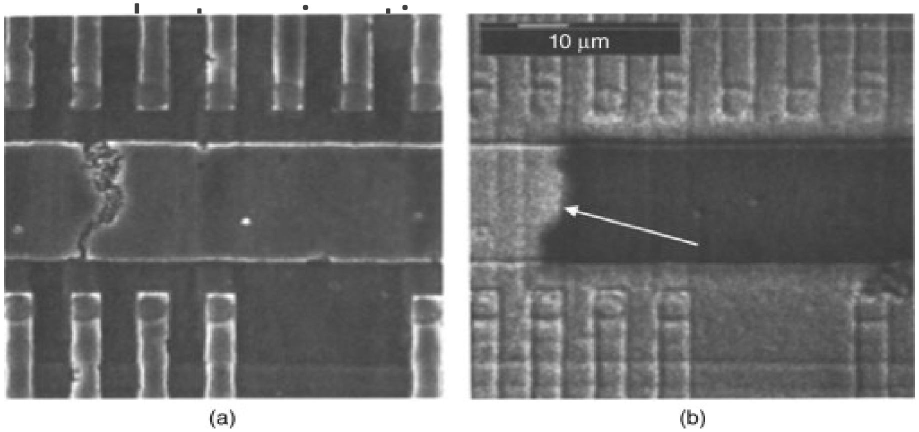
More Power

# Nanometer-Sized Electronic Devices

Speculation: Carbon Nanotubes will be useful for downsizing circuit dimensions



Current-induced



Scanning electron micrographs of the open circuit induced by EM in an n-MOS LSI (metal-oxide semiconductor for large-scale integration) bias metallization: (a) normal topographic image; (b) voltage contrast image.

Retrieved from: D.T. Read, V.K. Tewary, W.H. Gerstle. (2011) Modeling electromigration using the peridynamics approach. Pages 45-69. https://doi.org/10.1533/9780857093752.1.45.

# Nanometer-Sized Electronic Devices

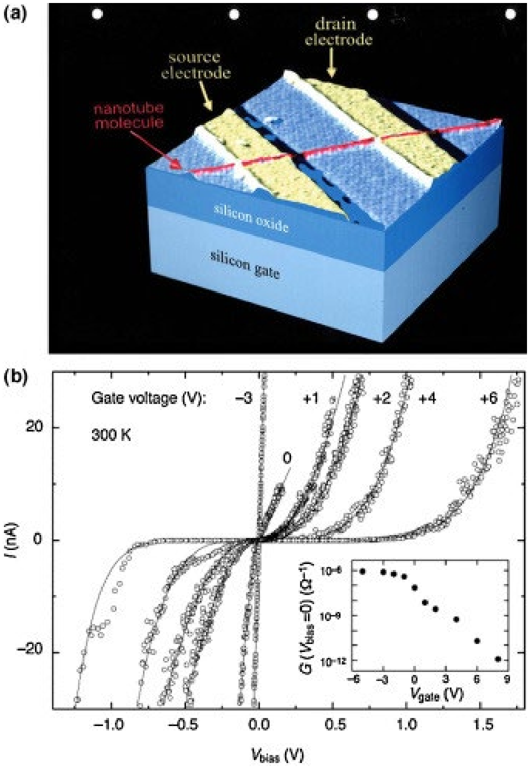
| Pros | Cons |
|---|---|
| CNT do not experience electromigration | Large contact resistances are necessary in current applications. |
| Because of ballistic transport, the intrinsic resistance of the nanotube is negligible | CNT would have a resistance of at least 6.5 kilohms. |
| SWNTs can carry up to 10^9 A/cm2<br>Normal metals can carry up to 10^5 A/cm2 | Contact resistance cannot be totally eliminated |

# Nanometer-Sized Electronic Devices

## Nanotube Field Effect Transistors (NT-FETs)

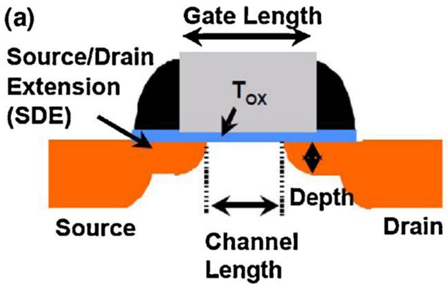
- First developed by Dekker's group at Delft university and by IBM in 1998
- Doping in CNT is not desirable as it would interfere with its perfect structure and compromise its electric properties

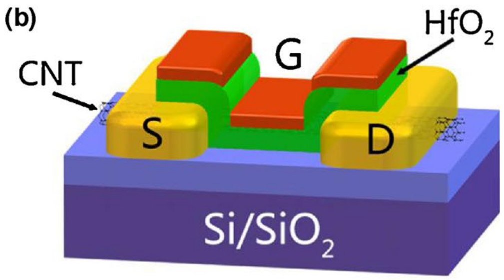
(a) Schematic depicting the first back-gate CNT FET developed by IBM group
(b) Output characteristics of the first CNT FET developed by Dekker's group for different gate voltages, and transfer characteristic of the device (inset).

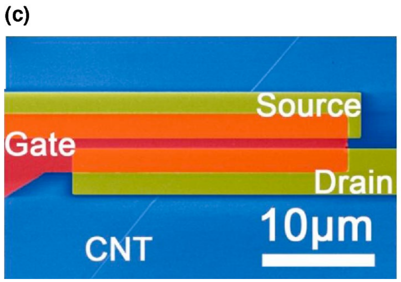


Lian-Mao Peng, Zhiyong Zhang, Sheng Wang (2014) Carbon nanotube electronics: recent advances. Materials Today. Volume 17, Issue 9. Pages 433-442. Recovered from: [https://doi.org/10.1016/j.mattod.2014.07.008](https://doi.org/10.1016/j.mattod.2014.07.008).

# Nanometer-Sized Electronic Devices:



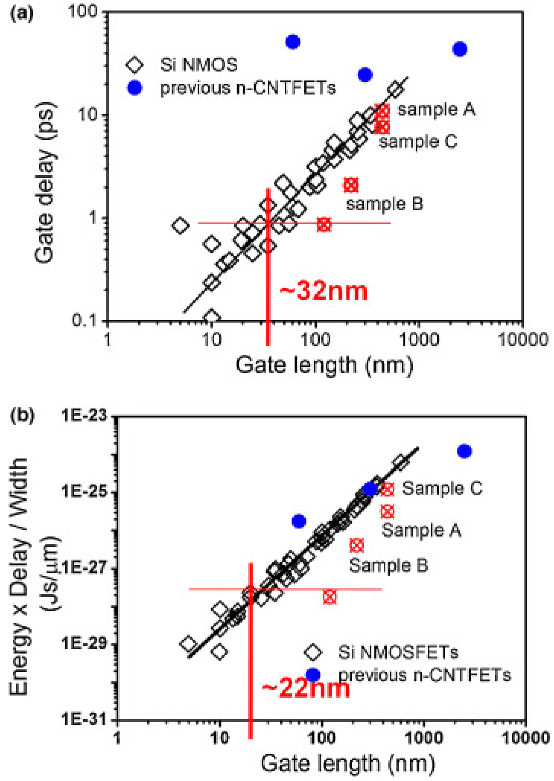




(a) Self-aligned gate structures for Si MOSFET

(b) Self-aligned gate structure for Carbon Nanotube Field Effect Transistor

(c) Top view SEM image of a real device



(a) Gate delay and (b) energy-delay

Lian-Mao Peng, Zhiyong Zhang, Sheng Wang (2014) Carbon nanotube electronics: recent advances. Materials Today. Volume 17, Issue 9. Pages 433-442. Recovered from: https://doi.org/10.1016/j.mattod.2014.07.008.