Ames Research Center

ELORET

Plasma Aided CVD of Carbon Nanotubes

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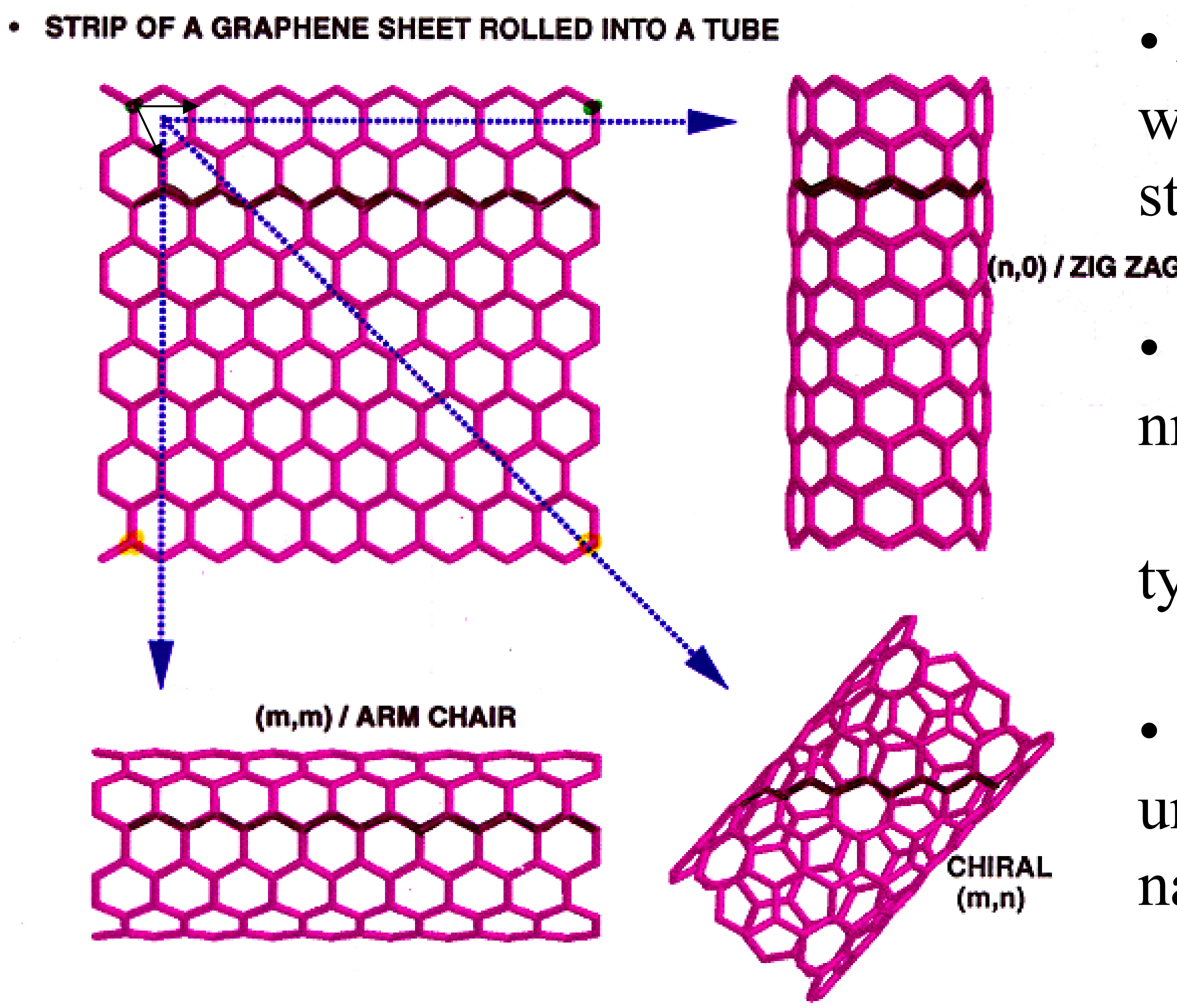
Outline

- Carbon Nanotube Introduction
  - What are they?
  - Properties
  - Applications
  - Different kinds of Nanotubes/Nanofibers
- Plasma CVD
  - Reactors for CVD
  - Operating Conditions
  - Alignment by Plasma CVD
  - Results and Studies
    - Catalyst Selection
    - Variation with Chemistry, Reactor Design
    - Microloading
    - Diagnostics

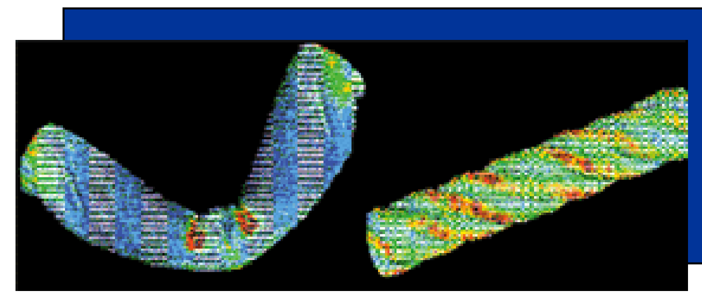
What is a Carbon Nanotube?



- A tubular form of carbon, with graphite bonding structure
- Diameters as small as 0.8 nm, up to tens of nm
  $$d = 0.78 \sqrt{n_1^2 + n_1 n_2 + n_2^2}$$
  typically 1.2-1.4 nm
- Length theoretically unlimited, typically several nanometers to microns
- Also can have concentric tubes – Multiwall Nanotube

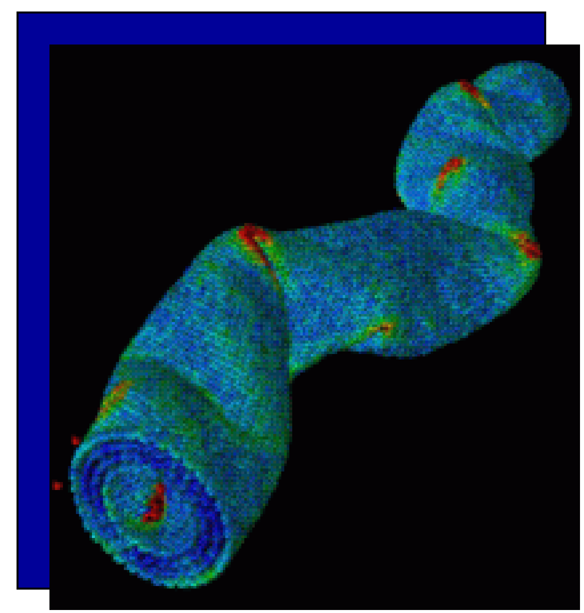
Carbon Nanotube: The Miracle Material

Mechanical/Thermal



- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture

- Young's modulus (stiffness) of over 1 TPa
  Steel: 200 GPa
  Carbon Fiber: 700 GPA
  Diamond: 1 TPa



- Maximum strain ~10%, much higher than any material

- Thermal conductivity: 2000 W/m-K
  Cu: 400 W/m-K

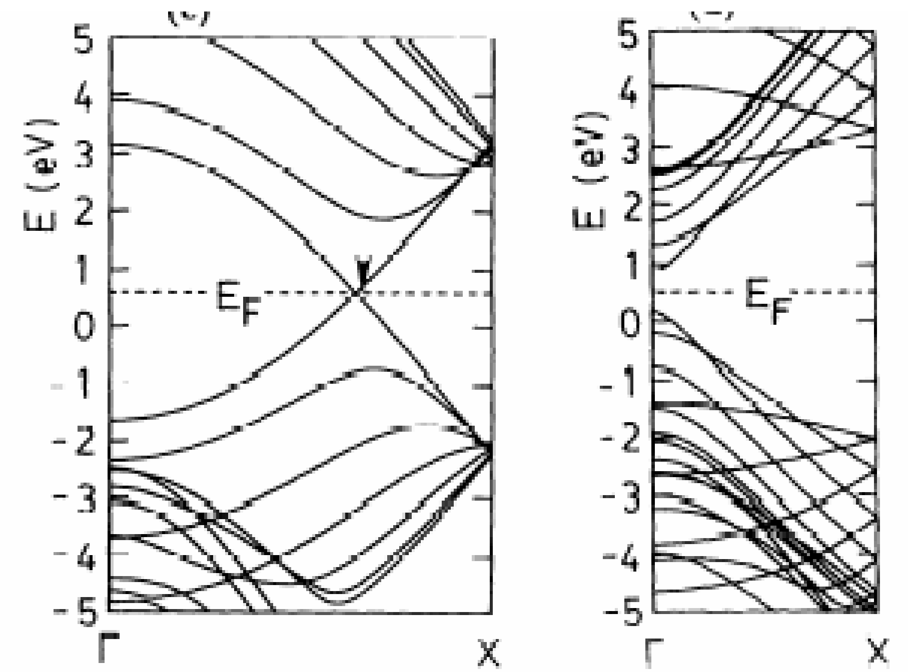
Carbon Nanotube: The Miracle Material

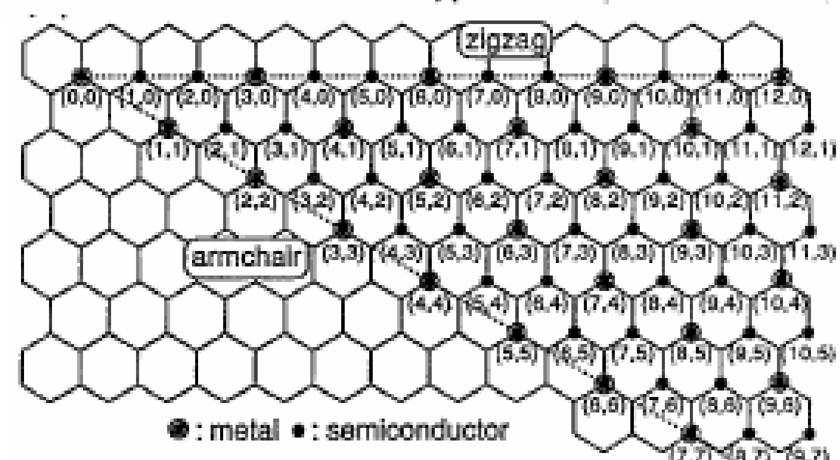
Electrical

- Can be metallic or semiconducting depending on chirality
  - Metallic: $2n_1 + n_2 = 0$
  - Narrow Band: $2n_1 + n_2 = 3j$
    ($E_g < 0.3$ eV, $\rightarrow 0$ larger dia.)
  - Semiconductor: $2n_1 + n_2 \neq 3j$
    ($E_g \sim 0.5$-1.3 eV)

- Ballistic Conductor:
  - Resistance independent of length
  - Intrinsic Resistance: 6.5 kΩ
    $\sim 8.6 \times 10^{-15}$ Ω-m^2
    equivalent to 0.5 μm of Copper

- High current carrying capacity ($\sim 10^{13}$ A/m^2)

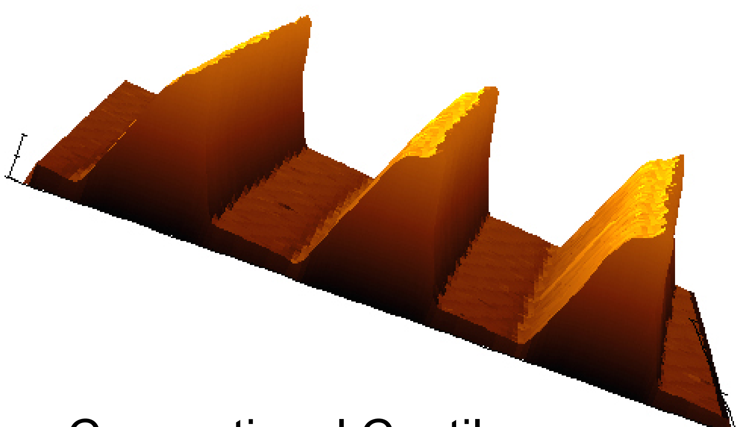




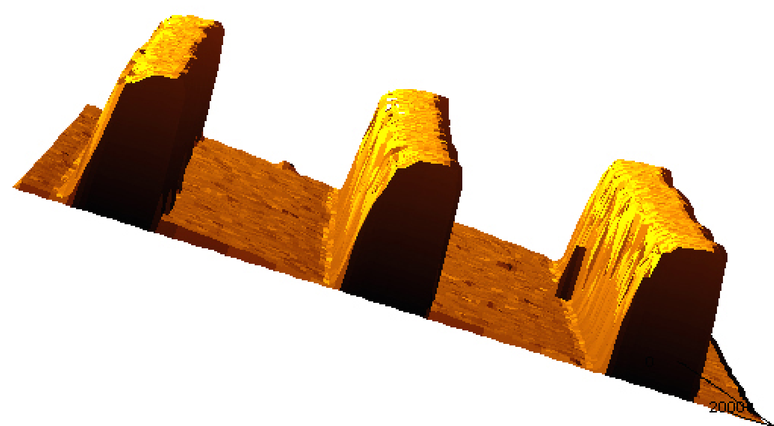
Carbon Nanotube Applications: Microscopy

- Attaching nanotube to AFM tips allows measurement of high resolution features, high aspect ratios

280 nm line and space pattern:



Conventional Cantilever

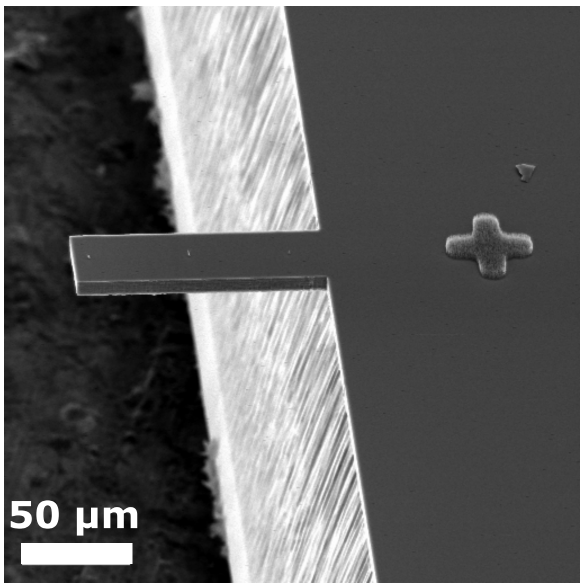


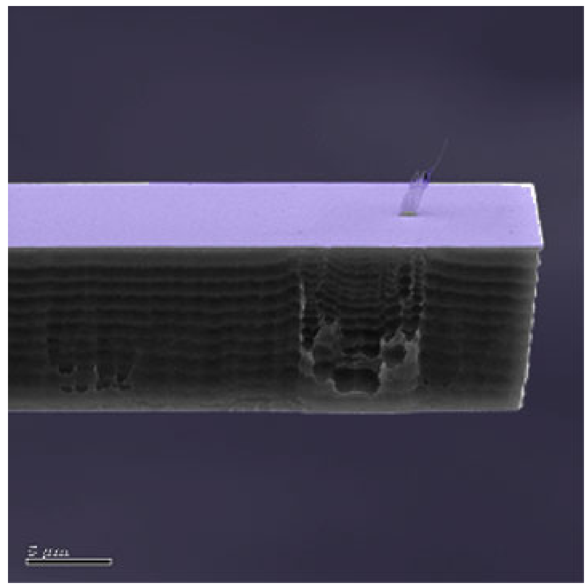
Tip with multiwalled nanotube

Nguyen et al., Nanotechnology, 12, 363 (2001).

Carbon Nanotube Applications: Microscopy

- Tubes fabricated directly on cantilever beam





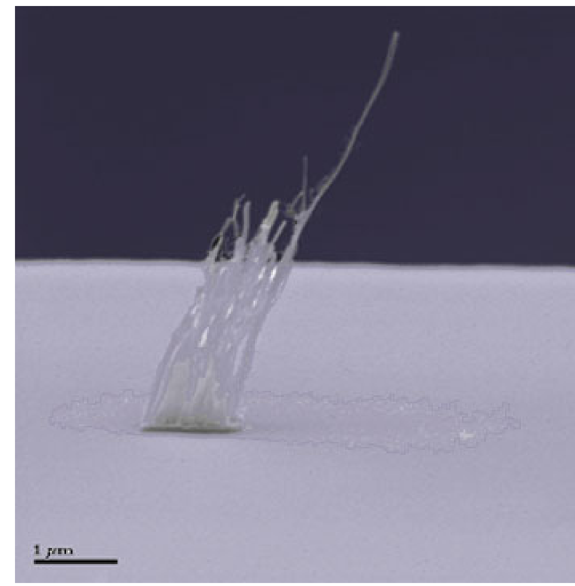
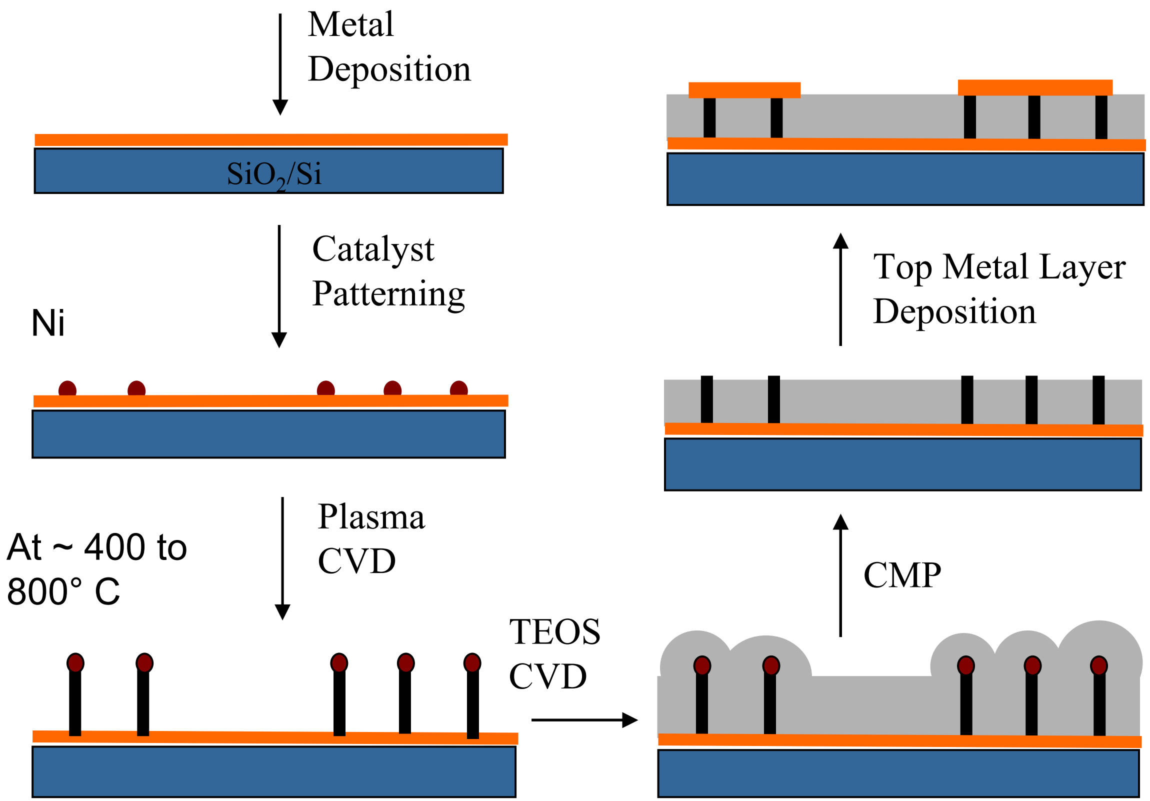
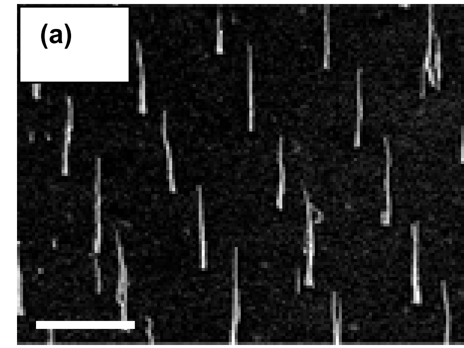
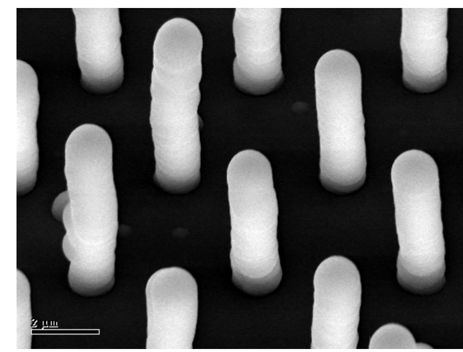


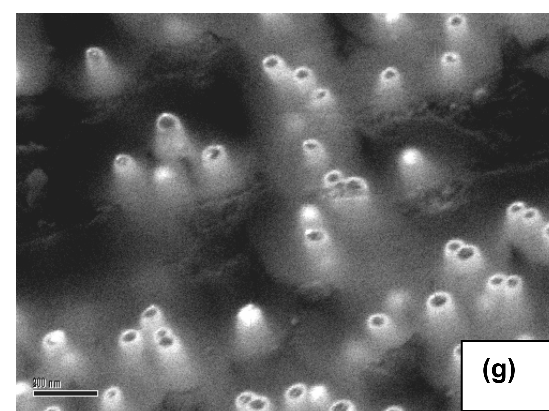
Image courtesy Alan Cassell, Integrated Nanosystems Incorporated

Carbon Nanotube Applications: Interconnect



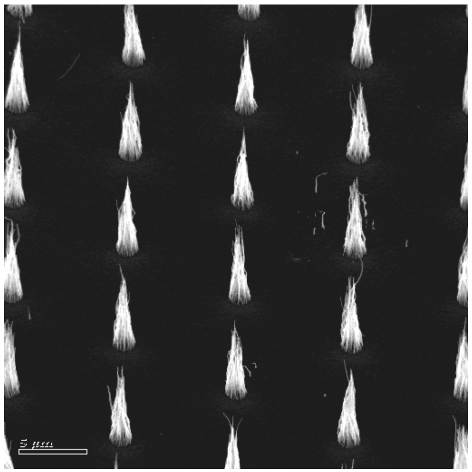


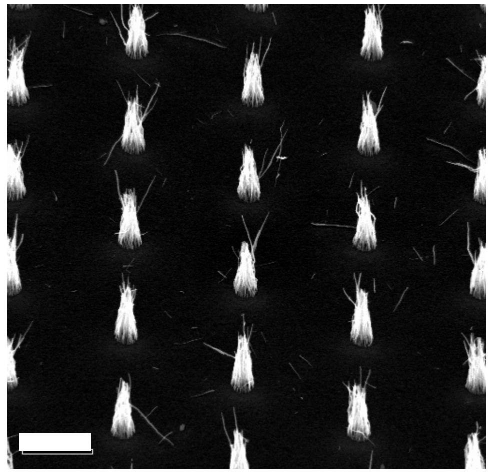




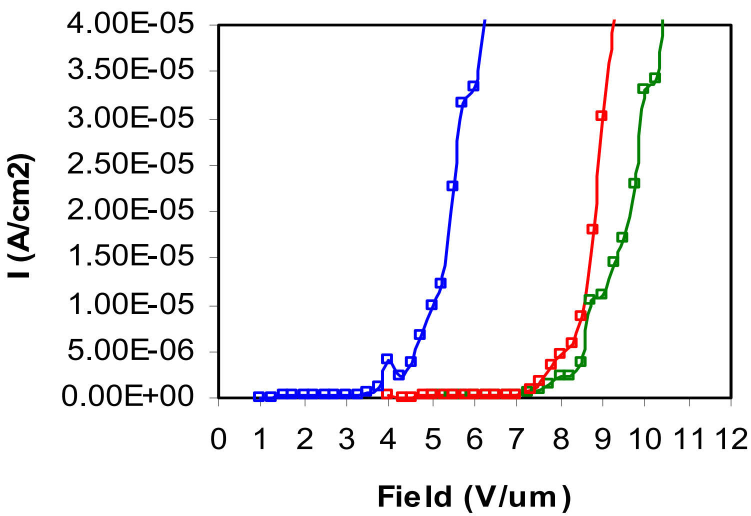
J. Li, Q. Ye, A. Cassell, H. T. Ng, R. Stevens, J. Han, M. Meyyappan, *Appl. Phys. Lett.*, **82**(15), 2491 (2003)

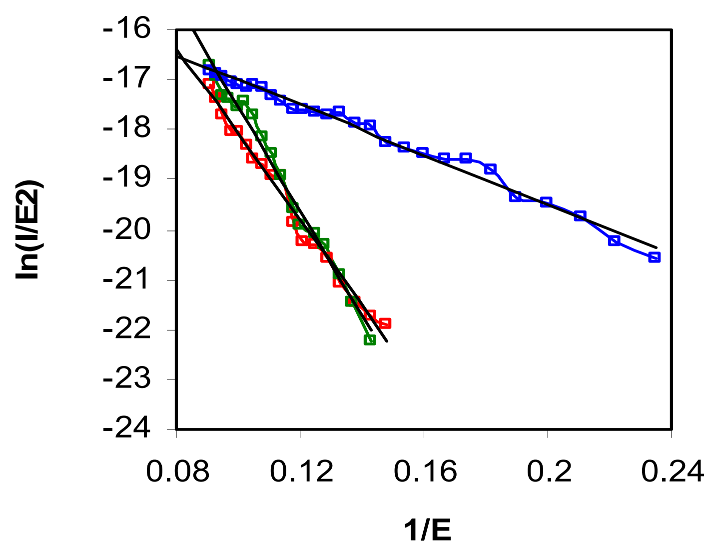
Carbon Nanotube Applications: Field Emission





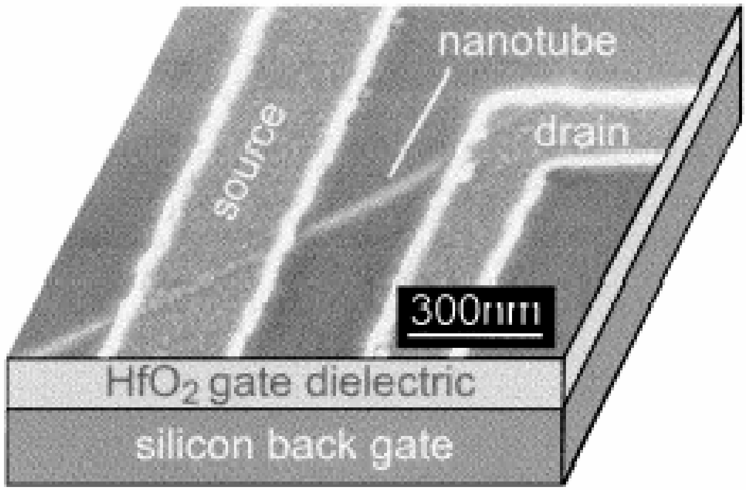
- **High Aspect Ratio of CNF allows field emission turn-on at lower Voltages**

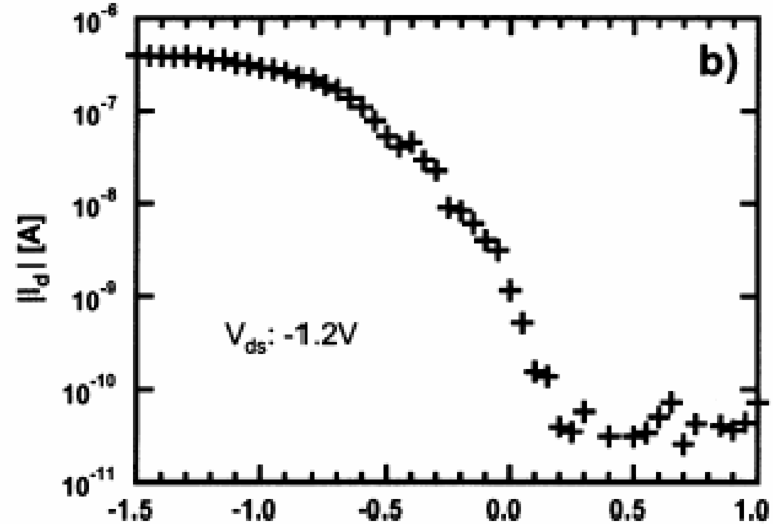




Cassell, et. al., Nanotechnology, submitted

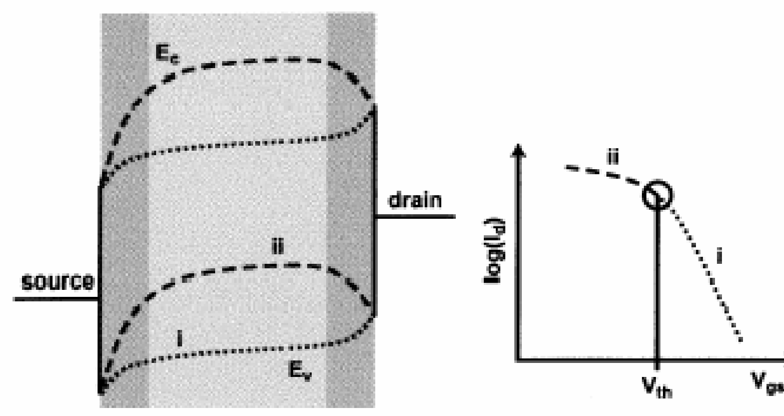
Carbon Nanotube Applications: Transistors





- Characteristics similar to modern transistors, but mass fabrication means are lacking

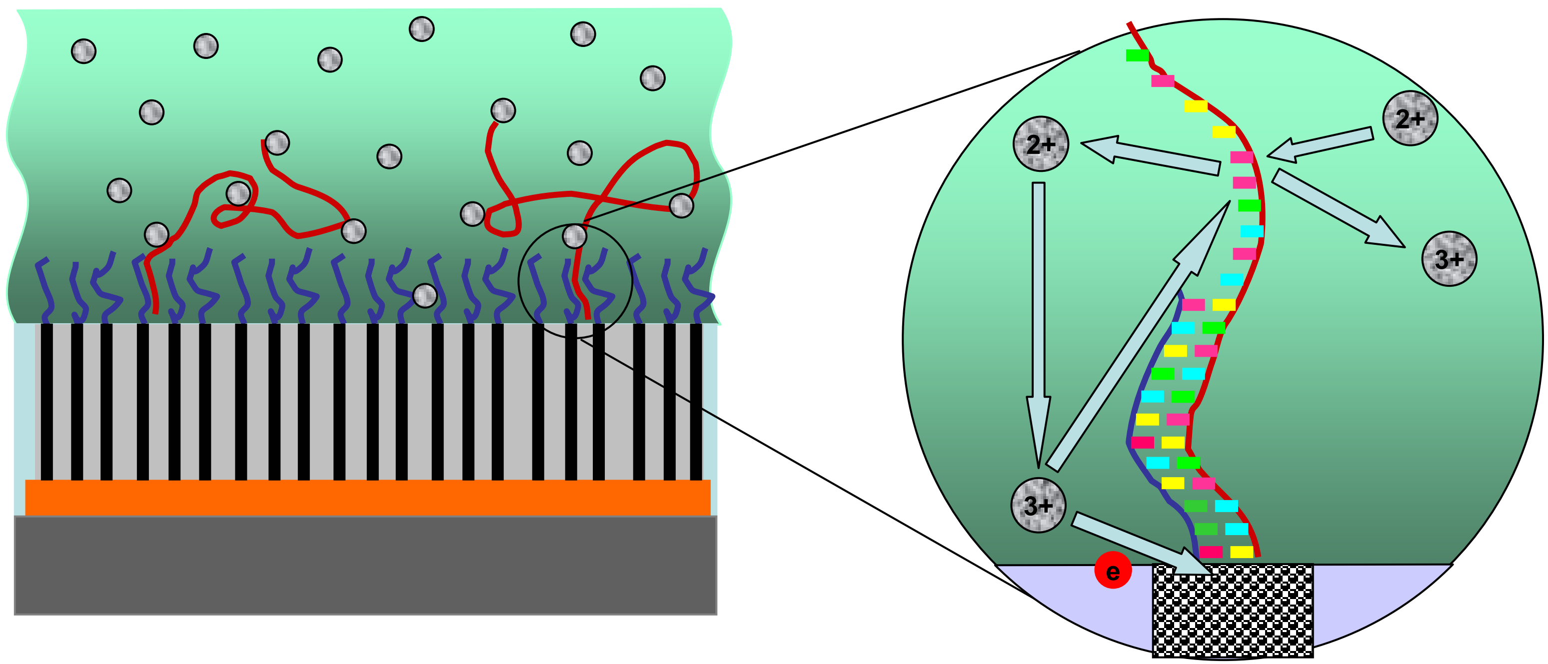
- FET switching controlled by modulation of Shottky barriers at nanotube contacts



(a) (b)

Appenzeller et al., *IEEE Trans. Nanotechnology*, 1, 184 (2002). (IBM Research)

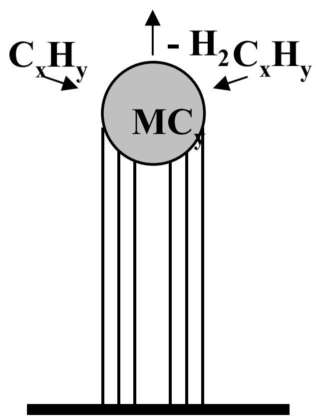
Carbon Nanotube Applications: Sensors



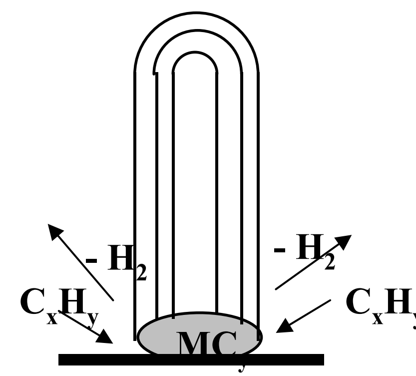
- **MWNT array electrode functionalized with DNA/PNA probe as an ultrasensitive sensor for detecting the hybridization of target DNA/RNA from the sample.**
  - Signal from redox bases in the excess DNA single strands
- **The signal can be amplified with metal ion mediator** $\left[Ru(bPy)_3^{2+}\right]$ **oxidation catalyzed by Guanine.**

CVD Growth Mechanisms

- Elevated Temperature allows catalyst diffusion and formation of nanoparticles
- Nanoparticles nucleate growth



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



Tip Growth

Typically occurs when there are very weak metal-surface interactions

Usually Larger Diameter

Base Growth

Occurs when the metal-surface interactions are strong

Usually Smaller Diameter

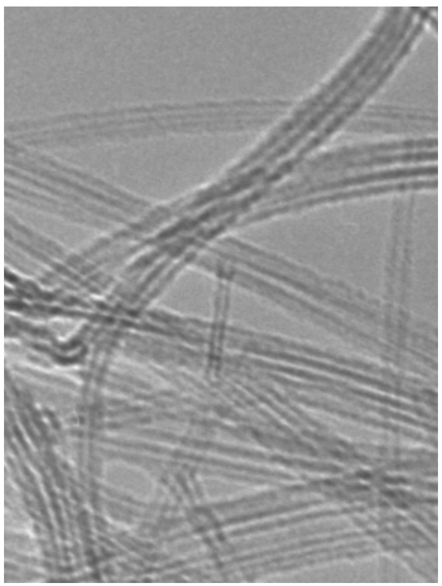
- Growth eventually halted by catalyst poisoning/amorphous C buildup

Types of Nanotubes/Nanofibers

Nanotubes

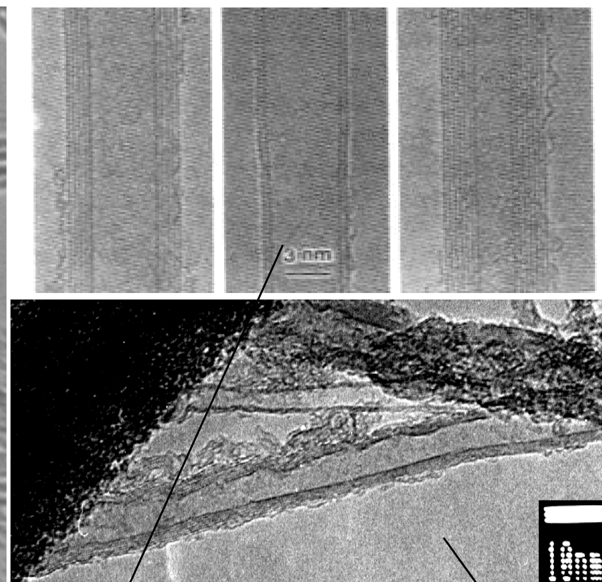
Nanofibers ("Defective Nanotubes")

Single Walled



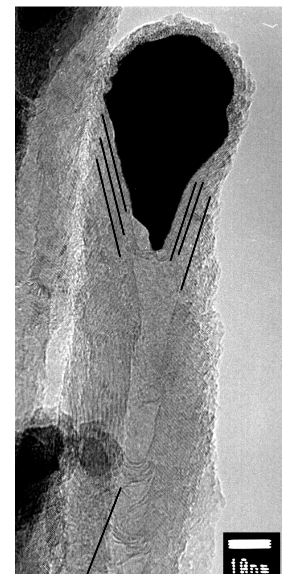
Thermal CVD

Multiwalled



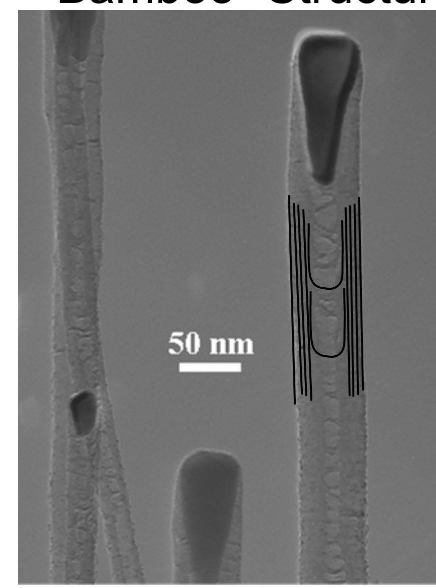
Arc Discharge

"Stacked Cone"



RF Plasma

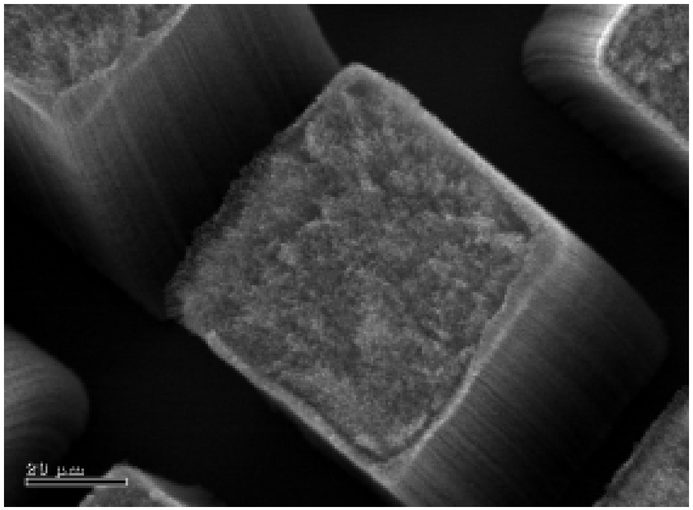
"Bamboo" Structure



DC Plasma

- Plasma CVD "Nanotubes" are actually overwhelmingly Nanofibers
  - Terminology is inconsistent in literature
- Nanofibers always grow in tip growth mode, Nanotubes typically base growth
- SWNTs have not been produced by Plasma CVD (thermal CVD)
- MWNTs produced by Plasma CVD often have many defects

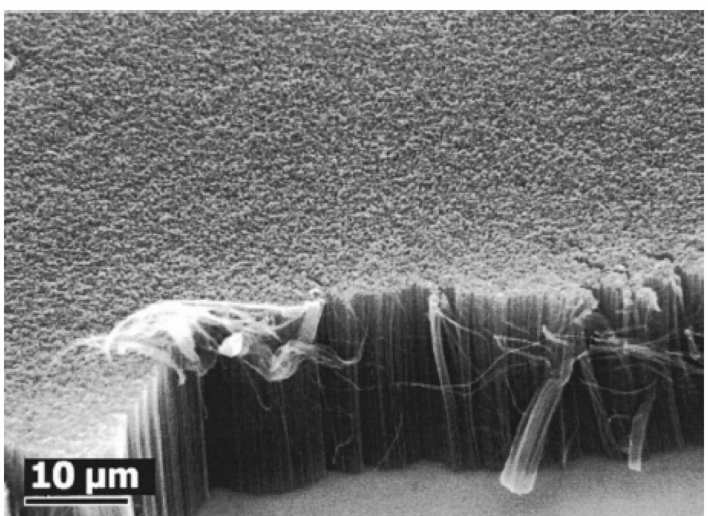
Alignment in Plasma CVD



Thermally Grown MWNT

Appears as Aligned Tower

Alignment achieved through van der Waals interaction of Nanotubes



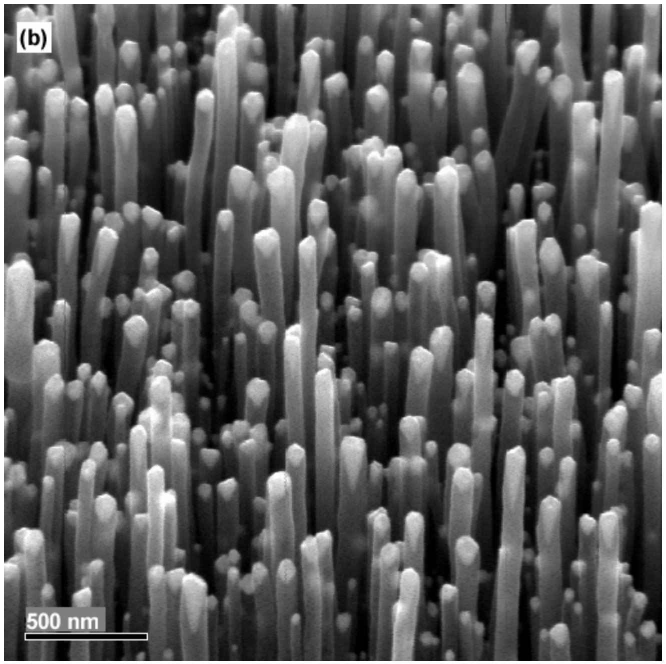
Plasma Grown MWNT

Appears similar to Thermal Case

In some cases, "straighter" tubes are observed in plasma CVD

Though advantage not always clear in this case

Alignment in Plasma CVD

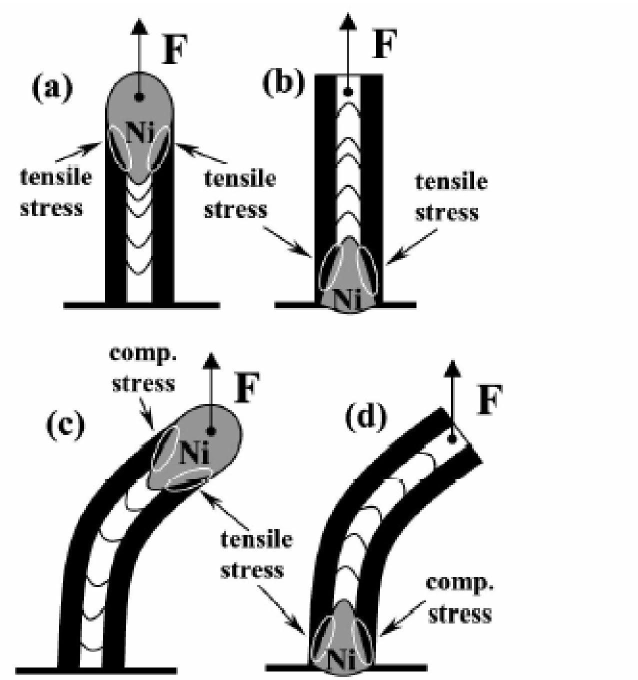


Plasma Grown Nanofibers

Fibers are Individually Aligned

Not close enough together for van der Waals Interaction

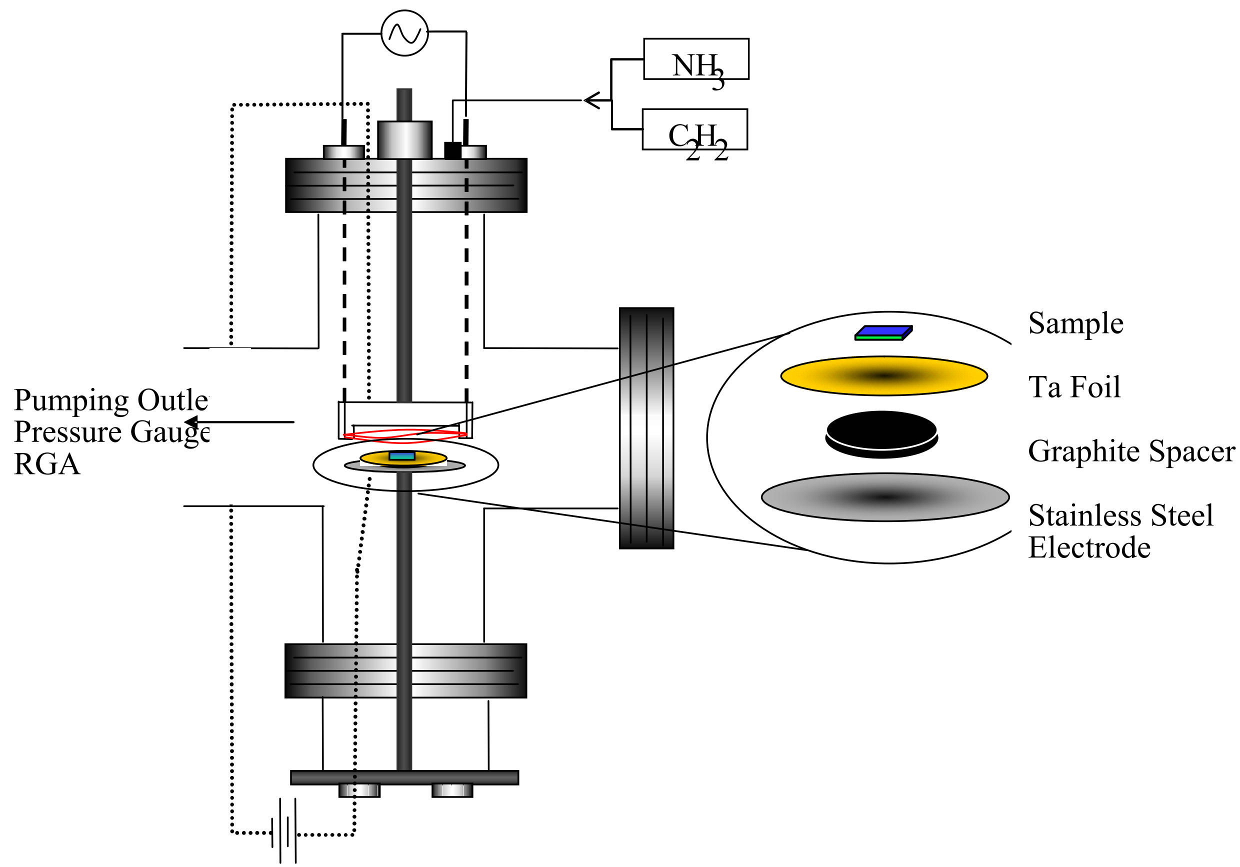
Fibers are straightened by Sheath Field!

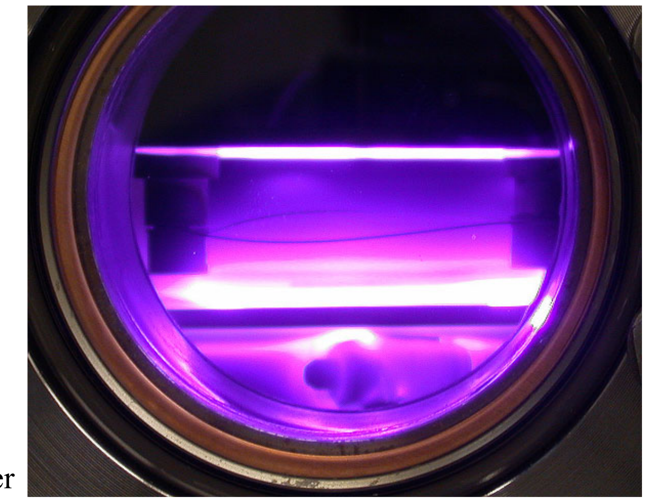


Mechanism proposed by Merkulov, et. al. (2001):

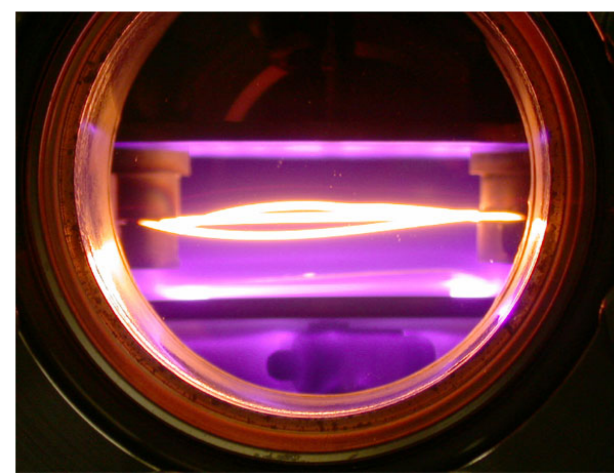
- **Field creates Stress at Particle/Nanofiber Interface**
- **Nanotube bending creates opposing stresses**
- **Tensile stress enhances growth rate, "straightens" fiber in tip growth mode**
- **In base growth, no straightening**

DC Plasma Reactor





DC Plasma CVD

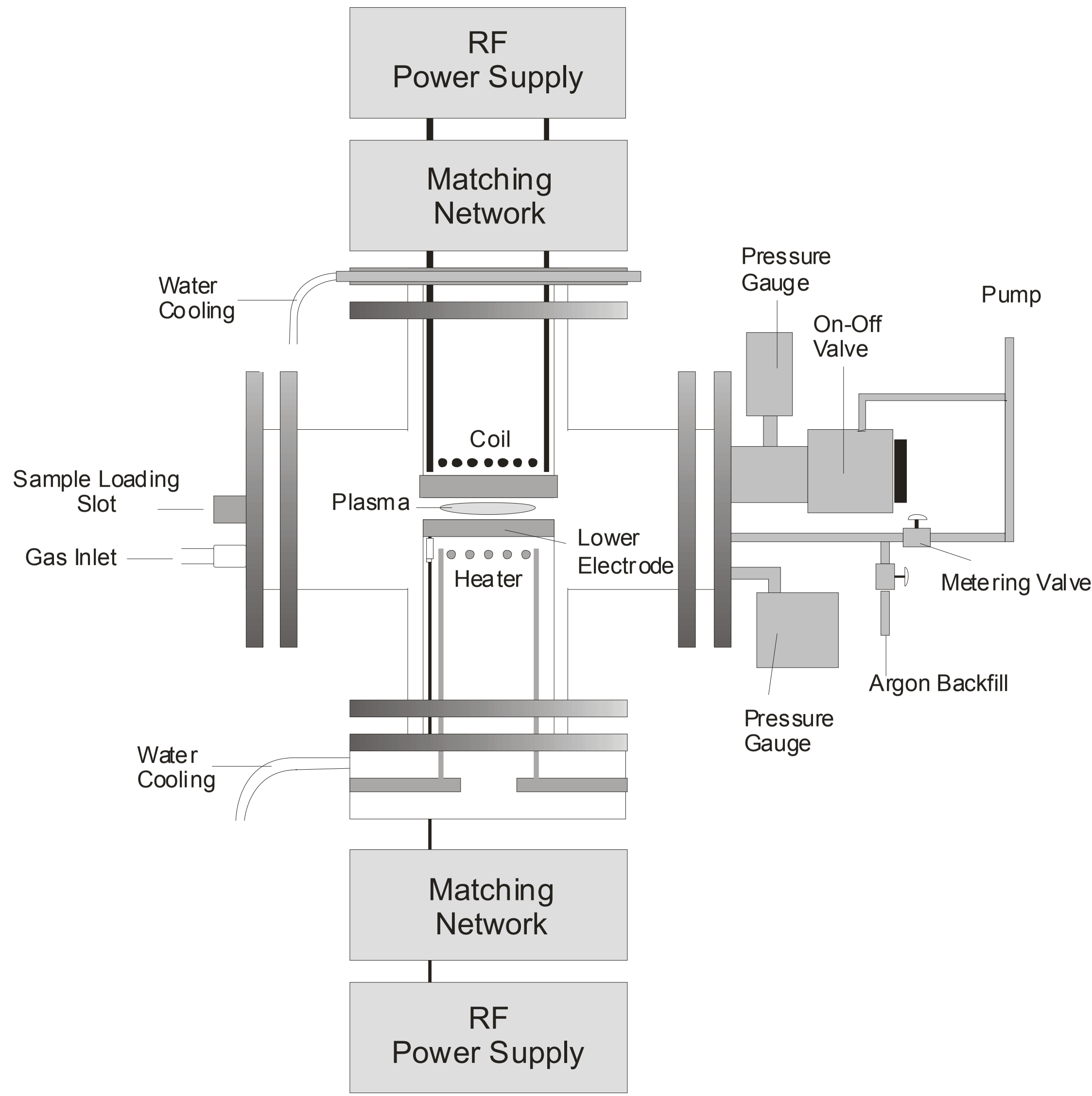


Hot Filament Assisted

Cruden et al., J Appl Phys, 12, 363 (2001).

"ICP" Reactor for Nanotube Growth

- Quartz/Steel chamber 10 cm in diameter with a window for sample introduction
- Inductive coil on the upper electrode
- 13.56 MHz independent capacitive power on the bottom electrode
- Heating stage on bottom electrode
- "Best" operating condition found to be in capacitive mode



Typical Plasma Operation Conditions

- Conditions Similar to Diamond-like carbon CVD

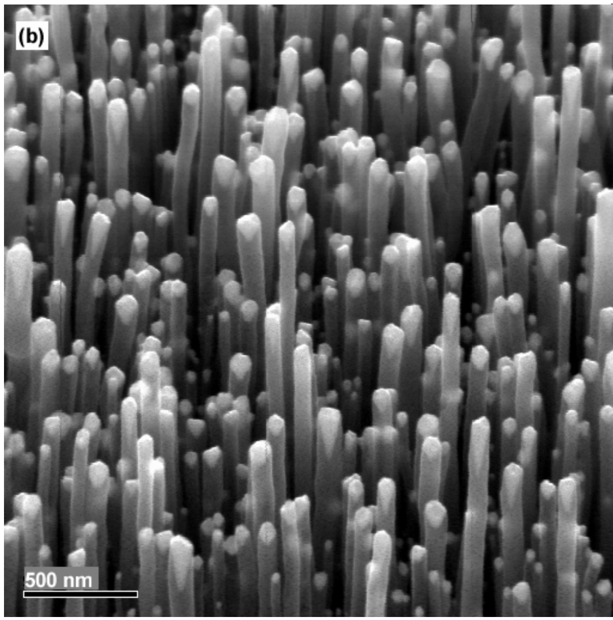
- Chemistries:
  - Requires carbon source: Methane (CH_4), Ethane (C_2H_4), Acetylene (C_2H_2)
  - Requires diluent/Co-etchant: Hydrogen (H_2) or Ammonia (NH_3)
  - Catalyst: Fe, Mo, Ni, Co

- Temperatures:
  High wafer temperatures required: 700-900 °C
  Often, heat is provided by plasma (and many researchers do not realize this)
  No researchers utilize clamping for wafer temperature control
  Few researchers measure actual wafer temperature

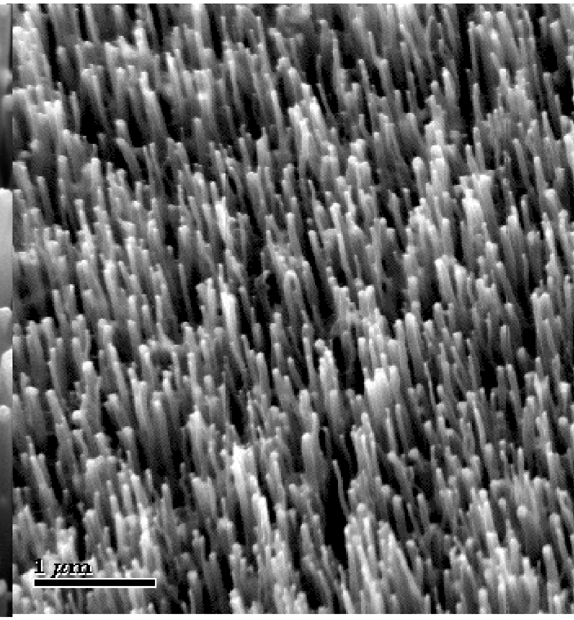
- Powers: 40 W – 400 W (system dependent)

- Pressures: Typically a few torr (optimum ~3-4 torr)

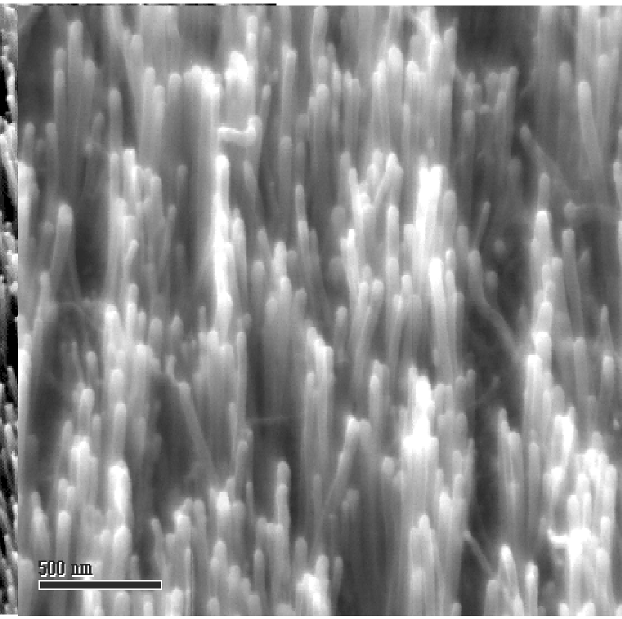
Variation with Plasma Systems



DC Plasma
Acetylene + Ammonia



RF Plasma
Ethylene + Ammonia

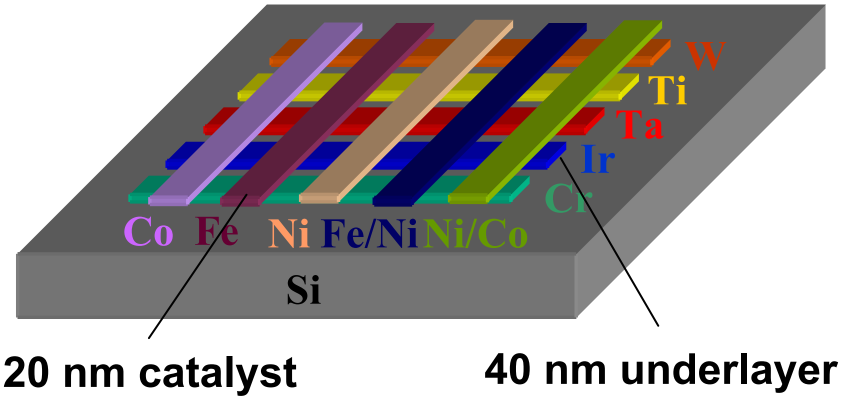


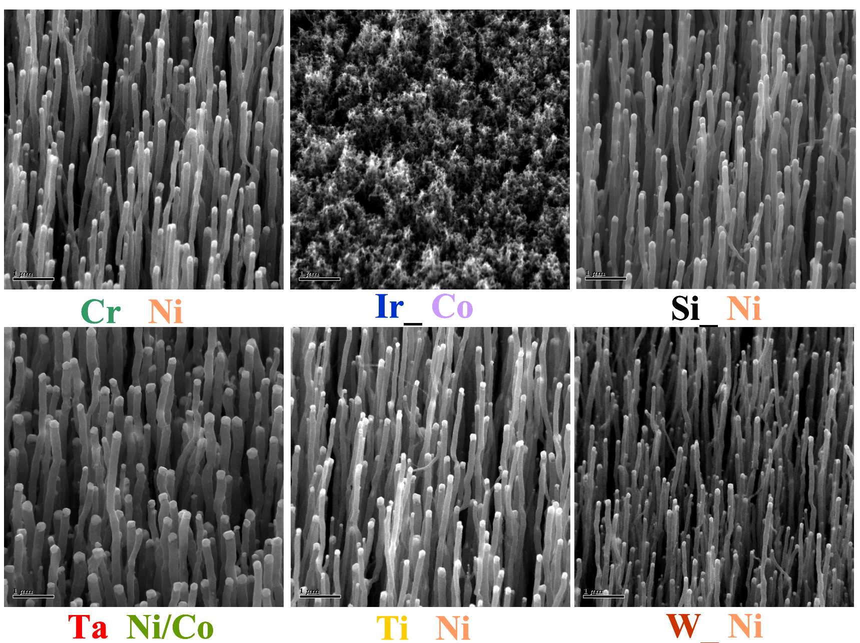
RF Plasma
Methane + Hydrogen

- **With proper system tuning, can get similar results on different systems**
  - **Plasma growth not too "finicky"**
  - **Catalyst preparation more important variable?**

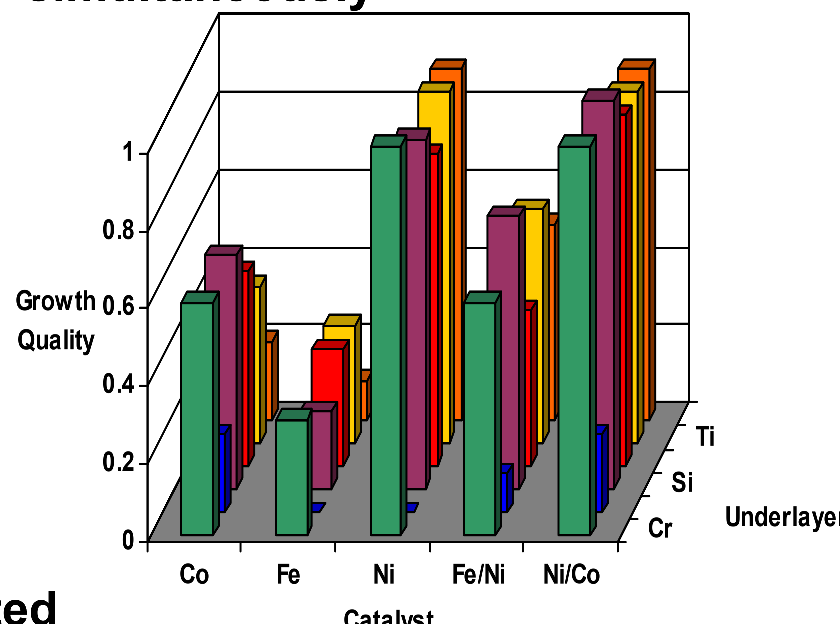
- **Reproducibility still an issue**
  - **Chamber wall effects**

Catalyst Selection: Combinatorial Approach



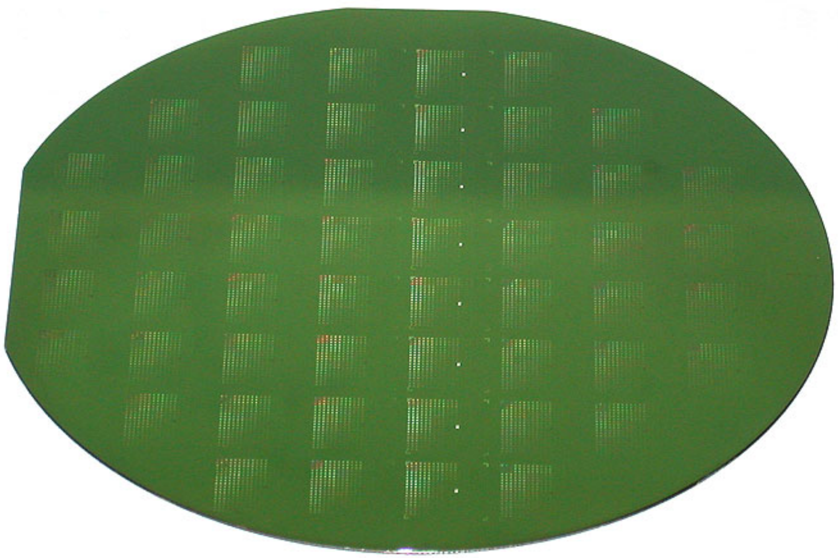


- Variety of Catalysts Applicable for Growth
- Growth sometimes enhanced by "layered" catalyst
- Using patterned metal lines, can examine growth for multiple catalysts simultaneously

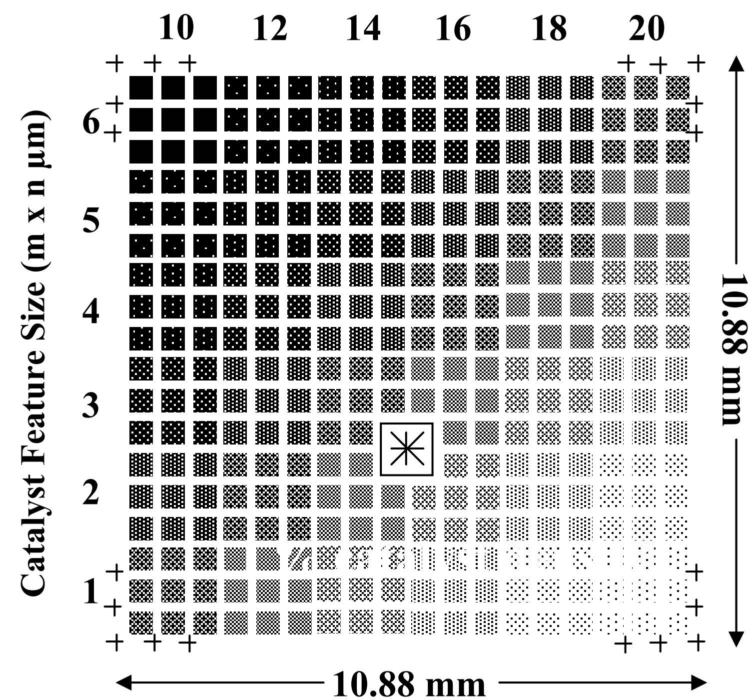


Cassell, et. al., Nanotechnology, submitted

Feature Density Dependencies: "Microarray" Chip



52 chips per 4” wafer



36 feature size/densities combinations per chip

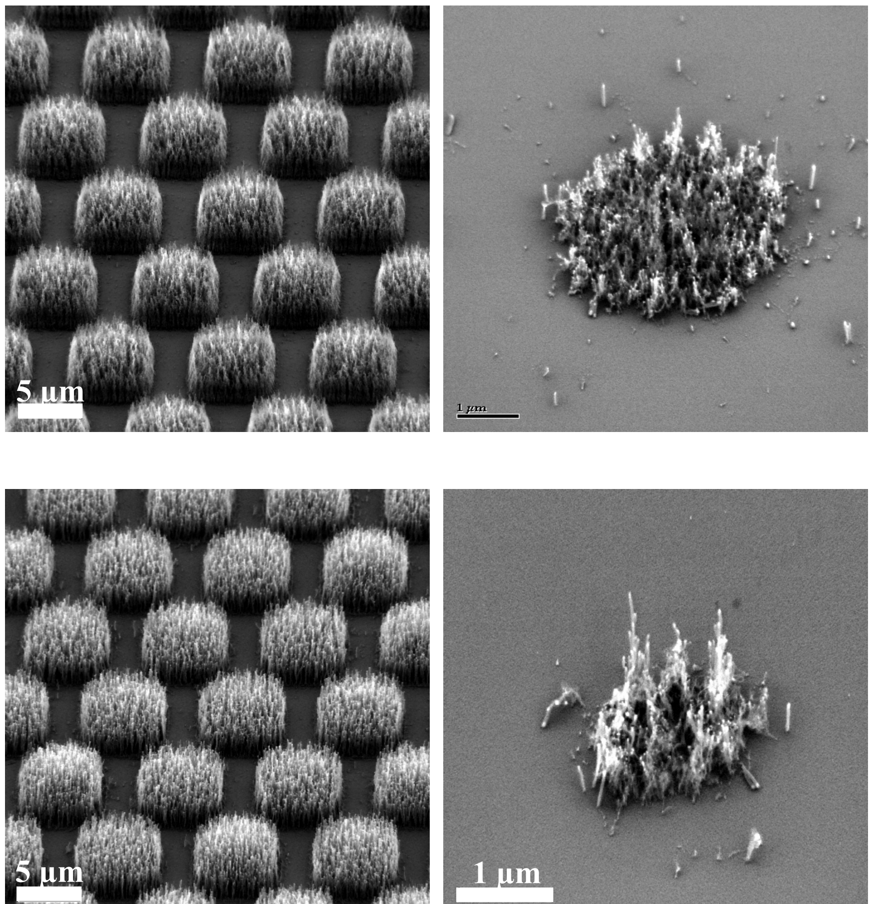
Cassell, et. al., Nanotechnology, submitted

Microloading

High Density Features: Coverage is Similar | Low Density Features: Poor coverage

525 V, 500 W

525 V, 250 W



Surface reactions create spatial variation in reactive species:

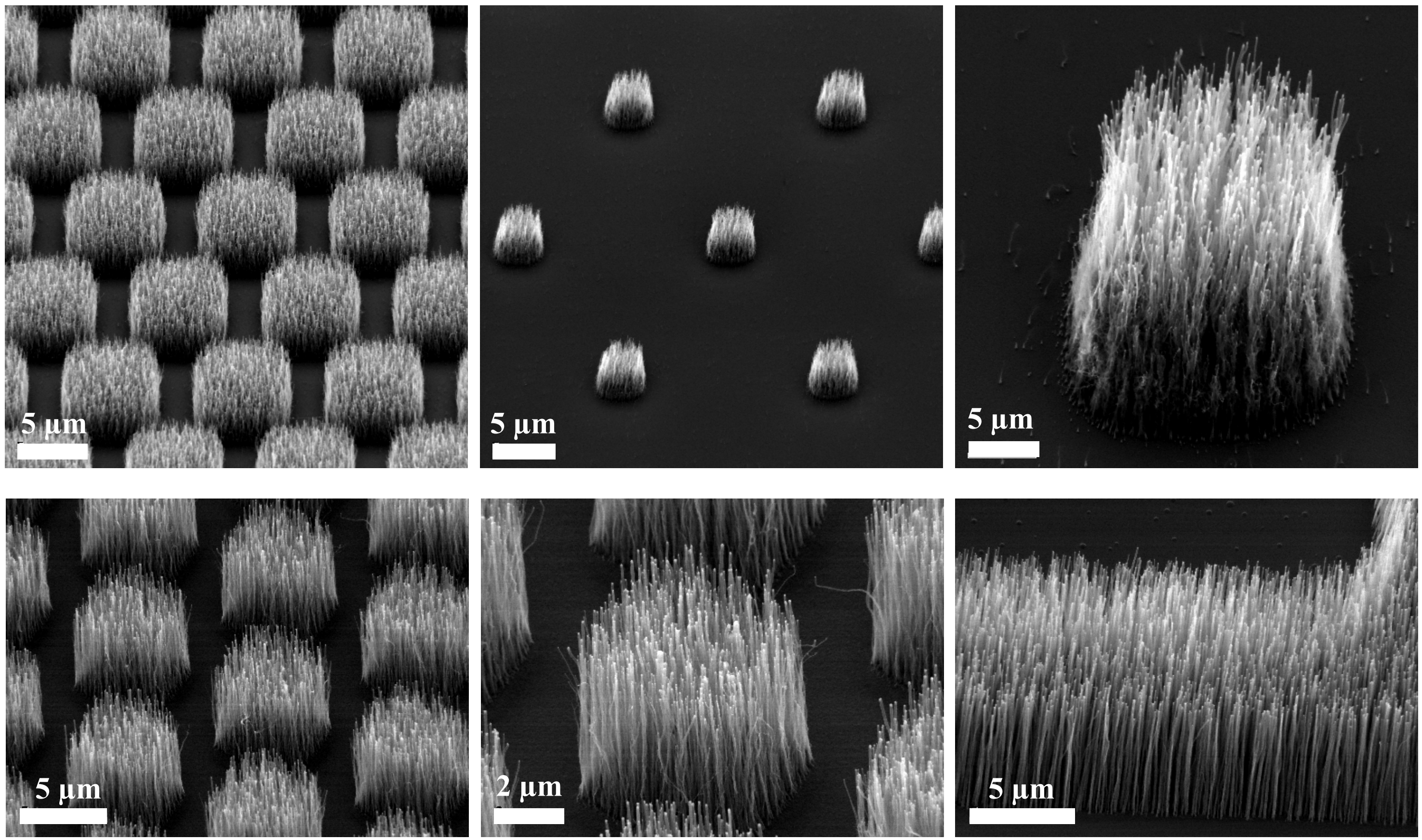
Too much power increases feedstock radicals, possibly poisoning catalyst or etching growth material.

Too little power decreases feedstock radicals, leading to poor growth uniformity.

Cassell, et. al., Nanotechnology, submitted

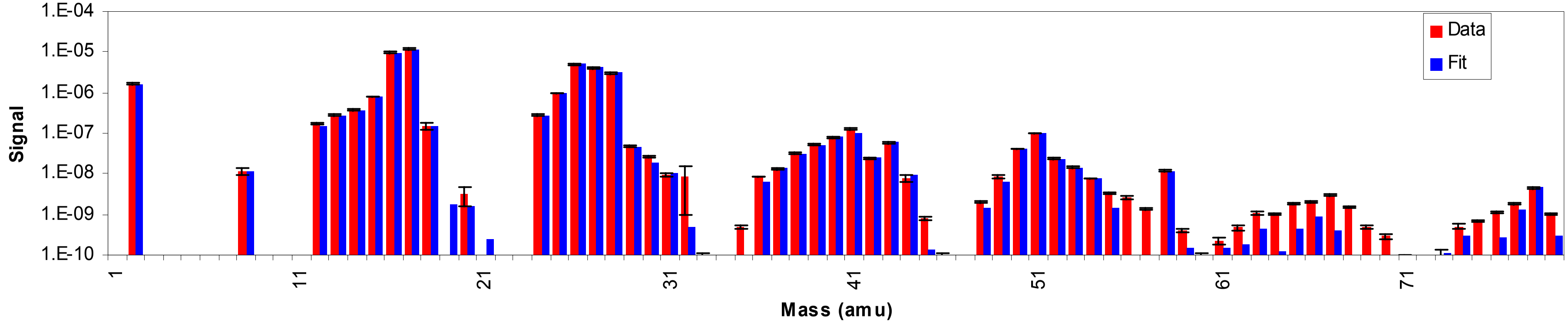
Microloading

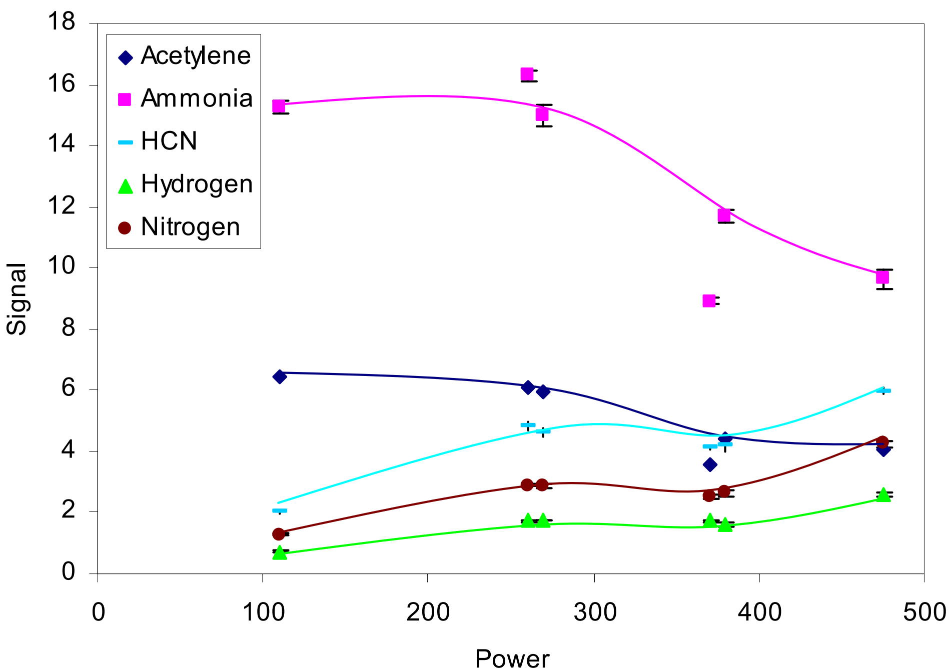
550 V, 350 W



Microloading minimized at intermediate power range

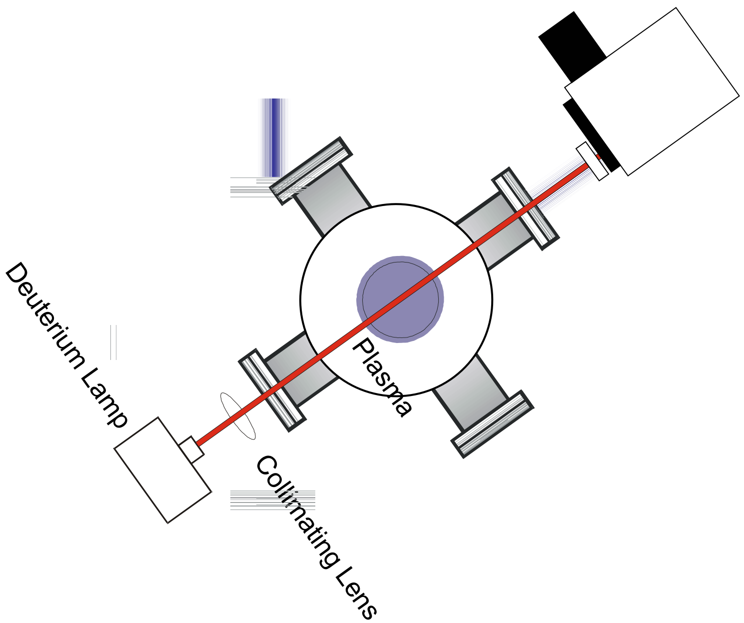
Diagnostics: Residual Gas Analysis

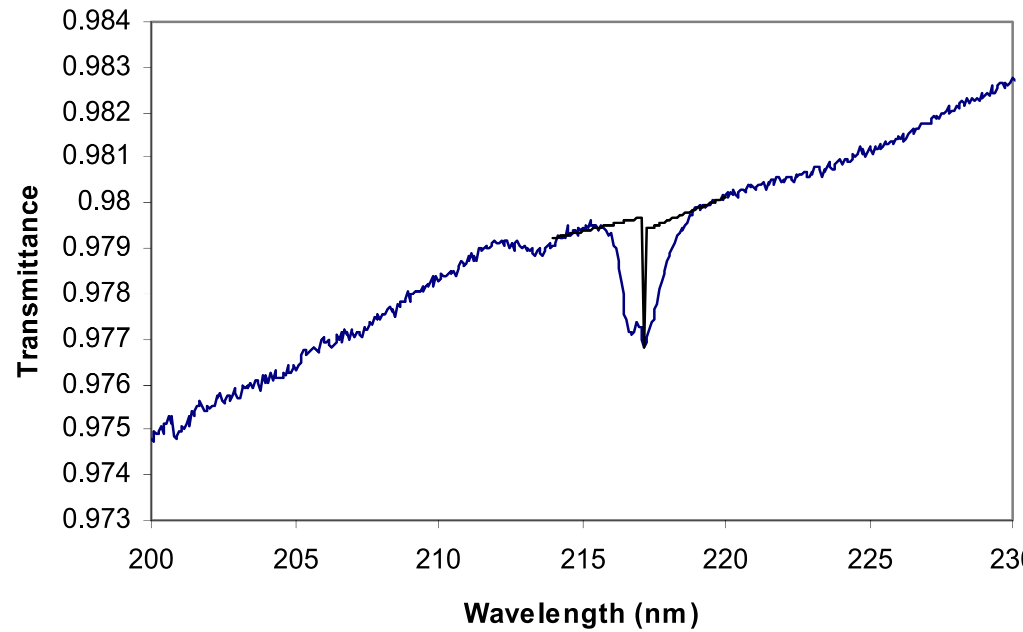




- **Downstream Chemistry Analysis**
- **Semi-quantitative analysis of stable discharge species**
- **Observe dissociation dependence on conditions**
- **Observe production of higher mass species (e.g. Benzene)**

Diagnostics: UV Absorption Spectroscopy



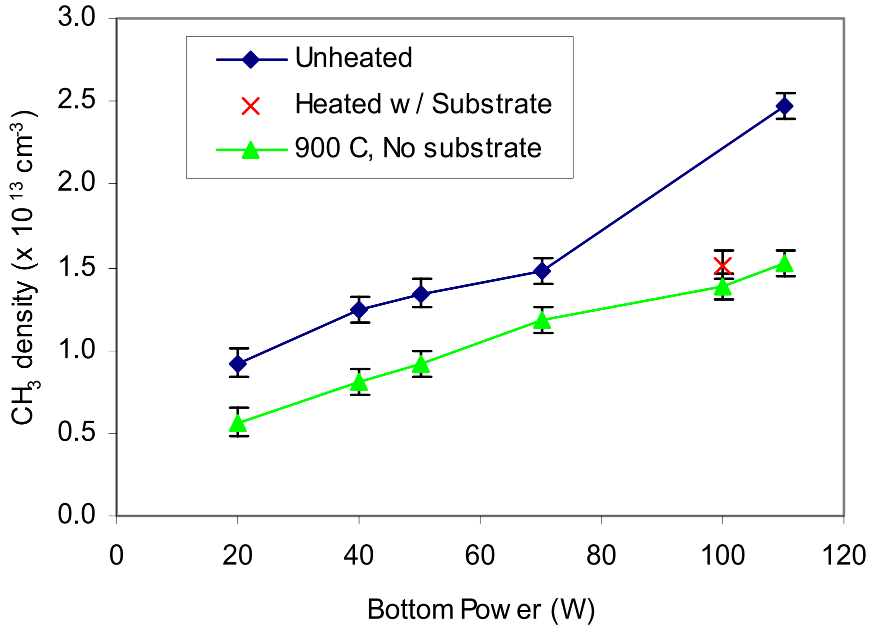


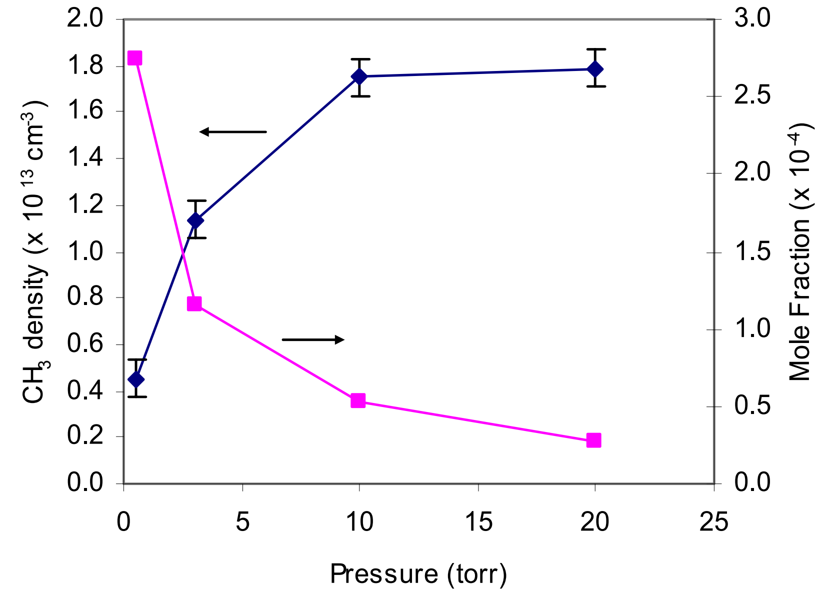
- **Quantitative measurement of CH_3 density via Beer's Law**

$$\ln\left(\frac{I - I_{plasma}}{I_{lamp} - I_{bkgd}}\right) = \sigma L n_{CH3}$$

- **Other species possible in visible: CH, C_2**

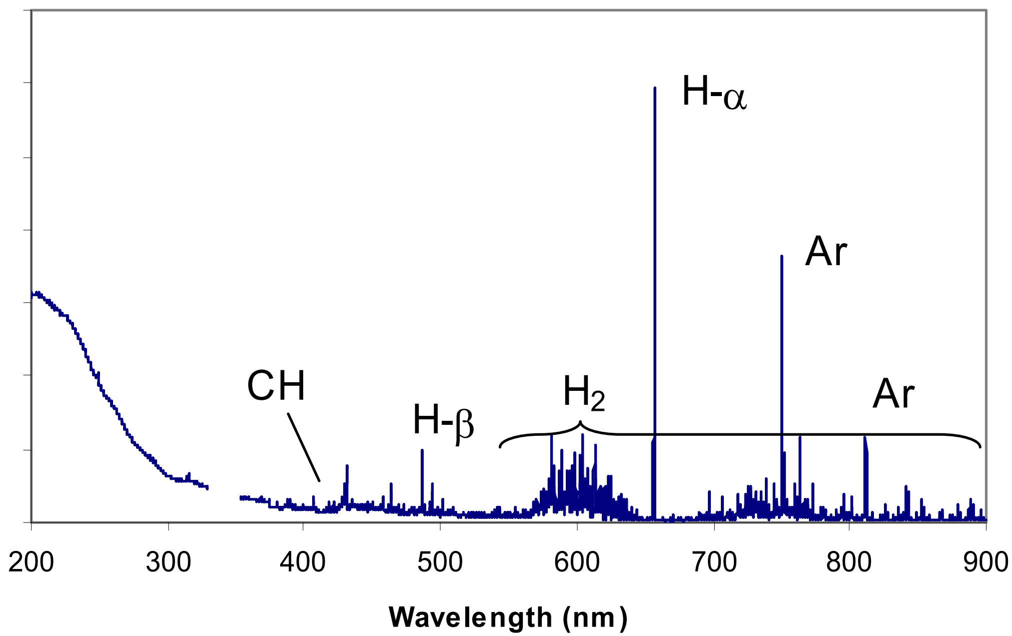
UV Absorption Spectroscopy cont.





- CH_3 densities near 10^{13} cm^{-3} (approx 1 mtorr)
- CH_3 increases with power, pressure. Saturates at high pressure
- Chemistry not seriously impacted by presence of catalyst
- Substrate heating does affect density (temperature/density relationship)

Diagnostics: Emission



• **Major features of emission: Atomic H peaks, H2 peaks, CH, continuum < 300 nm**

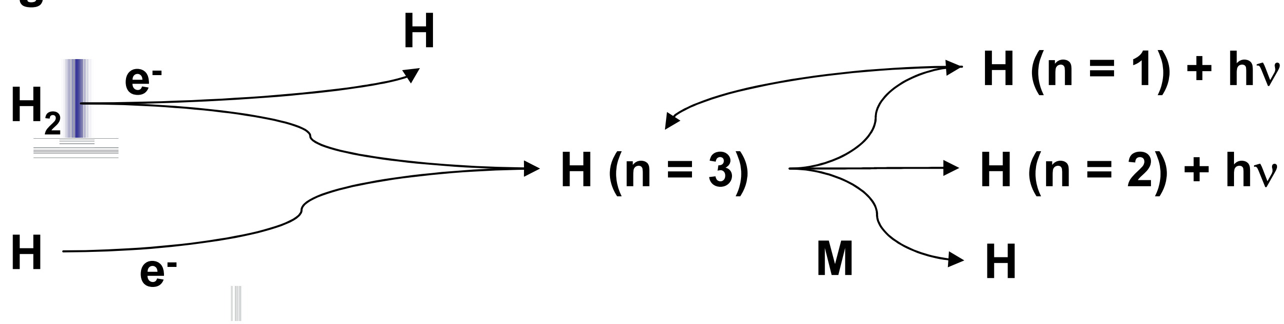
• **Ar added as actinometer: actinometry analysis not quite straightforward however**

• **Electron temperature determination from different H peak intensities ?**

• **Rotational temperature from H_2? There are thousands of H_2 peaks scattered throughout spectrum**

Emission Actinometry

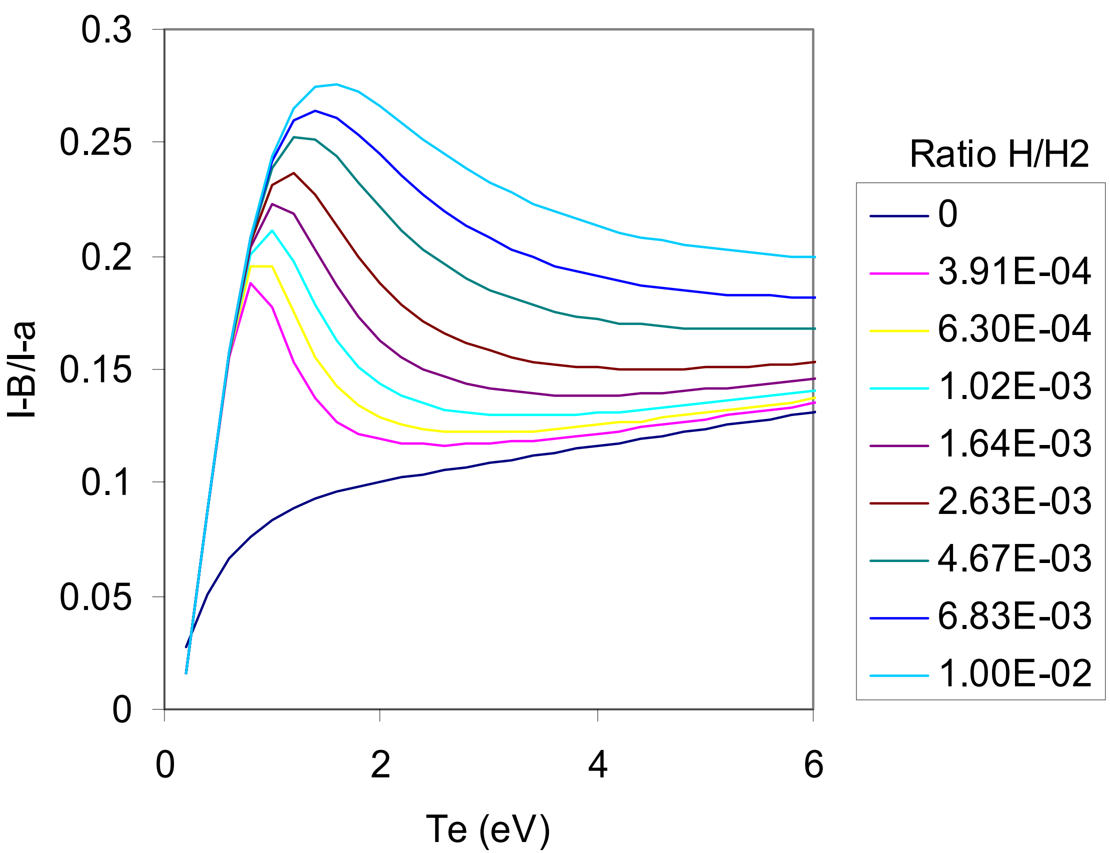
Hydrogen Emission



- **Emission is a competitive process between excitation and decay mechanisms**
  - **Dissociative vs. Direct Excitation**
  - **Radiative decay vs. collisional quenching (pressure dependent)**
  - **Radiation trapping (H density dependent)**

$$I_H \sim \frac{A_H^{3\to2}\left[k_{exc}^H\left(T_e\right)n_H + k_{diss}^H\left(T_e\right)n_{H_2}\right]n_e}{A_H^{3\to2} + A_H^{3\to1}\Lambda_{3\to1}\left(n_H\right) + \sum_i k_q n_i} \qquad I_{Ar} \sim \frac{A_{Ar}k_{exc}^{Ar}\left(T_e\right)n_e n_{Ar}}{A_{Ar} + \sum_i k_q^{Ar} n_i}$$

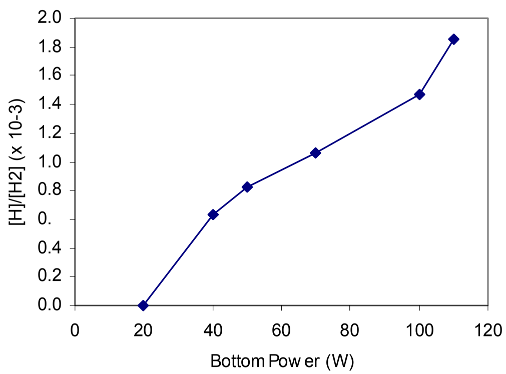
Electron Temperature through Emission

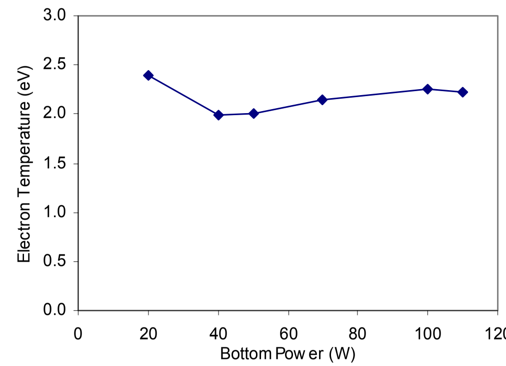


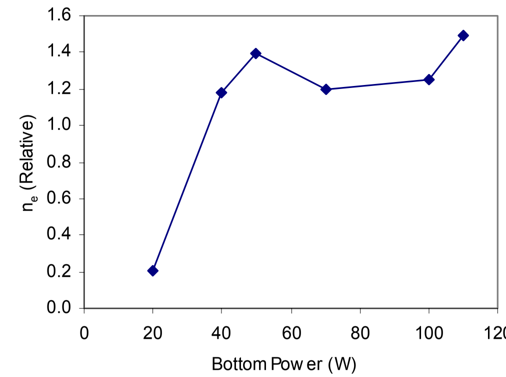
- **Ratio of H peaks varies with [H]/[H_2] ratio, T_e, pressure.**
- **Simultaneous solution of peak intensity equations for Ar, H (including all physics) allows estimate of H fraction, electron temperature and electron density**

Emission Data Analysis

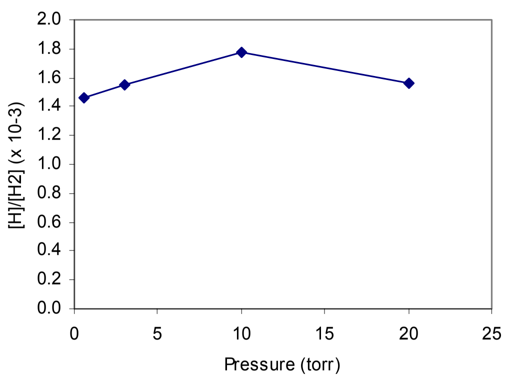
vs. Power (20-110 W)

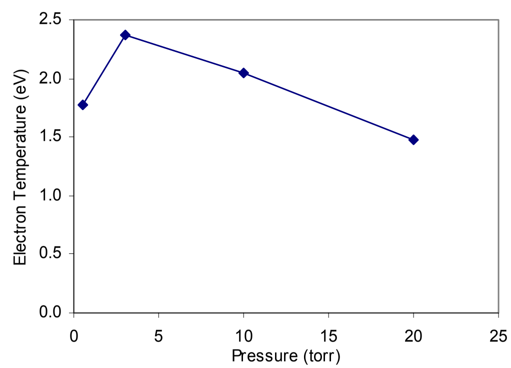


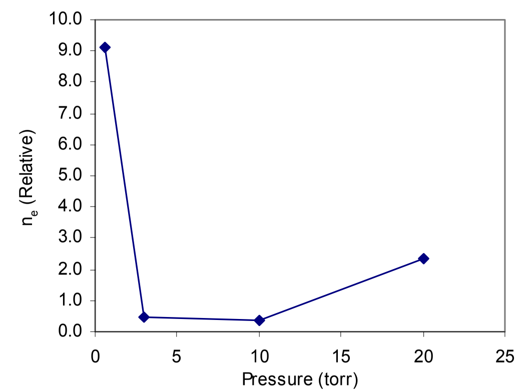




vs. Pressure (0.5-20 torr)







$[H]/[H_2]$
$0 – 2 \times 10^{-3}$

T_e
0 – 3 eV

n_e
(relative)

Summary

- Carbon Nanotubes Display remarkably physical properties that suit them to a wide array of applications
- Plasma CVD allows for better control of orientation of nanotubes/nanofibers
- Challenges remaining in Plasma CVD of Nanotubes
  - Understanding of growth mechanisms may lead to control of properties (e.g. chirality)
  - Temperatures of processing
    - Presently very high, limits use in microelectronics (esp. backend)
    - Proper measurement of substrate temperatures (how cold is "cold"?)
  - Manufacturability for mass integration
  - Understanding of relationships between controllable, measurable parameters and end products

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- Phillipe Sarazan (Field Emission)

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