# 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 chromatograph 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<sub>60</sub>-720 amu, C<sub>70</sub> – 840 amu.

NMR  $C_{60}$  1 line,  $C_{70}$  5 lines - symmetries.

2

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
G <sub>2</sub> Gl <sub>4</sub> 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 9. Collection rates of total soot,  $G_{60}$  and  $G_{70}$ , power = 55 kW.

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

# Fullerene synthesis by decomposition of CCl4 in rf dicharge in helium atmosphere



#### Growth of diamond layers – ultrananocrystalline diamond



- microwave power
  (2.45 GHz) 900–950 W
- pressure 7.5 kPa
- substrate temperature 800–950 °C
- CH<sub>4</sub>/H<sub>2</sub> gas mixture
  (2 and 9.4 % of CH<sub>4</sub>)
- deposition time
  1–40 min
- polished Si, no pretreatment

#### Nucleation of ultra-nanocrystalline diamond

#### Bias Enhanced Nucleation – BEN in-situ nucleation density ~ 10<sup>12</sup> cm<sup>2</sup>

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



#### 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<sup>2</sup> 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/ $\mu$ m)



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

DC glow discharge resistively heated carbon electrode – cathode with the sample (Si/SiO<sub>2</sub> 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<sub>2</sub> and held at this temperature for 15 minutes after that 200 sccm of NH<sub>3</sub> was introduced to pressure of 465 Pa. The deposition was carried out in mixture of  $C_2H_2$  and NH<sub>3</sub> for 15 minutes.



FIG. 1. SEM photographs of Ni films with varying thicknesses deposited using magnetron sputtering on 50 nm of ECR SiO<sub>2</sub> after annealing at 750 °C in 20 Torr of H<sub>2</sub> 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<sub>2</sub>H<sub>2</sub>:NH<sub>3</sub>=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





 $NH_3$  flow at 100 sccm



2 nm Ni catalyst



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  $\mu$ m 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<sub>2</sub>/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.



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

RF (13.56 MHz) capactive coupled discharge with 4 inch quartz tube. Sample Si/SiO<sub>2</sub>/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.



Figure 2. SWNTs grown at 600 °C. (a) AFM image of nanotubes grown from low-density ferritin deposition on a SiO<sub>2</sub> 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<sup>-1</sup>, due to splitting of the inplane graphene mode at 1580 cm<sup>-1</sup> from graphene to tubes). Raman data here was obtained with a SWNT mat grown on a uniform Fe film deposited on SiO<sub>2</sub>, and the data were sum of 75 spectra recorded over the sample.

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	diameter range	total # of	total # of	# of s-SWNTs	# of	s-SWNT
	RBM (cm <sup>-1</sup> )	(from Raman)	devices	Tubes (N <sub>T</sub> )	(N <sub>s</sub> )	m-SWNTs	% = (p)
PECVD	161 - 284	0.8 nm-1.5 nm	375	701	626	75	$\begin{array}{c} 89.3 \pm 2.3\% \\ 61.0 \pm 7.6\% \end{array}$
HiPco	201 - 264	0.8 nm-1.3 nm	80	164	100	64	

#### Possible negative influence of plasma in PECVD



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



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

#### PECVD at atmospheric pressure

- Plasma enhanced chemical vapor deposition with various sources
- Operation at 100 kPa without a vacuum system
- Plasma arcs, jets and torches mostly operated in floating catalyst regime, most often used with microwave sources
- Atmospheric pressure glow discharge (APGD) diffusion form of dielectric barrier discharge (DBD) – deposition on substrates with heated electrode

# Atmospheric pressure glow discharge

- Discharge configuration when one or both electrodes are covered with dielectric barrier (used for ozone production since 19<sup>th</sup> century)
- Filamentary DBD can be made diffusive with addition of He or Ne,which are both expensive gases, in can be also made homogeneous in Ar with certain hydrocarbons, N<sub>2</sub> or ammonia addition or special electrode structure.
- It was shown that during the current increase the discharge transits from a non-self-sustained discharge to a Townsend discharge and then to a subnormal glow discharge in He and Ar/NH3 and, therefore, can be called atmospheric pressure glow discharge (APGD).
- APGD has only 1 broad current pulse in each half period while DBD has many nanosecond current pulses, non-thermal plasma at atmospheric pressure



T. Nozaki, Y. Kimura and K. Okazaki, J. Phys. D: Appl. Phys. 35 (2002) 2779–2784

First CNTs growth published by T. Nozaki, Y. Kimura and K. Okazaki, J. Phys. D: Appl. Phys. 35 (2002) 2779–2784 Quartz substrate with 20 nm metal plated Ni, pretreatment in H<sub>2</sub> for 30 min at 600 °C Operation in kHz mode resulted in deposition of many defective structures





Figure 6. CNTs with uniform diameter of 40–50 nm and number density of  $10^9 {-} 10^{10}\,\rm cm^{-2}$  obtained after 30 min deposition.



• APG was also successfully used with modified electrode (pin to plate) by Y.-H. Lee, S.-H. Kyung, C.-W. Kim, G.-Y. Yeom. Carbon 44, 799 (2006) and capillary type by S.-J. Kyung, Y.-H. Lee, C.-W. Kim, J.-H. Lee, G.-Y. Yeom. Thin Solid Films 506–507, 268 (2006).



Ni (5 nm)/Cr (100 nm)/Si substrates He(6 slm)/NH<sub>3</sub>(90 sccm) plasma with pretreatment at 400 °C for 5 min He/C<sub>2</sub>H<sub>2</sub>(60 sccm) plasma He/N<sub>2</sub>(60 sccm)/C<sub>2</sub>H<sub>2</sub> plasma He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> plasma He/NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> with dc bias 1.2 kV

- In 2006 T. Nozaki et al. J. Appl.Phys. 99, 024310 used radio-frequency power source for CNTs growth
- APRFD creates stable continuous regime for CNTs growth, much lower operating voltage due to ion "trapping" between the electrodes, no dielectric barrier needed



Figure 1. APRFD reactor and image of APRFD during CNT growth.

**Parameters:** 2 inch Si wafer <100> coated with Cr/Ni (20 nm/20 nm(sputtered)), Discharge area: 12.6 cm<sup>2</sup> Deposition time: 5, 10, 20 min,  $He/H_2/C_2H_2$  (1000/4-10/2 sccm)





- Even with use of APRFD the growth of SWCNTs remained a challenge, key issue was the form of the catalyst
- In 2007 T. Nozaki, K. Ohnishi, K. Okazaki, U. Kortshagen. Carbon 45, 364 used densely mono-dispersed Fe–Co catalysts of a few nanometers size (first used by Maruyama) for aligned layers of SWCNTs
- Prepared nanoparticles were reduced in He/H<sub>2</sub> 1500/10 sccm at APRFD at 400 °C for 5 min, then 15 min at 700°C, deposition He/H<sub>2</sub>/CH<sub>4</sub> 1000/30/16 sccm for 5 min at 700 °C





Fig. 8. SEM micrographs of SWCNTs at different substrate temperatures.



Fig. 9. Raman scattering spectra of samples shown in Fig. 8.

T. Nozaki, K. Okazaki, Carbon Nanotube Synthesis in Atmospheric Pressure Glow Discharge: A Review, Plasma Process. Polym. 2008, 5, 300–321



Figure 4. Mass spectrum of the reacting gas obtained directly from the sheath; conditions:  $He/CH_4/H_2 = 1000/16/30 \text{ cm}^3 \text{ min}^{-1}$  and 700 °C.



 $\begin{array}{c} 80 \\ (\%) \\ (\%) \\ (7) \\$ 

Figure 6. CH<sub>4</sub> conversion and selectivity for the C<sub>2</sub> hydrocarbon:  $\Box$  20 kPa, H<sub>2</sub> = 0;  $\blacksquare$  100 kPa, H<sub>2</sub> = 0;  $\bigotimes$  100 kPa, H<sub>2</sub> = 90 cm<sup>3</sup> min<sup>-1</sup>; conditions: He/CH<sub>4</sub> = 3000/48 cm<sup>3</sup> min<sup>-1</sup> and 60 W.

Figure 5. Time-dependent change-of-mass spectrum for m/e = 16 and 28. See figure 4 caption for the conditions.

T. Nozaki, S. Yoshida, T. Karatsu and K. Okazaki, Atmospheric-pressure plasma synthesis of carbon nanotubes, J. Phys. D: Appl. Phys. 44 (2011) 174007 (9pp).

## CNTs growth in APG in $Ar/H_2/C_2H_2$



FIG. 1. Electrode configuration. 1—Simax glass dielectric, 2—upper electrode, 3—distance pillar, 4—discharge, 5—substrate, 6—AlN dielectric, 7—thermocouple, 8—bottom electrode, 9—heater, 10—gas inlet.





FIG. 3. The time dependence of applied voltage (dotted line) and discharge current (full line) at room temperature for (a) DBD in pure Ar, (b) DBD in Ar/CH<sub>4</sub>, and (c) APGD in Ar/C<sub>2</sub>H<sub>2</sub>. The concentration of CH<sub>4</sub> or C<sub>2</sub>H<sub>2</sub> in Ar was 0.41 vol. %. Discharges were operated slightly above the ignition voltage in particular gas mixture.



FIG. 5. ICCD images of discharges at room temperature with  $80\,\mu s$  (one half-period) exposure time: (a) filamentary DBD in Ar, (b) filamentary DBD in Ar/CH<sub>4</sub>, (c) APGD in Ar/C<sub>2</sub>H<sub>2</sub>, and (d) APGD in Ar/C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub>. The concentration of CH<sub>4</sub> or C<sub>2</sub>H<sub>2</sub> was 0.41 vol. %. Horizontal lines indicate the dielectric surfaces and the upper electrode is the instantaneous cathode in all images.

FIG. 2. The dependence of ignition voltage  $U_0$  on the concentration or acetylene or methane added to Ar or Ar/H<sub>2</sub>. The discharge was operated at room temperature 22 °C. Argon and hydrogen flow rates were 7 slm and 100 sccm, respectively.

6,8 kHz power supply with 0.8–4.0 kV (peak-to-peak) voltage , electrode distance of 1,75 mm, 10x15 mm Si/SiO2 (300 nm)/5 nm Fe catalytic layer. Ar/H2/CH<sub>4</sub> or  $C_2H_2$  mixture.

Eliáš M., Kloc P., Jašek O., Mazánková V., Trunec D., Hrdý R., Zajíčková L., Atmospheric pressure barrier discharge at high temperature: Diagnostics and carbon nanotubes deposition, Journal of Applied Physics 117(10) (2015) 103301.

#### CNTs growth in APG in $Ar/H_2/C_2H_2$ – diagnostics at high temperature



current (full line) for (a) DBD in Ar/CH<sub>4</sub>/H<sub>2</sub> at 22 °C, (b) APGD Ar/C<sub>2</sub>H<sub>2</sub>/ H<sub>2</sub> at 22 °C, and (c) APGD Ar/C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> at 680 °C. The concentration of CH<sub>4</sub> or C<sub>2</sub>H<sub>2</sub> in Ar/H<sub>2</sub> was 0.41 vol. %. Discharges were operated slightly above

the ignition voltage in particular gas mixture.



FIG. 8. ICCD images of APGD in Ar/C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> with 0.41 vol. % admixture of C<sub>2</sub>H<sub>2</sub> and bottom electrode heated to 680°C: (a) 80  $\mu$ s (one half-period), instantaneous cathode at upper electrode, (b) 80  $\mu$ s (one half-period), cathode at bottom electrode, (c) 5  $\mu$ s, cathode at upper electrode, and (d) 5  $\mu$ s, cathode at bottom electrode. Horizontal lines indicate the dielectric surfaces.



FIG. 7. The ignition voltage  $U_0$  in dependence on the concentration of acetylene or methane added to Ar/H<sub>2</sub> for the temperature of bottom electrode 680 °C. Argon and hydrogen flow rates were 7 slm and 100 sccm, respectively.

If the bottom electrode was heated up to 680 °C the ignition voltage decreases due to the decrease of neutral gas concentration. Substrate temperature is 40 °C lower then heated electrode and upper electrode temperature is 250 °C lower. Due to the temperature profile the behaviour in instantaneous cathode or anode is different in each half period.

## CNTs growth in APG in $Ar/H_2/C_2H_2$



FIG. 13. Cross sectional SEM micrographs of deposited carbon nanostructures for (a) 0.1%, (b) 0.2% of C<sub>2</sub>H<sub>2</sub> in Art/C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> APG discharges, and (c) 0.2%, (d) 0.4% of CH<sub>4</sub> in Ar/CH<sub>4</sub>/H<sub>2</sub> DBD discharges. The substrate temperature was 710°C. The micrographs were made using TESCAN LYRA microscope.



FIG. 12. TEM micrograph of the carbon nanostructures deposited from (a), (b) 0.2% of C<sub>2</sub>H<sub>2</sub> in Ar/C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub> mixture and (c), (d) 0.2% of CH<sub>4</sub> in Ar/CH<sub>4</sub>/H<sub>2</sub> mixture. The substrate temperature was 610°C for (a) and (c) and 710°C for (b) and (d) images. The micrographs were made using Philips CM12 microscope.

## CNTs deposition by plasma arcs/jets/torches at atmospheric pressure



H. Takikawa et al. *Physica B* 323, 277 (2002)., O. Smiljanic et al., Chem. Phys. Lett. 356, 189 (2002).

## CNTs deposition by plasma arcs/jets/torches at atmospheric pressure





Fig. 9. SEM images of CNTs obtained from the atmospheric microwave plasma-torch. (a) at a furnace temperature of 700, (b) 800, (c) 900, and (d) 1000 °C.

Y. Ch. Hong, H. S. Uhm, Physics of plasmas 12, 053504 (2005)



Microwave plasma torch operating at 2,45 GHz, max. 2 kW power, dual gas flow Center - Ar(500-1500 sccm)/ Outer - H<sub>2</sub>(250-500 sccm)/CH<sub>4</sub>(10-50 sccm) Si/Fe, Si/SiO<sub>x</sub>/Fe, Si/Al<sub>x</sub>O<sub>y</sub>/Fe substrates Fe(1-10 nm) vacuum evaporated, SiO<sub>x</sub> PECVD O. Jašek, M. Eliáš, L. Zajíčková et al., Materials Science and Eng. C, 26, 2006, 1189







Substrate type Si/SiO<sub>2</sub>/Fe 10 nm ( $Q_{CH4}$ =40 sccm,  $Q_{H2}$ =400 sccm, Ar=1500 sccm,  $T_S$ =700°C,  $t_d$ =15 min.).



Material contrast analysis – comparison of micrographs in secondary and backscattered electrons. White points correspond to catalytic particles – tip growth mode.



#### TEM micrograph



CNTs growth a) SiO<sub>x</sub> b) Al<sub>x</sub>O<sub>y</sub> and c) without barrier layer. Ar/H<sub>2</sub>/CH<sub>4</sub> 1540/430/42 sccm, 60 s, 400W, 700-750 °C



Growth pattering without barrier layer

WD 8.1mm

# CNTs growth in microwave plasma torch with floating catalyst



TEM micrograph of MWCNTs/SWCNTs deposited from mixture of Ar/H<sub>2</sub>/CH<sub>4</sub> and Fe(CO)<sub>5</sub> Deposition of SWCNTs on the substrate using ethanol admixture



Raman spectra of deposited nanostructures