Carbon Nanotubes by Microwave Plasma-Enhanced Chemical Vapor Deposition

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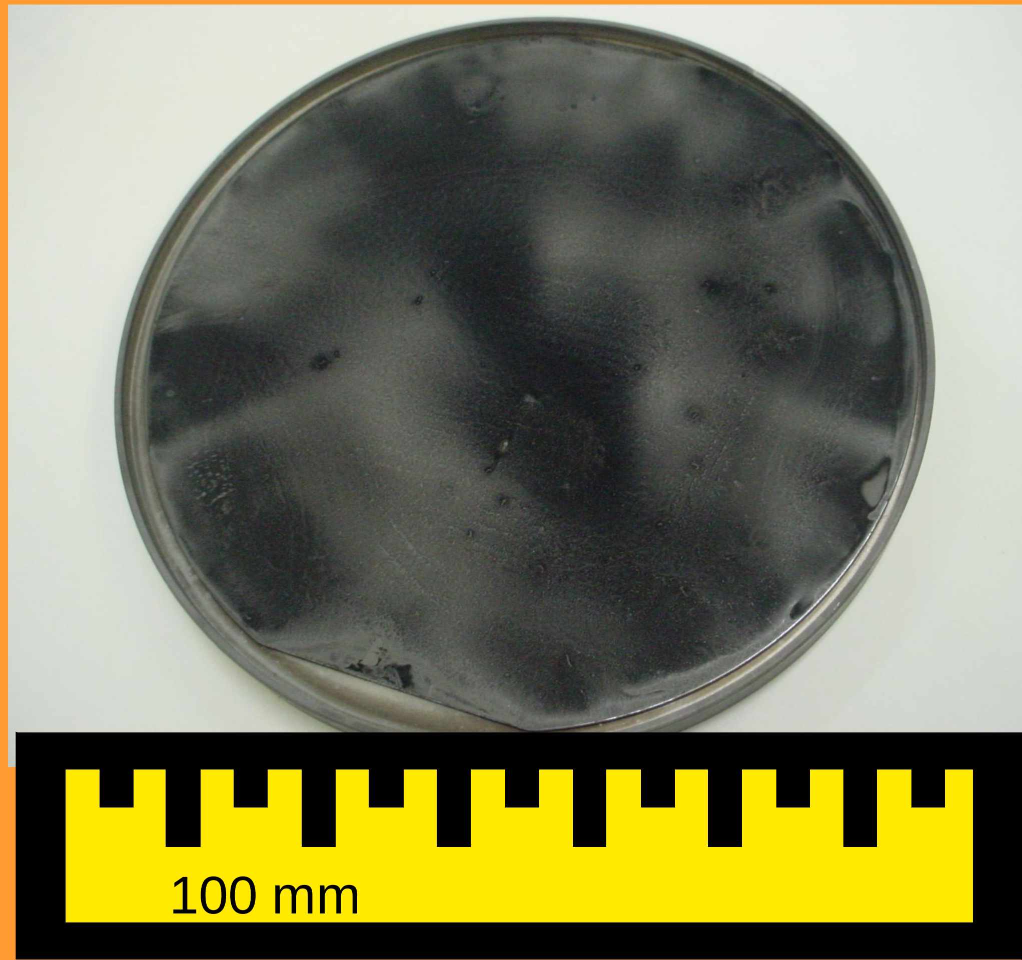
MWCNT- 100mm wafer

- Spin on multiwall catalyst- no sputtering
  - 6nm Fe particles suspended in oil
- Process:
  - 50% CH_4 in H_2,
  - 300 W,
  - 5 Torr,
  - 850 C



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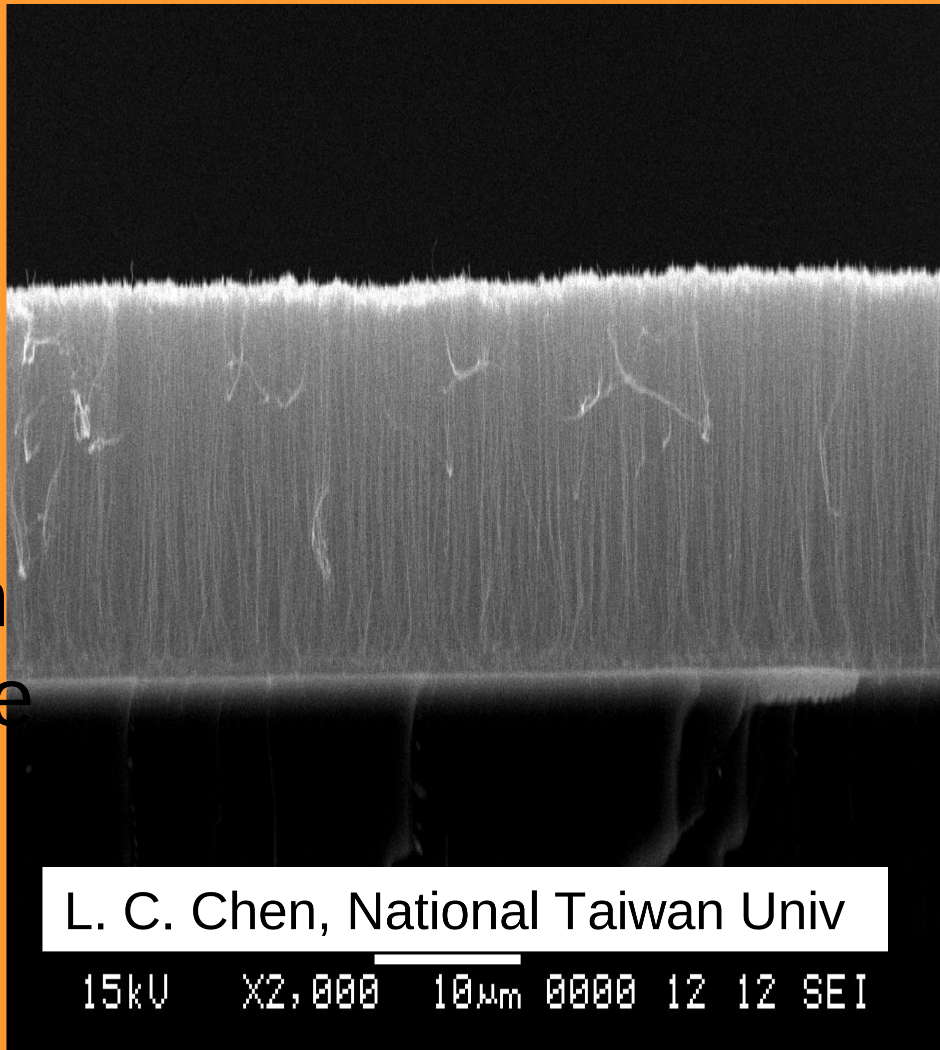
Significance of PECVD

- Plasma dissociates hydrogen/methane mix into reactive radicals mostly atomic hydrogen (H), and methyl (CH_3)
- Plasma CVD has shown vertically oriented, dense forests of carbon nanotubes.



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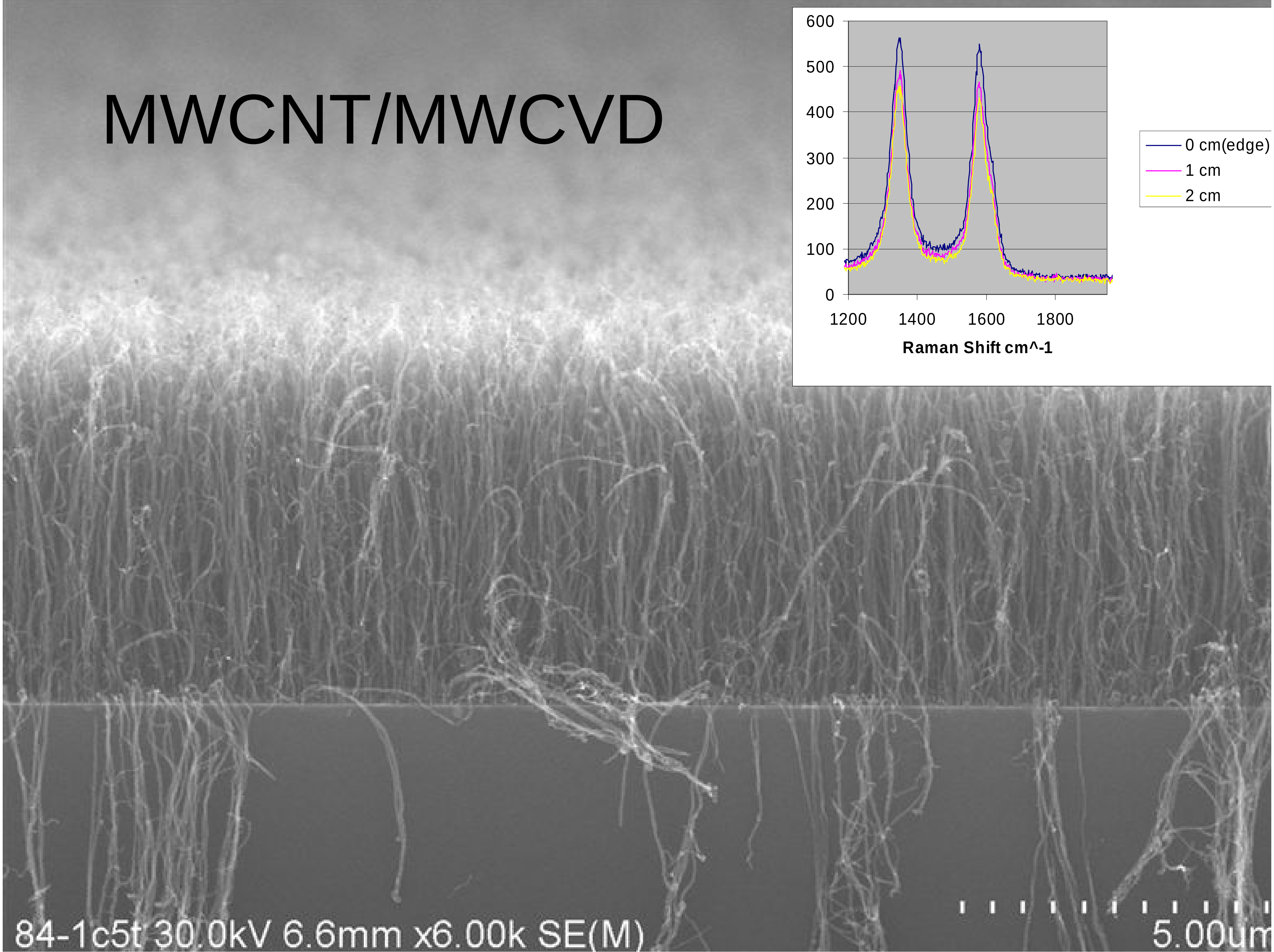
MWCNT/MWCVD


84-1c5t 30.0kV 6.6mm x6.00k SE(M)
5.00um
600
500
400
300
200
100
0
1200
1400
1600
1800
Raman Shift cm^-1
0 cm(edge)
1 cm
2 cm

Motivation

- Provide microwave plasma deposition technology to enable:
  - Large area 200-300mm
  - deposition temperature <450C.
  - Particle and impurity control
  - Reliable, reproducible
  - Semiconductor process compatible

- Reduce required growth temperatures for SWCNTs by thermal CVD from 900-1200 ^{o}C.

- MICROWAVE Plasma generates radical density characteristic of 2000C at much lower effective temperature e.g < 450C and can be highly ionized (Low pressure ECR mode) or highly neutral (high pressure mode).

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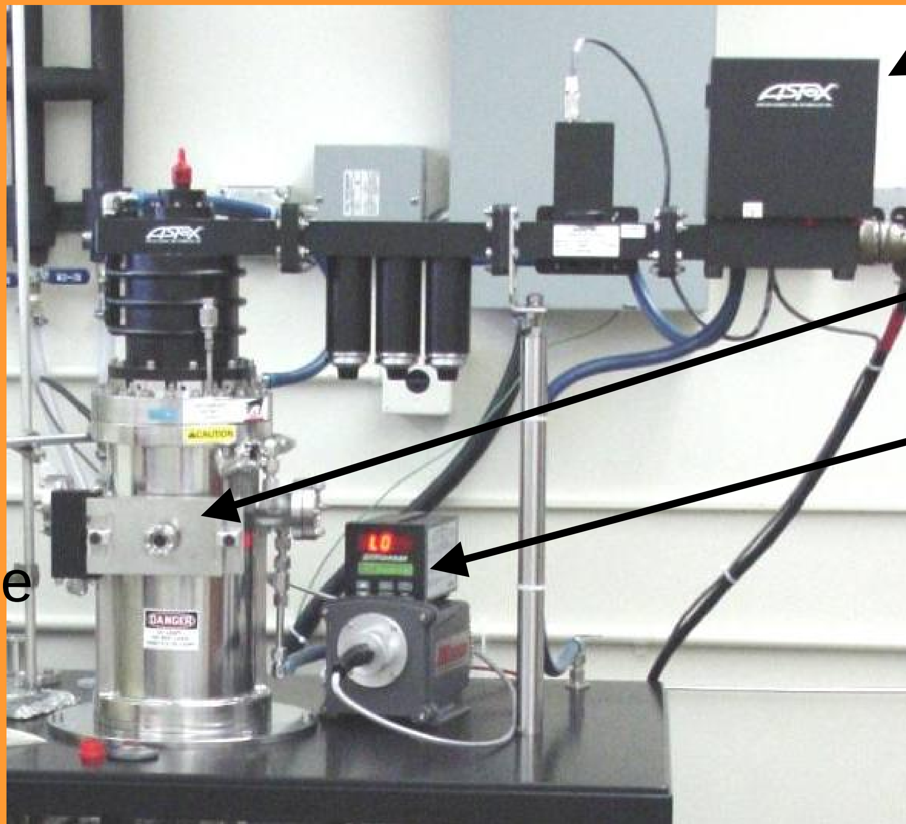
Microwave PECVD System

<u>Process Gasses:</u>
H_2: 0-1000 sccm
CH_4: 0-10 sccm

<u>Substrate DC Bias:</u>
0 – 600 V; 0 – 1.7 A

3.5 Kilowatt, 900C RF Heating of 4” Substrate

External Interlocks for Safe Hands-Free Operation



1.5kW and 2.5GHz Microwave Generator

Vacuum Chamber

Dual Wavelength Pyrometer Measures Surface Temperature

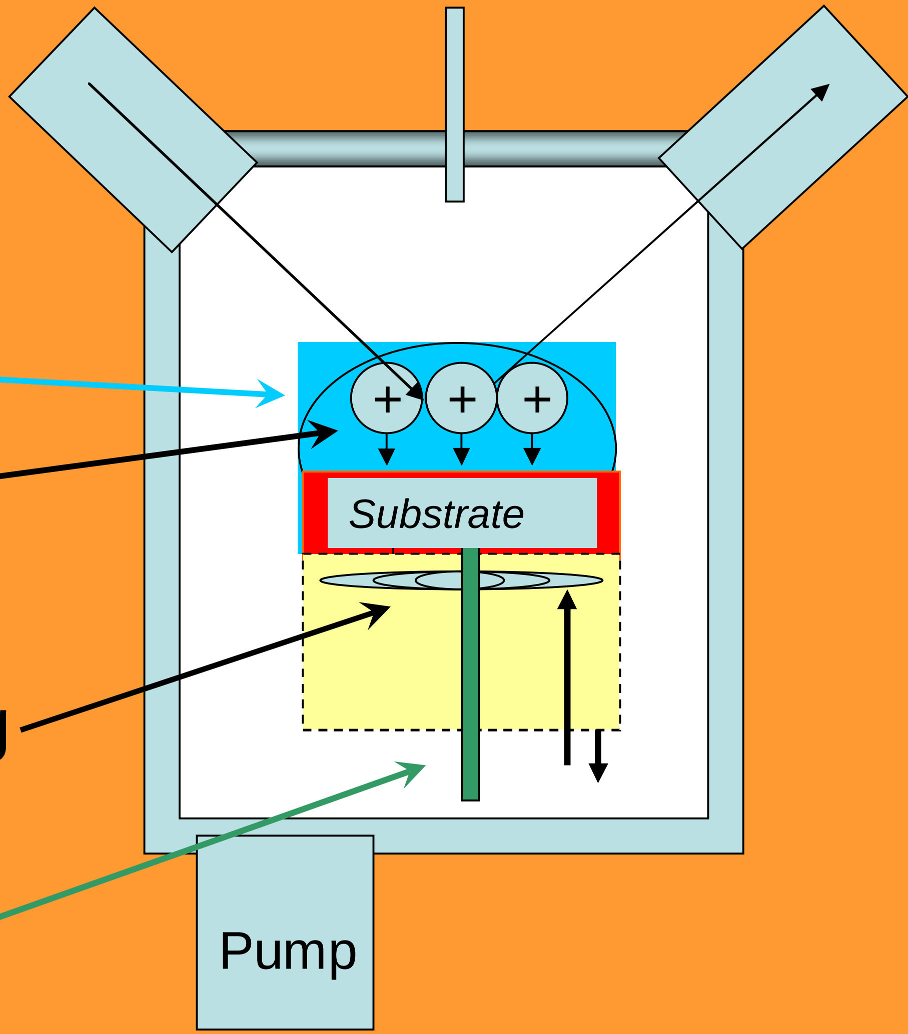
Embedded K-type thermocouple monitors stage temperature

Seki Technotron Corp.
AX5200 Series

Plasma Deposition system

- Ellipsometry, IR Pyrometry and laser interferometry

- Microwave plasma
- DC bias
- RF induction heating – water cooled coil
- thermocouple



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SWCNT Catalyst Synthesis

- Catalyst/support made by sol-gel method:
- Mix powders and form ‘Sol’:
  - Magnesium Nitrate $Mg(NO_3).6H_2O$, 0.5g
  - Cobalt Nitrate $Co(NO_3).6H_2O$,
  - Ammonium Heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$,
  - citric acid, 3g
  - distilled water
- typically 4:1 Mo:Co supported on MgO: $MgO_{(1-x-y)}Co_xMo_y$

Catalyst/support Synthesis

- Solution placed in ceramic boat and loaded into 550 ^{o}C furnace for 5 minutes in air
- Resulting bimetallic Mo:Co catalyst and MgO support was ground to a fine powder using a mortar and pestle
- 0.030 grams of powder added to 25mL and ultrasonically agitated for 3 hours before being dispersed onto silicon substrates

Synthesis Conditions

Current work

Catalyst	Temperature	Pressure	Feedstock Gasses	Plasma
Mo / Co catalyst with MgO support	**600 - 800 C**	**10 Torr**	**10:1 $H_2 : CH_4$**	**200 W**

Prior PECVD SWCNT but not MICROWAVE plasma:

1) T. Kato et a., Chem. Phys. Lett.**, 381**, 422 (2003).

2) Y. Li et al., Nano Lett., **4**, 317 (2004).

	Catalyst	Temperature	Pressure	Feedstock Gasses	Plasma
1	Fe / Co catalyst with Faujasite-type zeolite support	550 - 850 C	0.5 Torr	7 : 4 **$H_2 : CH_4$**	900 W
2	Ferratin nanoparticles and sub-monolayer e-beam evaporated iron	600 C	0.5 Torr	1 : 4 **$Ar : CH_4$**	75 W

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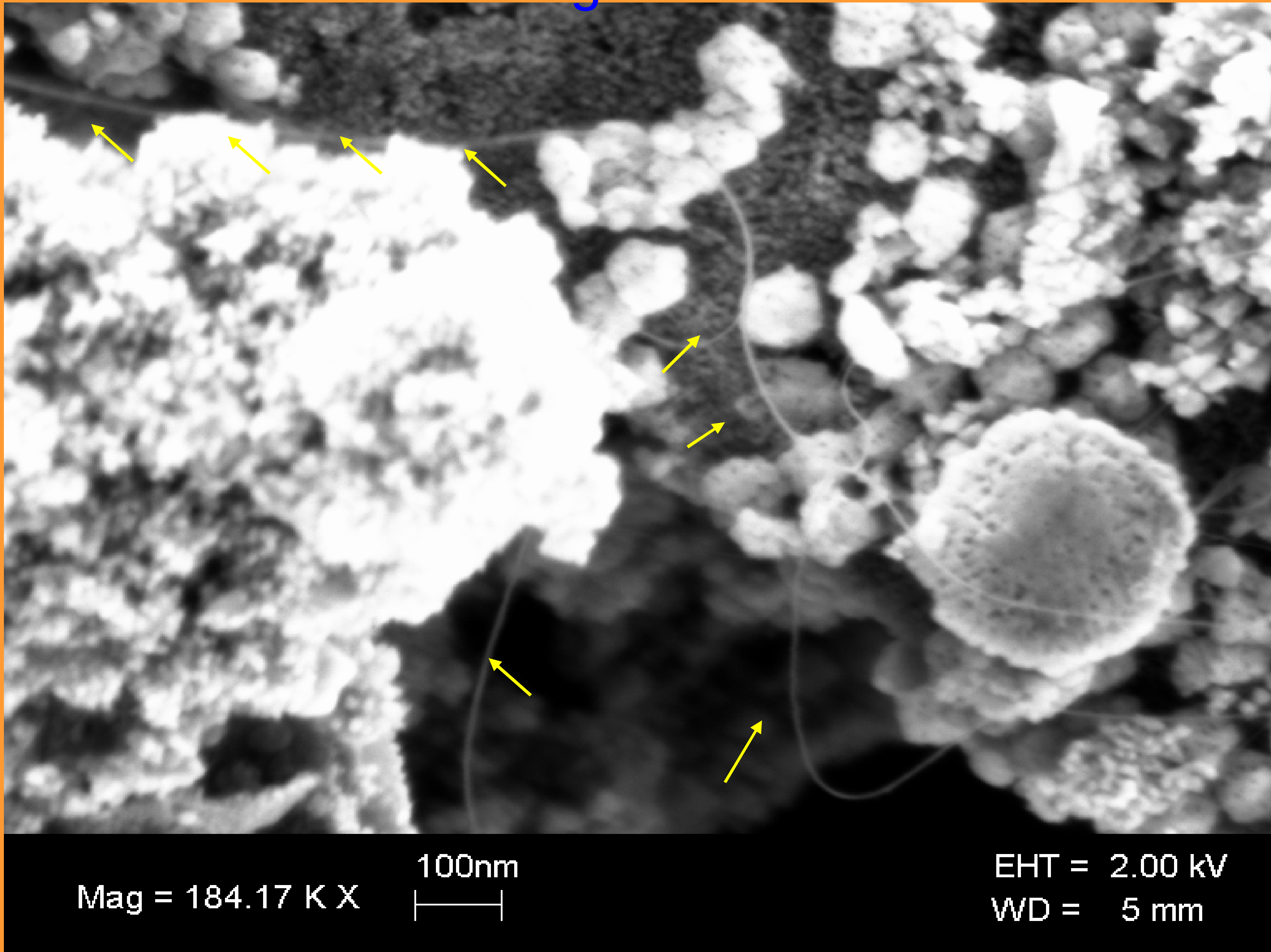
SEM – Microns long bundles of SWCNTs



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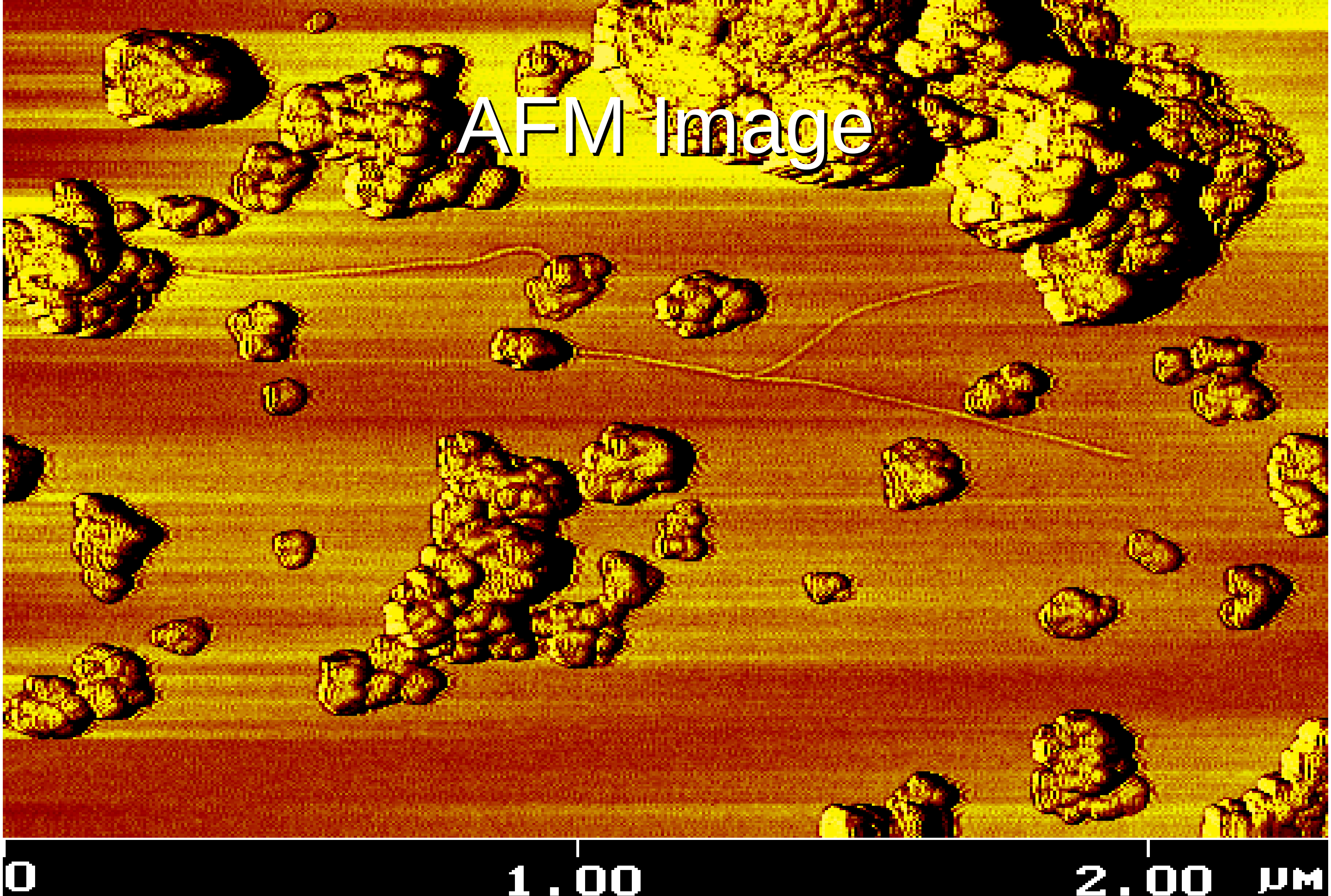
AFM Image



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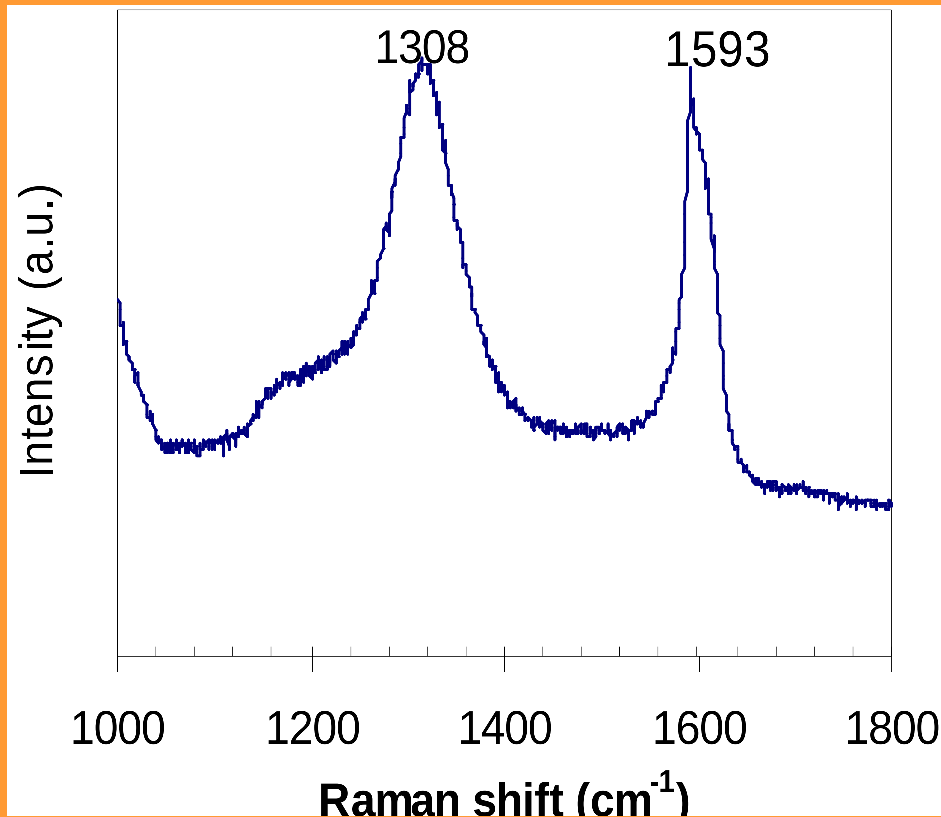
Deposition temperature 800 ºC

- D (disorder)-band at 1308 cm^{-1} – High intensity consistent with a:C or poor resonance condition
- G (graphite)-band at 1593 cm^{-1}



Horiba/Jobin Yvon LabRam system with cooled CCD (charge coupled device) detection and 632.8 nm laser excitation with 15 mW intensity at the source and approximately 1.5 mW at the sample

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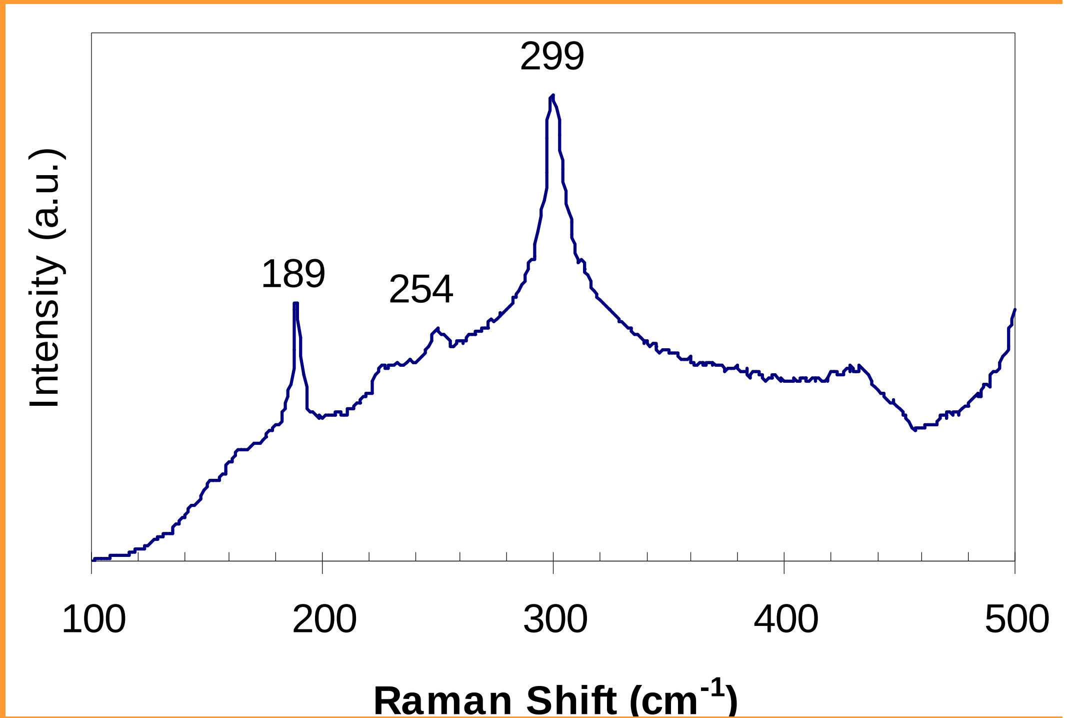
Deposition temperature 800 ºC

- Radial breathing modes at 189 and 254 cm^{-1} correspond to 1.3 and 0.9 nm diameter, respectively*
- Based on laser excitation energy and Raman shift, 0.9 nm CNTs are semiconducting while 1.3 nm CNTs are metallic**



*S. M. Bachiloet al., Science, **298**, 2361 (2002).
H. Kataura et al., Synth. Met., **103, 2555 (1999).

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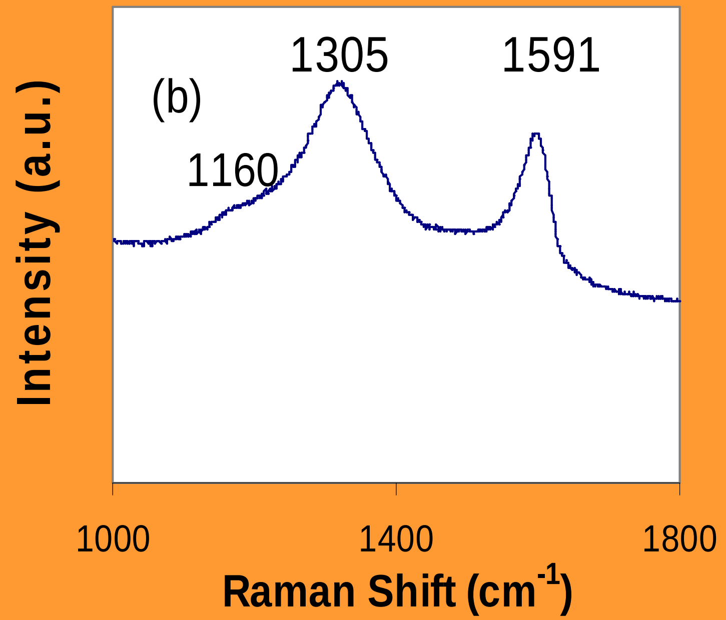
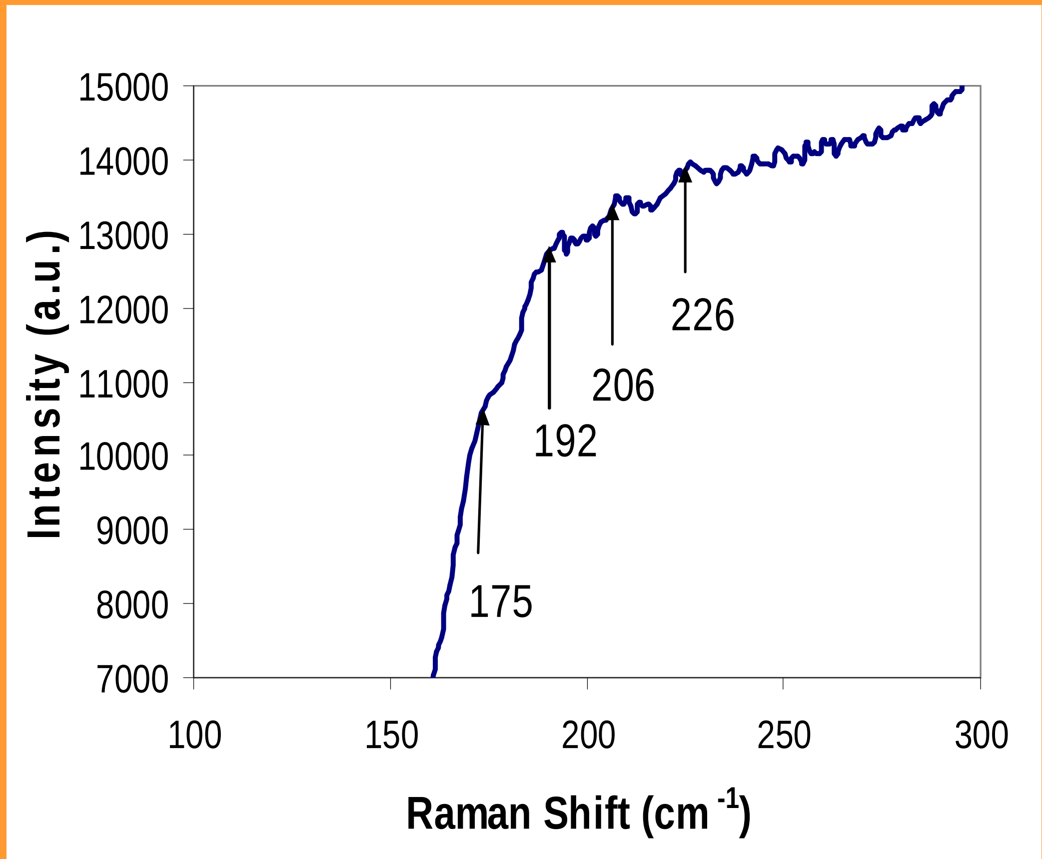
Deposition temperature 600 ºC

- Weak Radial breathing modes at 175, 192, 206, and 226 cm^{-1} corresponding to diameters from 1.2 to 1.5 nm.
- Strong D band likely a:C





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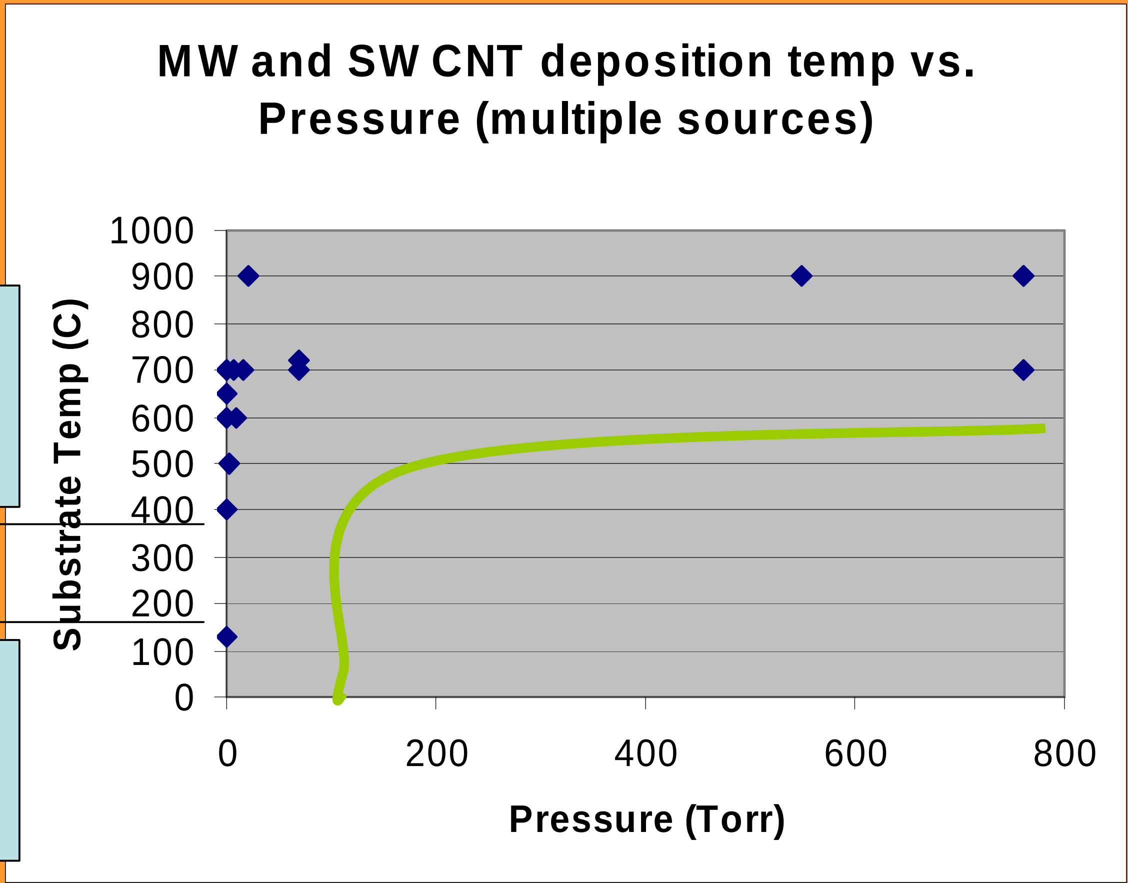
Data: ‘Diamond 2003’, 14th European Conference on Diamond, Diamond-like Materials, Carbon Nanotubes, Nitrides and Silicon Carbide

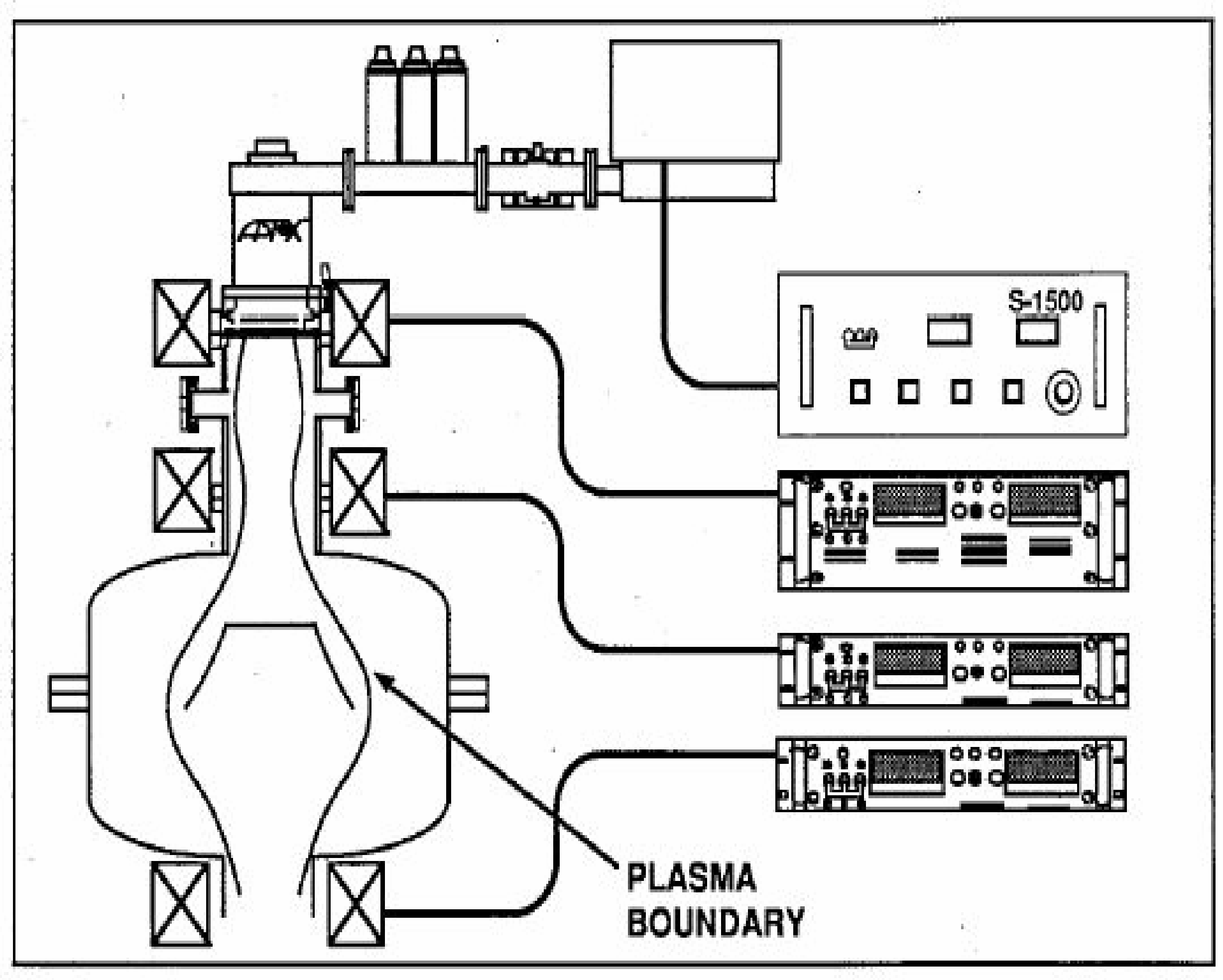


Woo, KIST, Korea, ECR-MW plasma

Robertson, Cambridge U., UK, DC plasma

Electron Cyclotron Resonance ECR

- mTorr Operation
- Room temperature deposition
- High rate
  - plasma density
  - radical flux



ECR- CNT Deposition System

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Conclusions

- Multiwall and Single wall CNT were deposited using Sekitechnotron/ASTeX microwave PECVD.
- Deposition area 100mm diameter wafers
- Both semiconducting and metallic SWCNTs were synthesized at 600C and higher temperatures.

Acknowledgements

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