FB100 Plasma Chemical Processes

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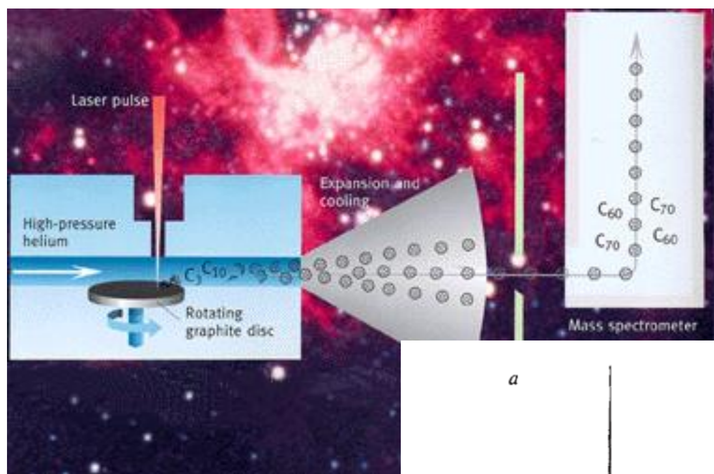
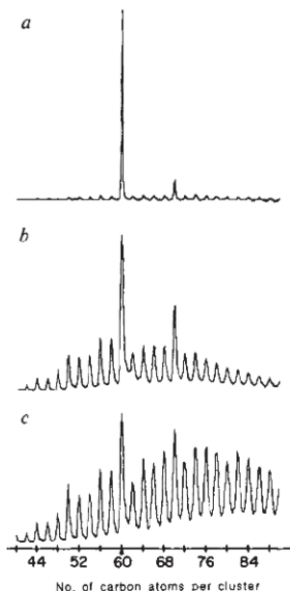
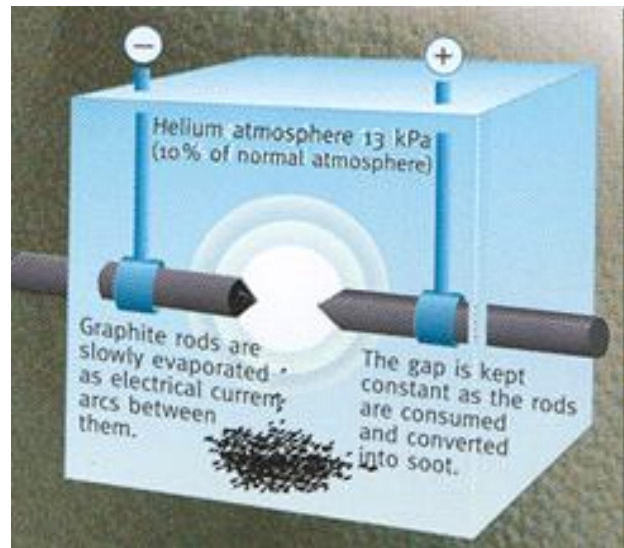
Fullerene synthesis



Laser ablation of graphite target in He atmosphere pressure ~ 100 Torr (13 kPa)
Separation in centrifuge and liquid chromatography
Fast detection by color in fullerene/toluene suspension C_{60} – wine red, C_{70} brown.





Arc discharge
He atmosphere, 13 kPa,
Arc discharge electric parameters: ~100 A, 24V.
Deposit collected on reactors cooled reactor walls
Analysis – mass spectrometry
C_{60}-720 amu, C_{70} – 840 amu.
NMR C_{60} 1 line, C_{70} 5 lines - symmetries.

Lawrence T. Scott, Methods for the Chemical Synthesis of Fullerenes, Angew. Chem. Int. Ed. 2004, 43, 4994 – 5007.

Fullerene synthesis

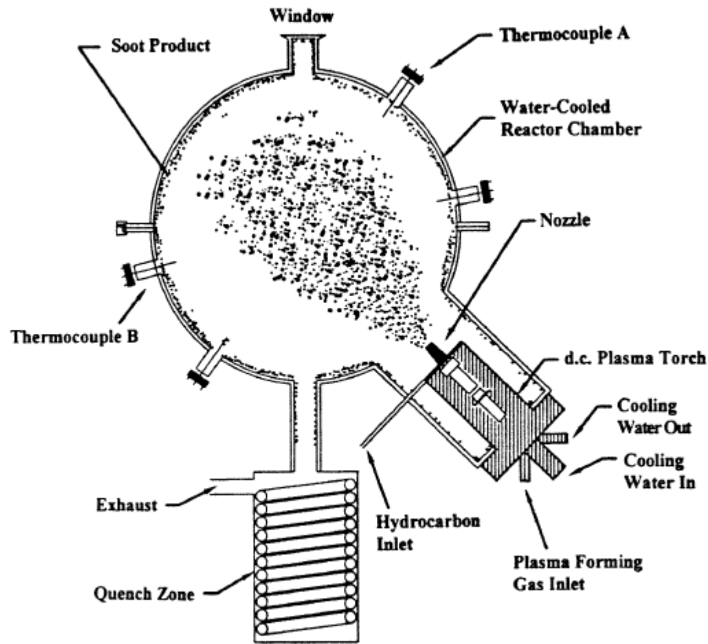


Figure 1. Set-up of fullerene synthesis reactor.

Table 1. Experimental conditions for fullerene soot production.

Torch power (kW)	55, 65
Helium flow rate (slpm)	225
C_2Cl_4 feed rate (mol/min)	0.29
He carrier gas flow rate (slpm)	20
Run duration (min)	4

J.-F. Bilodeauyx, T. Alexakisyz, J.-L. Meuniery and P. G. Tzantrizosz, Model of the synthesis of fullerenes by the plasma torch dissociation of C2Cl4, J. Phys. D: Appl. Phys. 30 (1997) 2403–2410.

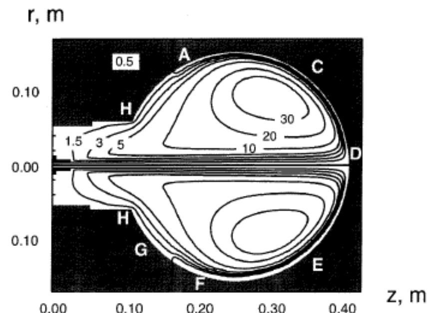


Figure 3. Isocontours of the helium stream function, normalized by the torch flow rate.

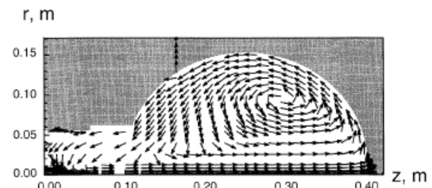


Figure 4. Direction of velocities in the reactor.

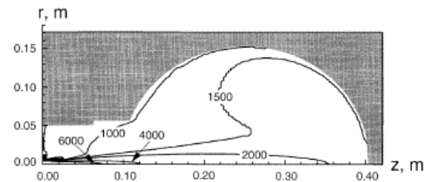


Figure 5. Isocontours of temperature (K).

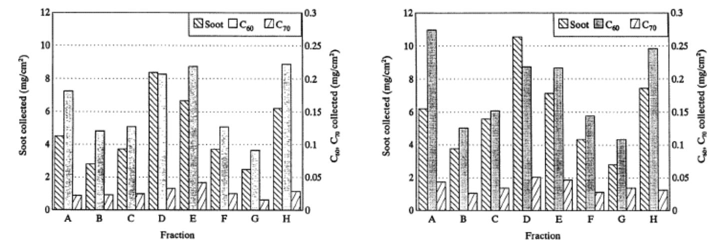
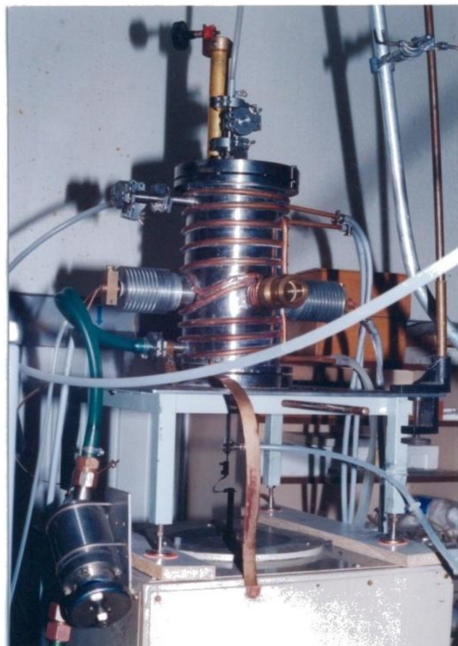
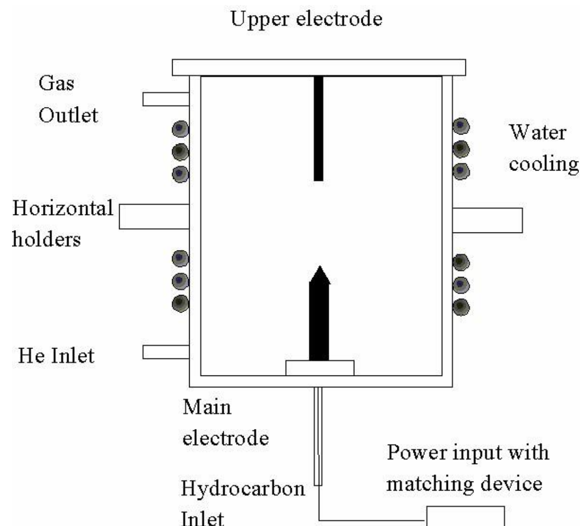


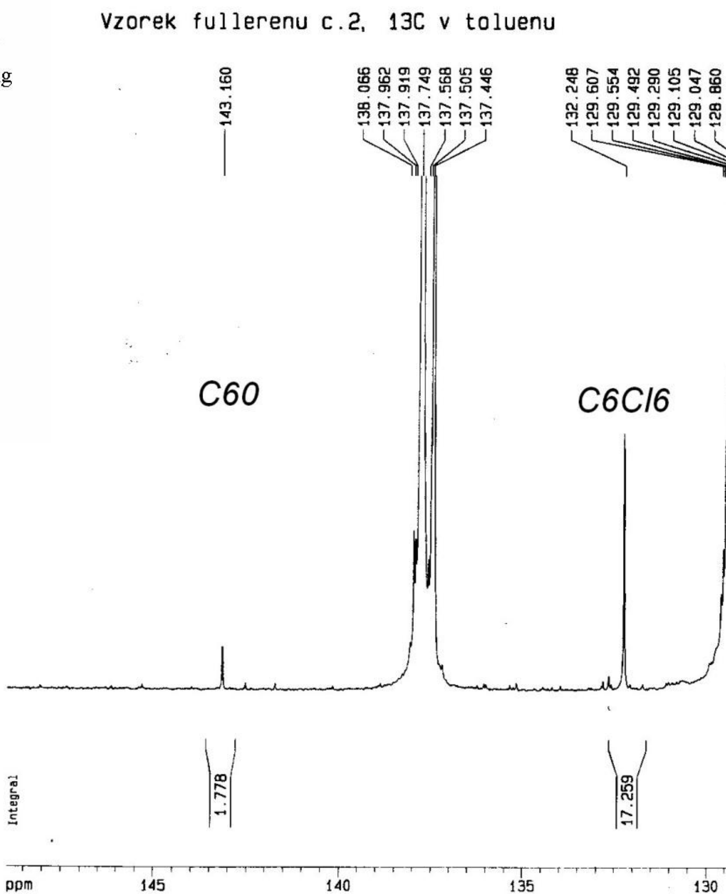
Figure 9. Collection rates of total soot, C_{60} and C_{70}, power = 55 kW.

Figure 10. Collection rates of total soot, C_{60} and C_{70}, power = 65 kW.

Fullerene synthesis by decompostion of CCl4 in rf dicharge in helium atmosphere

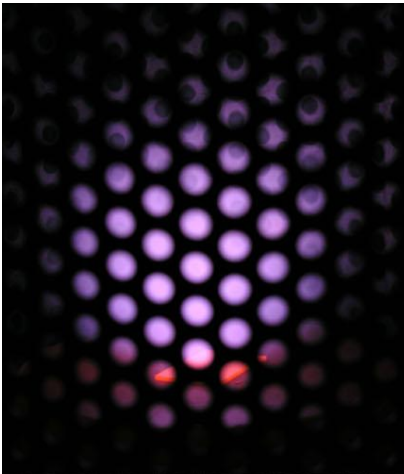


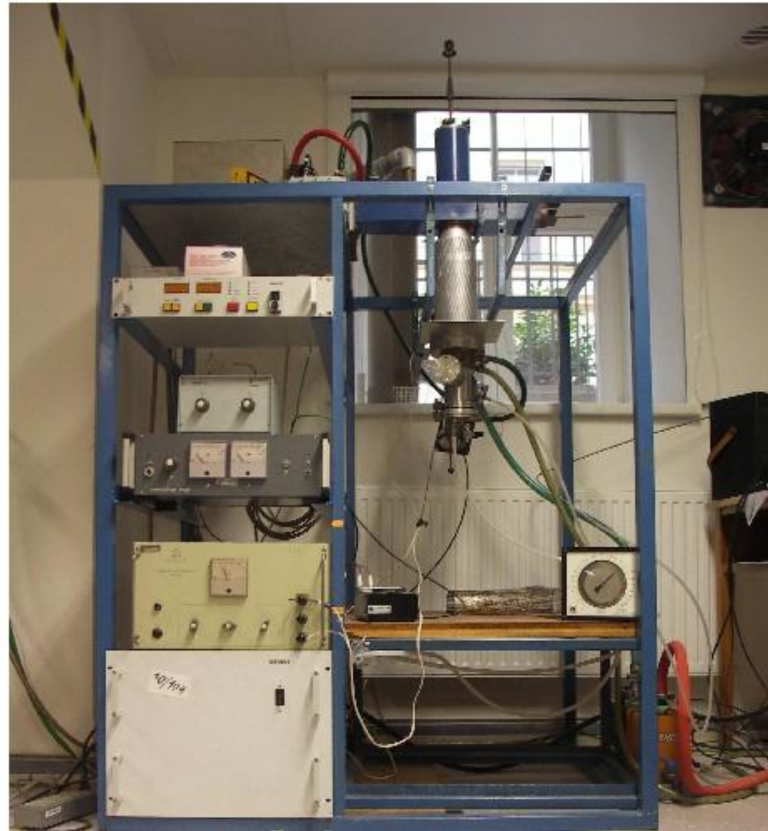




Stainless steele water cooled reactor 20 cm diameter
25 cm height
Precursors toluene, benzene, CCl_4 (0,2 – 0,3 cm^3/min)
RF power - 27 MHz,2 kW, dep. time 10 -30 minut
Helium atmosphere 60 – 150 Torr

Growth of diamond layers – ultrananocrystalline diamond



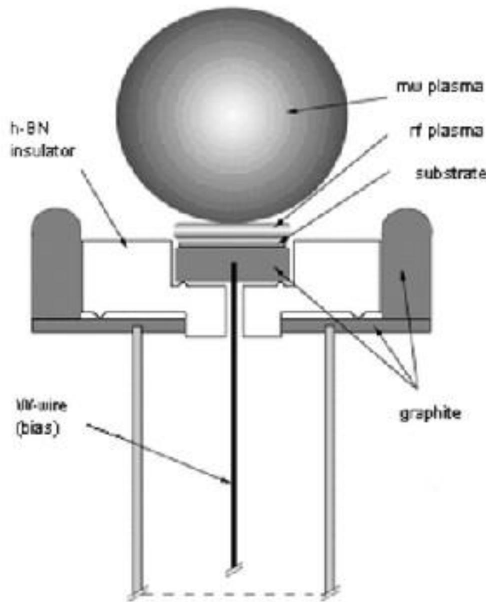


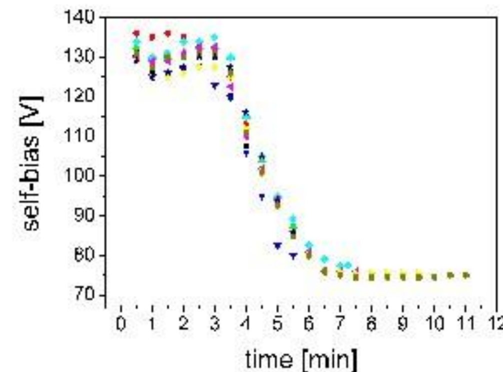
- microwave power (2.45 GHz) 900–950 W
- pressure 7.5 kPa
- substrate temperature 800–950 °C
- CH_4/H_2 gas mixture (2 and 9.4 % of CH_4)
- deposition time 1–40 min
- polished Si, no pretreatment

Nucleation of ultra-nanocrystalline diamond

Bias Enhanced Nucleation – BEN in-situ nucleation density ~ 10^{12} cm^2

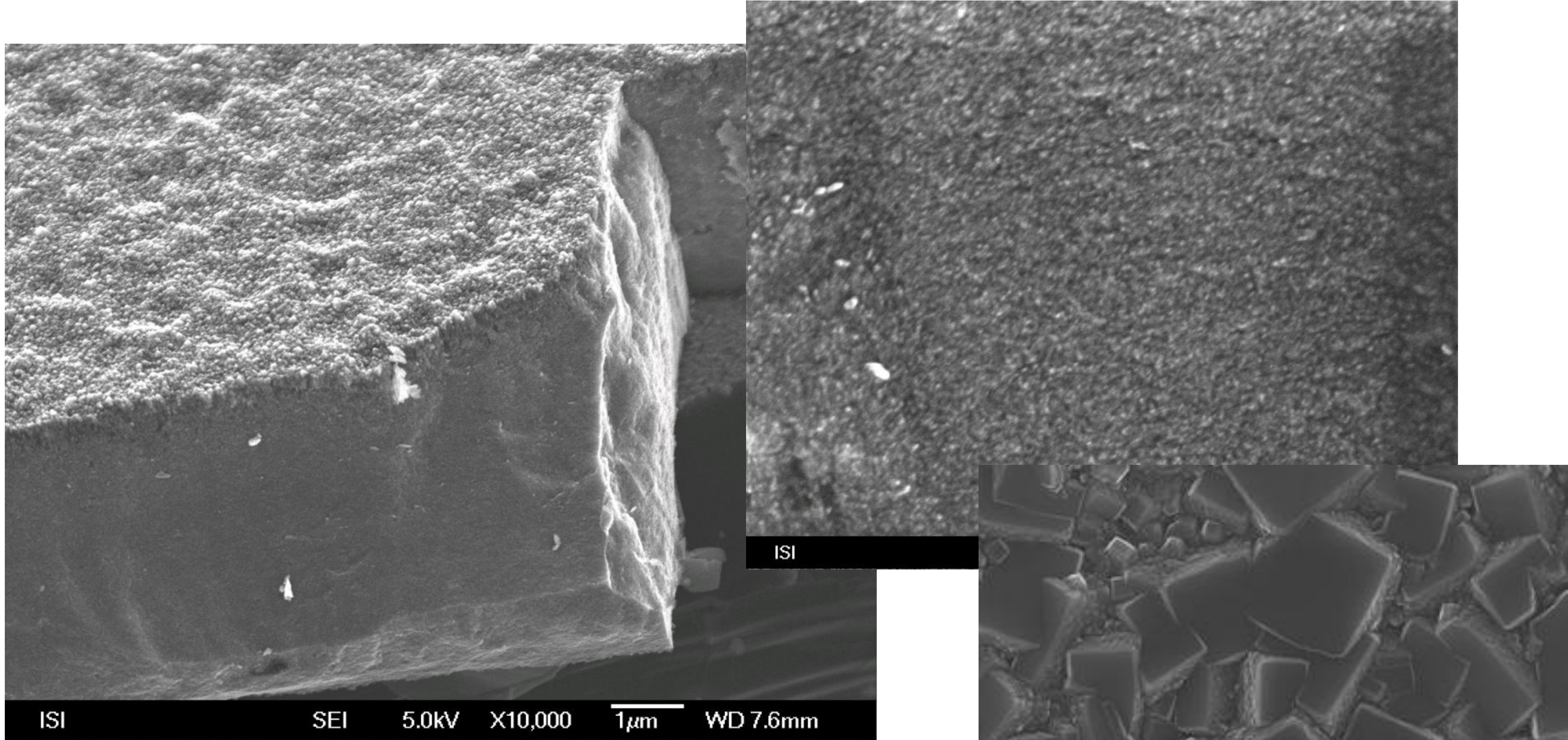
- BEN is traditionally used with DC bias and during nucleation phase
- our approach combined MW (900 W) and RF (35 W) discharges, DC bias was a result of RF sheath properties
- ion bombardment during the deposition phase was necessary for high renucleation rate





Ultra-nanocrystalline diamond

High concentration of CH_4 – 10 % against 1-2 % traditionally used, 2x lower layer roughness



H/N/C mixtures – T. Frgala, PhD Thesis
Preferential growth of <100> orientation

Nucleation of ultra-nanocrystalline diamond

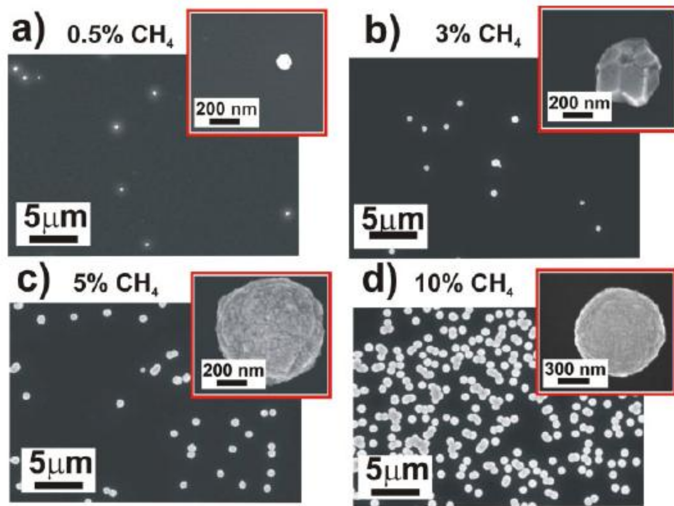


Figure 1 SEM images of the Si substrates nucleated for 1 h in the hot plasma system at different ratios of CH_4 to H_2 (inserted images show details of the diamond cluster morphology).

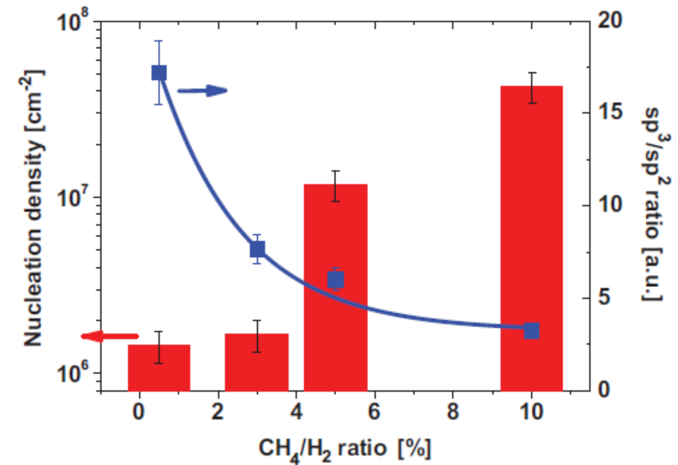


Figure 2 Nucleation densities of the samples nucleated in the hot plasma (red columns) and corresponding diamond (sp^3) to non-diamond (sp^2) ratio (blue curve) calculated from Raman spectra at various methane concentrations.

Astex type reactor MW power 2500 W, pressure 50 mbar, and process time 1 h. Si substrate (10 x 10 mm) is 1-2 cm from plasma ball and is heated by plasma to 750 C.

The diamond can also be nucleated from CO_2/H_2 mixture in the remote mw plasma reactor. The nucleation density is higher and sp^2 content lower but time of nucleation is 15 hours. At high CO_2 concentrations (40 %) the diamond seeds are etched away.

Tibor Izak, Alexey Sveshnikov, Pavel Demo, and Alexander Kromka, Enhanced spontaneous nucleation of diamond nuclei in hot and cold microwave plasma systems, Phys. Status Solidi B 250, No. 12, 2753–2758 (2013).

Low temperature diamond synthesis

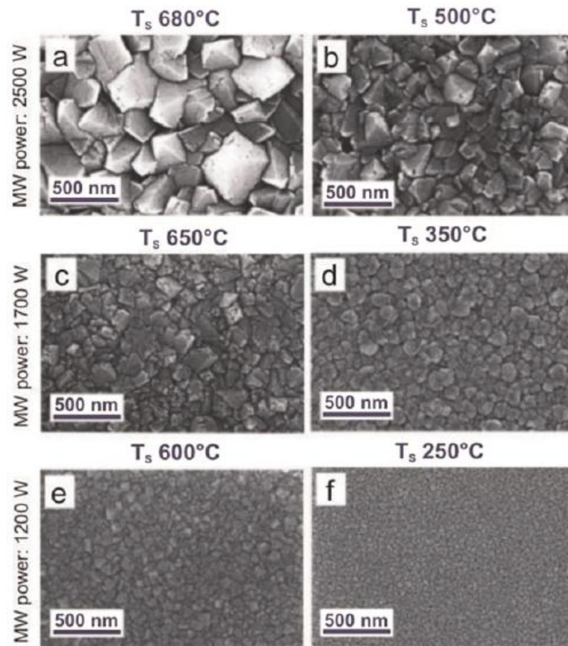
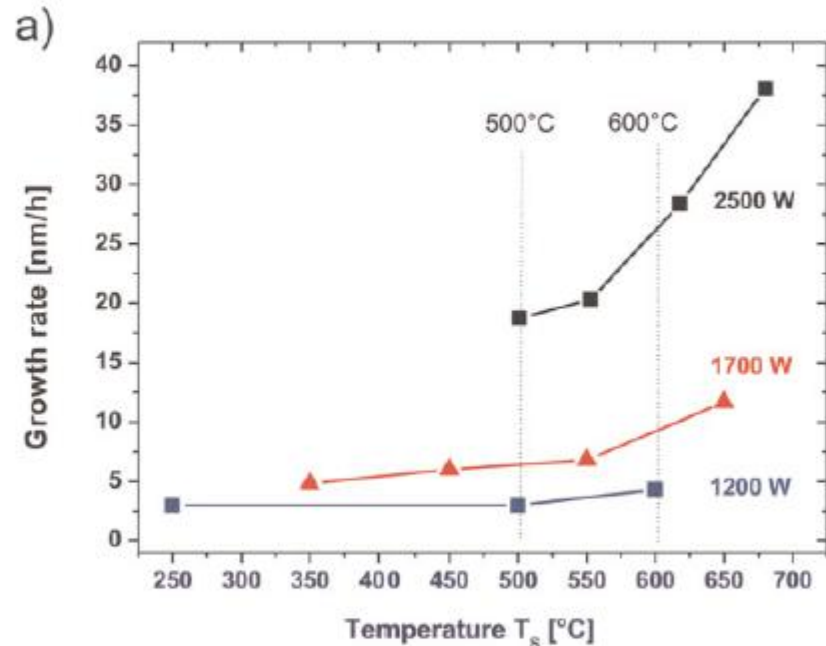


Figure 1 (online colour at: www.pss-b.com) Top-view SEM images of diamond film morphology deposited at different substrate temperatures (T_S); upper row: diamond films deposited at 2500 W, middle row: 1700 W, bottom row: 1200 W of MW power. The right column represents the minimal substrate (or deposition) temperature at corresponding MW power without external ohmic substrate heating.



Diamond layer ultrasonically seeded by ultradispersed detonation diamond (UDD) powder on Si (10x10 mm). Pressure 0.1 mbar, deposition time 15 h, gas mixture 2.5% of CH_4 and 10% of CO_2 in H_2. Temperature regulated by plasma power and table heater.

Tibor Izak, Oleg Babchenko, Marian Varga, Stepan Potocky and Alexander Kromka, Low temperature diamond growth by linear antenna plasma CVD over large area, Phys. Status Solidi B 249, No. 12, 2600–2603 (2012).

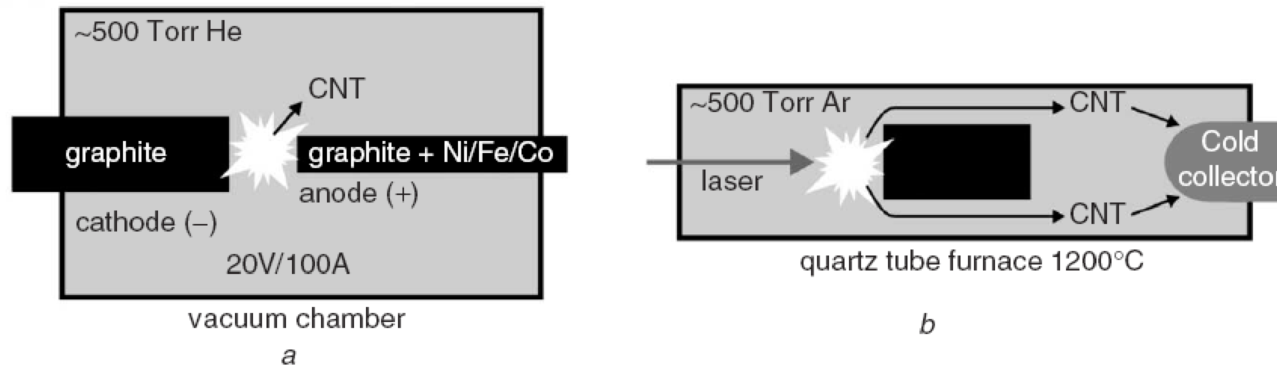
Carbon nanotubes synthesis

High temperature methods

-Arc discharge between grapthite electrodes

-Graphite target laser ablation

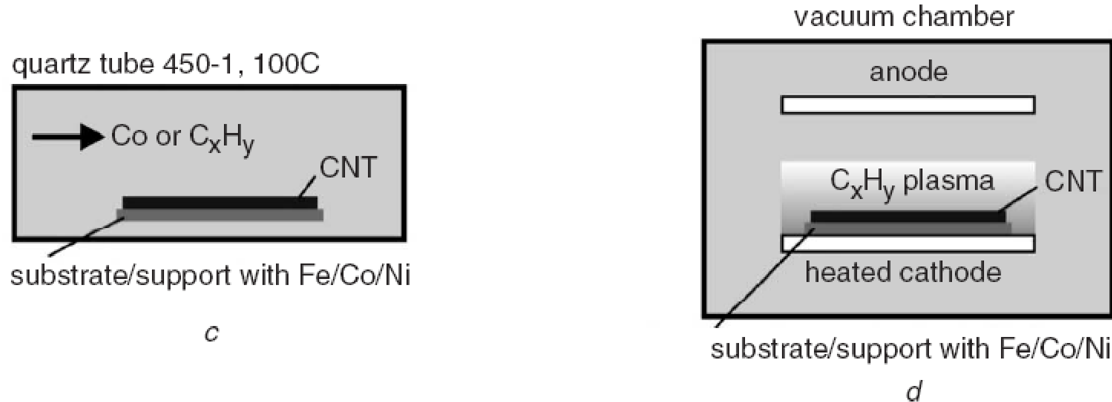
-high temperature (3500 °C), short growth time ms, SWCNTs require catalyst – transition metal (Fe,Ni,Co,Mo), carbon diffuses into catalytic particle and precipitates out in the form of nanotube, several nanotubes can growth from one particle



K.B.K. Teo, R.G. Lacerda et al.. "*Carbon Nanotube Technology for Solid State and Vacuum Electronics*" IEE Proceedings in Circuits, Devices and Systems (Nanoelectronics issue) **151**, 443 (2004).

Carbon nanostructures synthesis

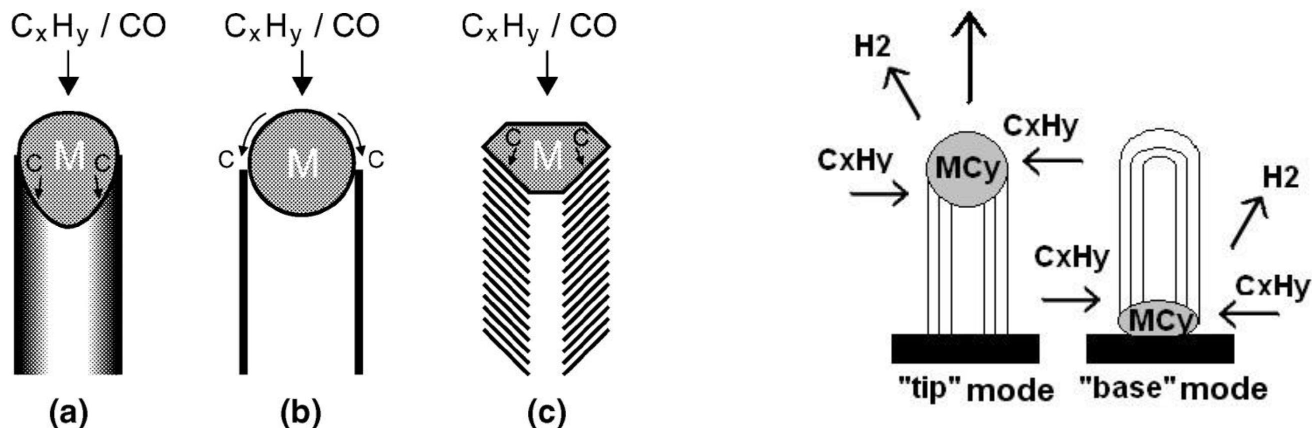
Low temperature methods *– thermal CVD, PECVD (rf, mw, dc, hf)*
hydrocarbon decomposition in presence of catalyst
Temperature 500-1200 °C, longer deposition times- minutes even hours, transition metal catalyst plays significant role and serves as template for nanotube growth
PECVD *– lowering deposition temperature, compatibility with microelectronics industry, electric field vertical alignment (0.15 V/μm)*



M. Meyyappan, L. Delzeit, A. Cassell, D. Hash. *Plasma Sources Sci. Technol*. **12**, 205 (2003), M. Meyyappan, J. Phys. D: Appl. Phys. **42** (2009) 213001

Catalyst in PECVD

- *Transition metal catalyst – Fe,Co,Mo,Ni or combination - finite solubility in C leads to CNTs growth by diffusion, saturation and precipitation mechanism*
- *Catalyst must be in the form of particles, particles and their surface atoms have high mobility in nm scale even if the metal is in solid state and can behave like liquid*
- *in lower temperature surface diffusion dominates, in higher volume diffusion*
- *Support catalyst (evaporation, sputtering, wet catalyst, colloids etc.) or floating catalyst – decomposition of organometallics*
- *Catalyst poisoning effect – covering the particle with amorphous carbon*



K. B.K. Teo, C. Singh, M. Chhowalla, W. I. Milne, Encyclopedia of Nanoscience and Nanotechnology, Vol. 10, Eds. H.S. Nalwa, American Scientific Publishers, Los Angeles, 2003

CNTs growth in PECVD systems

DC glow discharge resistively heated carbon electrode – cathode with the sample (Si/SiO_2 buffer layer and Ni catalyst 0.5-20 nm) Anode (2 mm diameter by 1 cm length copper wire) was 2 cm from cathode. Sample heated to 750 C under H_2 and held at this temperature for 15 minutes after that 200 sccm of NH_3 was introduced to pressure of 465 Pa. The deposition was carried out in mixture of C_2H_2 and NH_3 for 15 minutes.

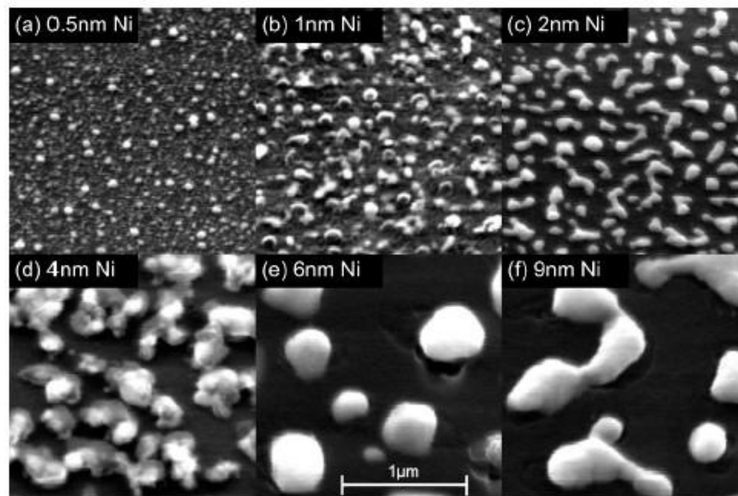


FIG. 1. SEM photographs of Ni films with varying thicknesses deposited using magnetron sputtering on 50 nm of ECR SiO_2 after annealing at 750 °C in 20 Torr of H_2 for 15 min.

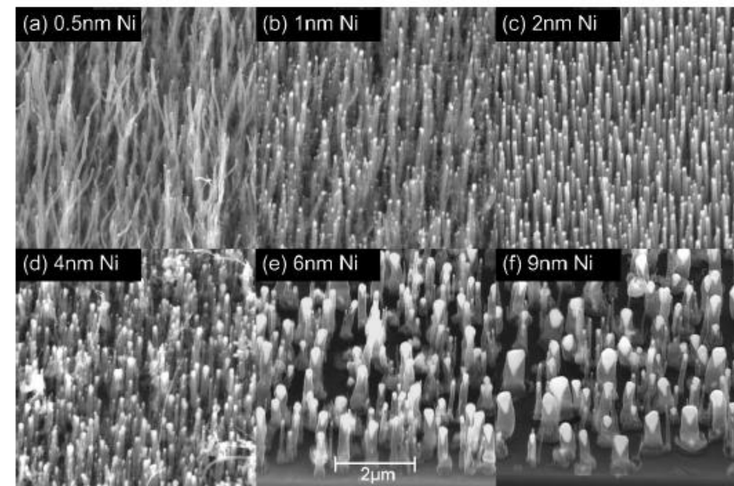
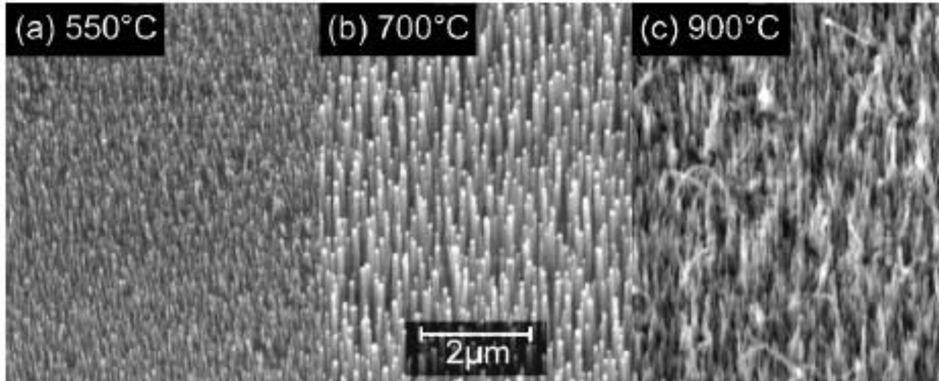
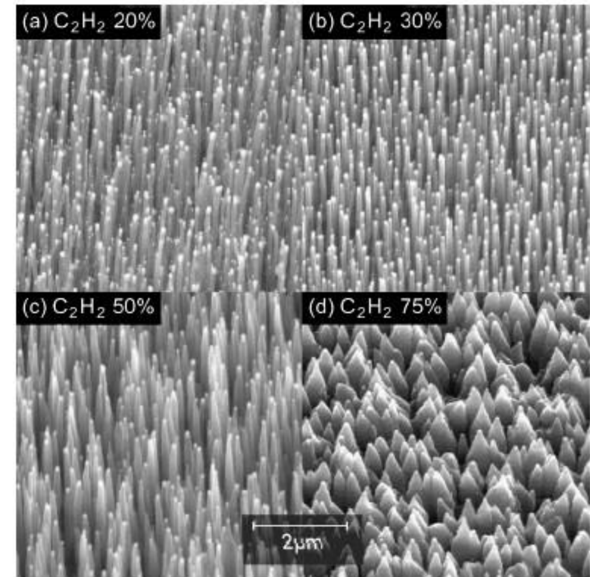


FIG. 4. SEM photographs of nanotubes grown on Ni layers of various initial thicknesses shown in Fig. 1. Standard growth conditions (bias voltage = −600V, C_2H_2:NH_3=75:200, time=15 min) were used for all depositions.

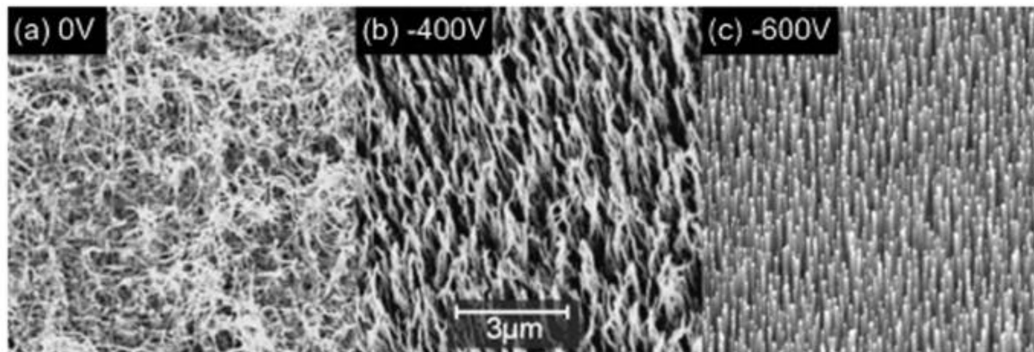
Chhowalla et al., Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor depositionJ. Appl. Phys., Vol. 90, No. 10, 2001,5308

CNTs growth in PECVD systems





NH_3 flow at 100 sccm



2 nm Ni catalyst

CNTs growth in PECVD systems

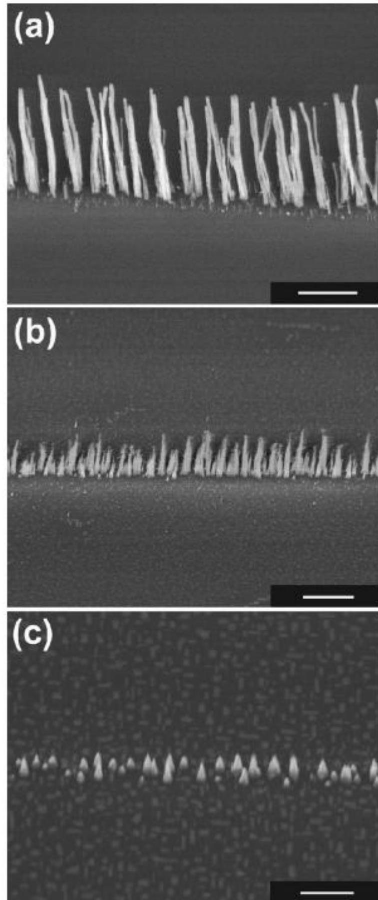


FIG. 2. SEM photographs of vertically aligned CNFs grown from e-beam patterned Ni lines at (a) 500 °C, (b) 270 °C, and (c) 120 °C. A tilt angle of 40° was used for imaging [scale bars: (a) and (b) 1 μm and (c) 500 nm].

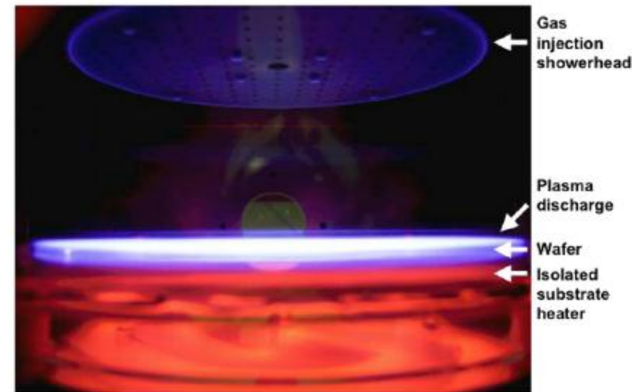


Figure 4. Wafer scale PECVD reactor. (Image courtesy of K B K Teo.)

DC discharge between the heater stage (cathode) and the gas shower head (anode), 2 cm above the stage was ignited by applying a fixed voltage of 600 V.

$Si/SiO_2/Ni$ (6 nm) substrate

Samples annealed in 120 Pa NH_3 for 15 minutes. Deposition carried out in $C_2H_2:NH_3$ 50:200 sccm at 150 Pa for 30 minutes.

S. Hofmann, C. Ducati, and J. Robertson, B. Kleinsorge, Low-temperature growth of carbon nanotubes by plasma-enhanced chemical vapor deposition, Appl. Phys. Lett., Vol. 83, No. 1, 135.

CNTs growth in PECVD systems

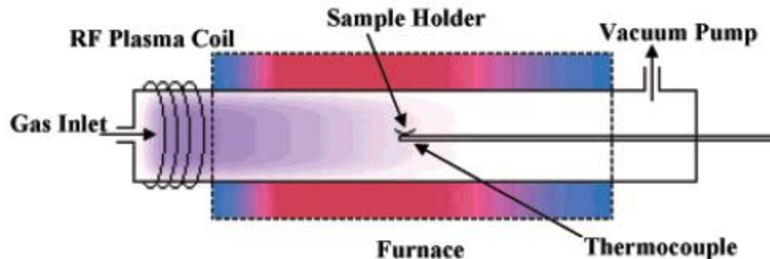
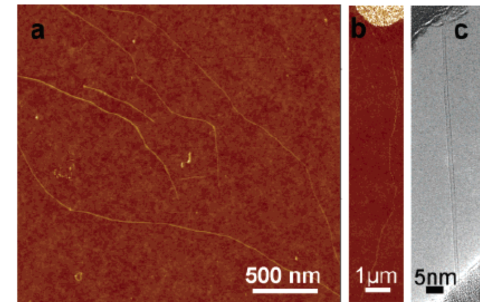


Figure 1. Schematic drawing of the PECVD reactor used for the synthesis of SWNTs.



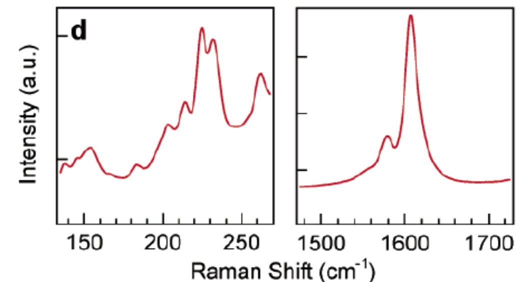


Figure 2. SWNTs grown at 600 °C. (a) AFM image of nanotubes grown from low-density ferritin deposition on a SiO_2 substrate. (b) AFM image of a tube grown from an iron-film island (nominal thickness 1 Å). (c) TEM image of an as-grown SWNT (diameter = 1.2 nm). (d) Left panel: Raman data for the RBMs of SWNTs grown by PECVD. Right panel: The G-band of SWNT vibration (clear peaks at 1578 and 1608 cm^{-1}, due to splitting of the in-plane graphene mode at 1580 cm^{-1} from graphene to tubes). Raman data here was obtained with a SWNT mat grown on a uniform Fe film deposited on SiO_2, and the data were sum of 75 spectra recorded over the sample.

RF (13.56 MHz) capactive coupled discharge with 4 inch quartz tube. Sample Si/SiO_2/Fe Ferritin or 0.1 nm Fe by electron beam evaporation of Fe 40 cm from the coil in the furnace. Sample annealed in in Ar to 600 °C and then 60 sccm Ar/CH4 (80%) at 67 Pa. Plasma was turned on for 3 minutes with 75 W power.

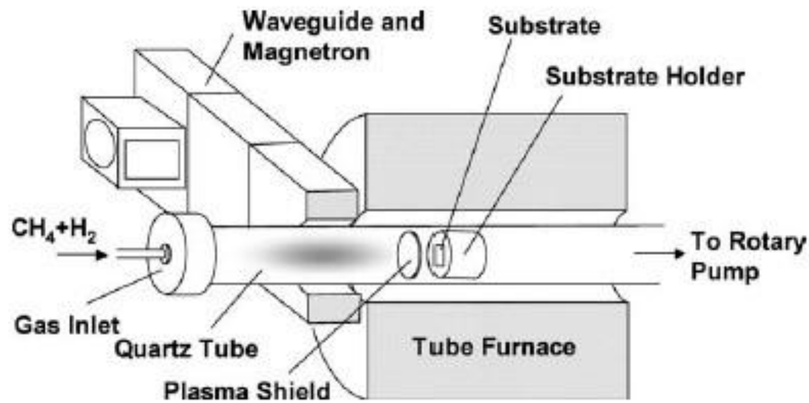
No CNTs without the plasma.

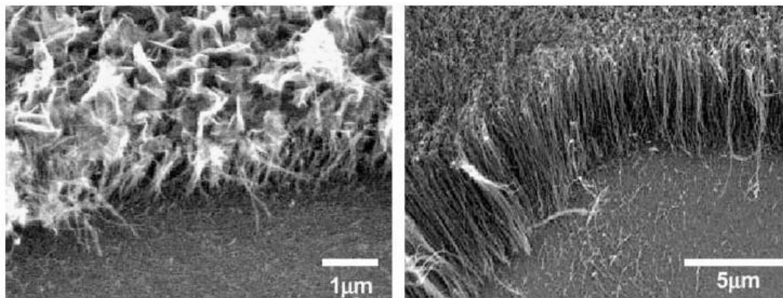
Y. Li et .al. , Preferential Growth of Semiconducting Single-Walled Carbon Nanotubes by a Plasma Enhanced CVD Method, Nano Lett., Vol. 4, No. 2, 2004, 317.

Table 1. Summary of the Diameter Distributions and Percentages of s- and m-SWNTs Grown by PECVD (with several batches of devices) and HiPco

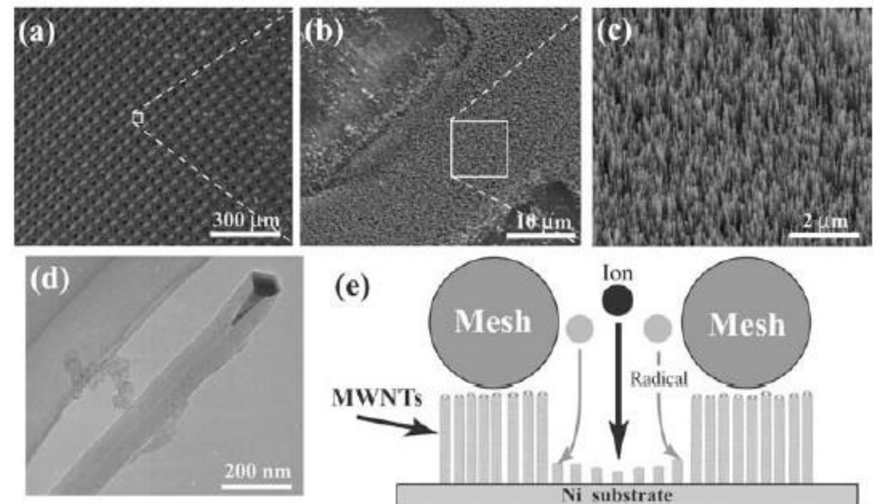
	measured Raman RBM (cm^{-1})	diameter range (from Raman)	total # of devices	total # of Tubes (N_T)	# of s-SWNTs (N_s)	# of m-SWNTs	s-SWNT % = (p)
PECVD	161−284	0.8 nm−1.5 nm	375	701	626	75	89.3 ± 2.3%
HiPco	201−264	0.8 nm−1.3 nm	80	164	100	64	61.0 ± 7.6%

Possible negative influence of plasma in PECVD





Kinoshita H. et.al., Carbon 42 (2004) 2735



Jeong et al., Appl. Phys. A 79, 85 (2004)