

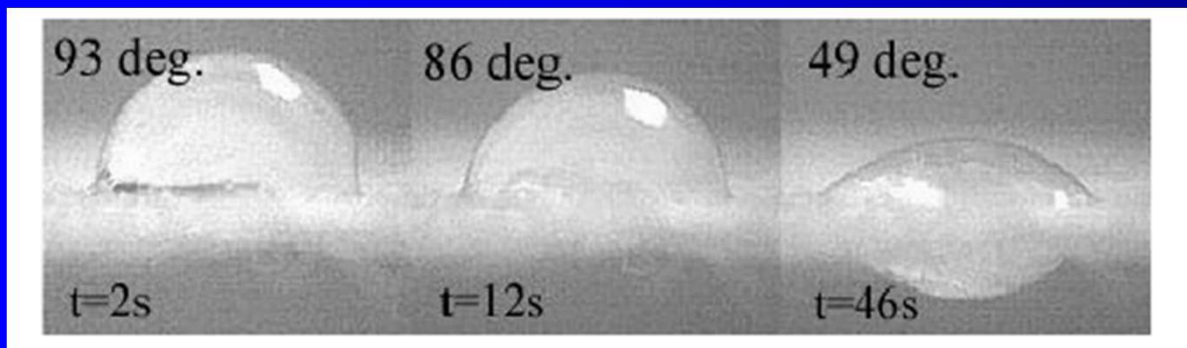
7.4 Plasma Surface Modification

What can happen after surface modification?

- change of surface roughness
- change of surface chemistry

What these changes are used for?

- change of surface free energy, i.e. wettability
- improved adhesion of further coatings
- immobilization of biomolecules



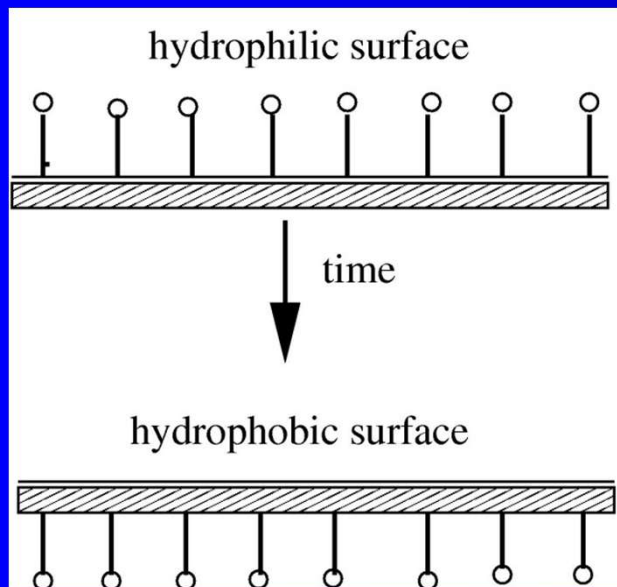
Plasma Treatment

combination of various processes (chemistry, ions, UV) results in:

- removal of material
- modification of original material (especially important for polymers)
- grafting of new functional groups

In contrary to depositions the changes are limited to a very thin surface layer (in the order of nm) but please note that the term “surface” is a matter of definition!

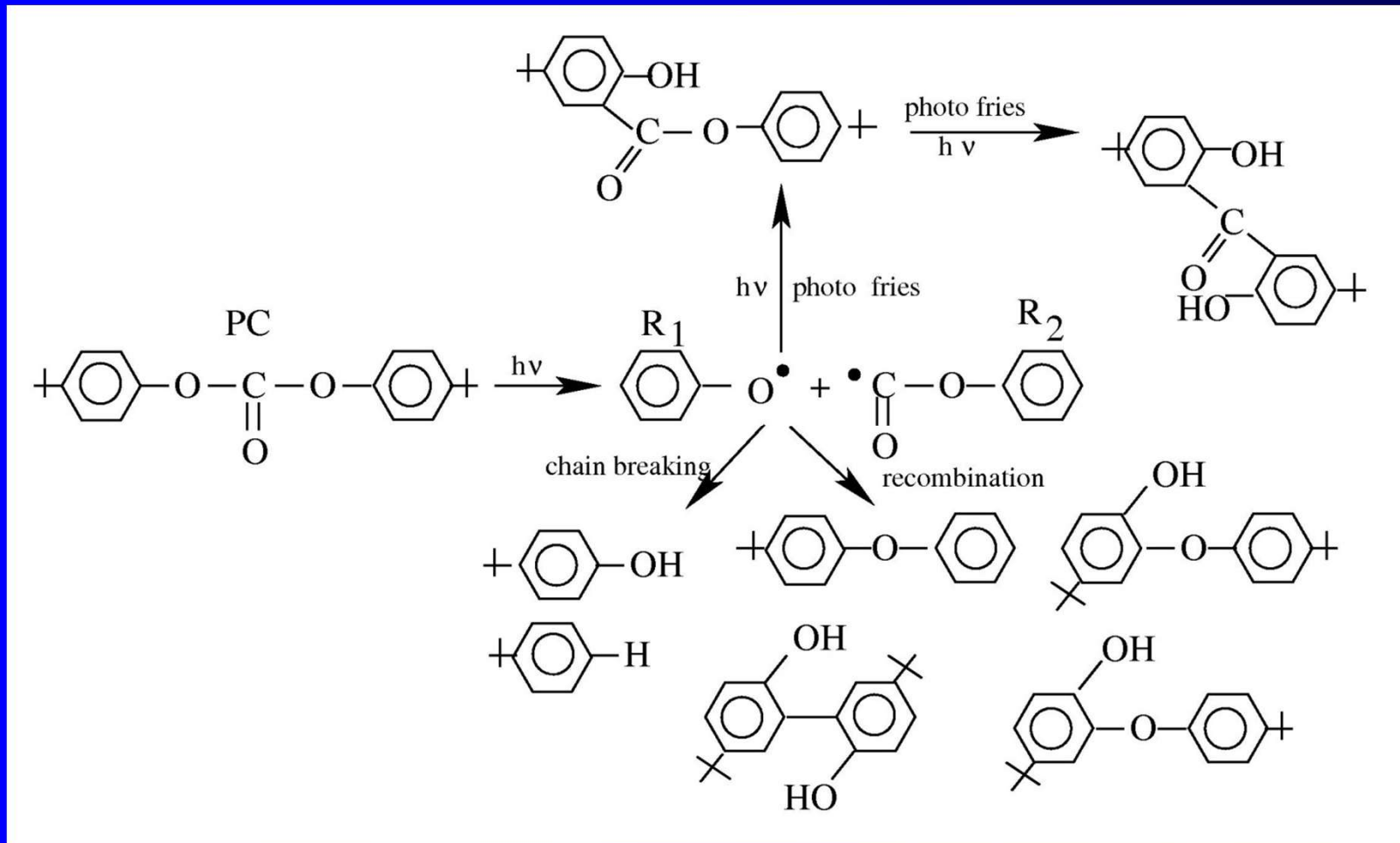
ageing of treated surfaces



important issue of any surface treatment processes

Effect of UV Radiation on Polycarbonate

suggested mechanism of carbonate bond breakage due to UV radiation:



Plasma generates also UV photons and this effect is often forgotten!

Plasma modifications of polymers in inert gas

➤ discharge in argon, helium:

chemical bonds, such as C-H, C-C, C=C, are broken

↳ generation of free radicals at or near the surface

↳ radicals react with each other either directly (if polymer chain is flexible enough) or due to migration along polymer chain („chain-transfer“)

↳ **cross-linking, branching, removal of low molecular weight material or its conversion into high molecular weight one (no new functional groups)**



(cross-linking by activated species of inert gas)

R. H. Hansen, H. Schonhorn, J. Polym. Sci. B 4 (1966) 203

H. Schonhorn, R. H. Hansen, J. Appl. Polym. Sci. 11 (1967) 1461



increase of surface hardness, improvement of adhesive forces at the interface

Additionally, changes of surface roughness

Plasma treatment in reactive gases

➤ plasma containing oxygen (O_2 , H_2O , CO_2 ...)

- etching of surface carbon radicals by atomic oxygen
- new functional groups, e.g. C-O, C=O, O-C=O, C-O-O, CO_3 , OH



hydrophilic surface, change of roughness

➤ plasma containing nitrogen (N_2 , NH_3 ...)

- new functional groups such amine (N-C), imine (N=C), nitrile ($N\equiv C$), amide (N-C=O)
- incorporation of oxygen and its functional groups
- grafting of amine groups $-NH_2$



hydrophilization, biocompatibility, immobilization of biomolecules

➤ plasma containing fluorine (SF_6 , CF_4 , C_2F_6 ...)

F and CF_x radicals react with surface and two different processes compete:

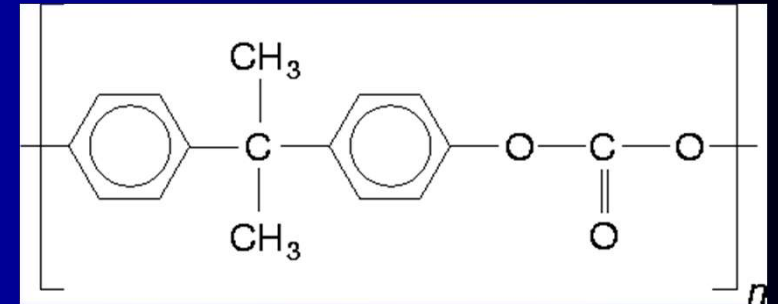
- etching
- grafting and deposition



hydrophobization, change of roughness

Why Plasma Modification of Polycarbonate?

Polycarbonates are attractive business article, the most important PCs are based on on bisphenol A (Diflon[®], Macrolon[®], Lexan[®])



Properties

- excellent breakage resistance (15-20x than acrylate, 250x than glass)
- good transparency (3 mm thick – 90 %)
- low inflammability, good workability, lighter than glass

- low hardness (0.2 GPa)
- low scratch resistance
- degradation by ultraviolet light

replace glass and metals in:

- automobile headlamps, stoplight lenses,
- corrective lenses,
- safety shields in windows, architectural glazing

can be applied to:

- plastics vessels, parts of machines
- in optical grades for compact discs (CDs, CD-ROMs and DVDs), optical fibers

modification of PC surface properties is necessary

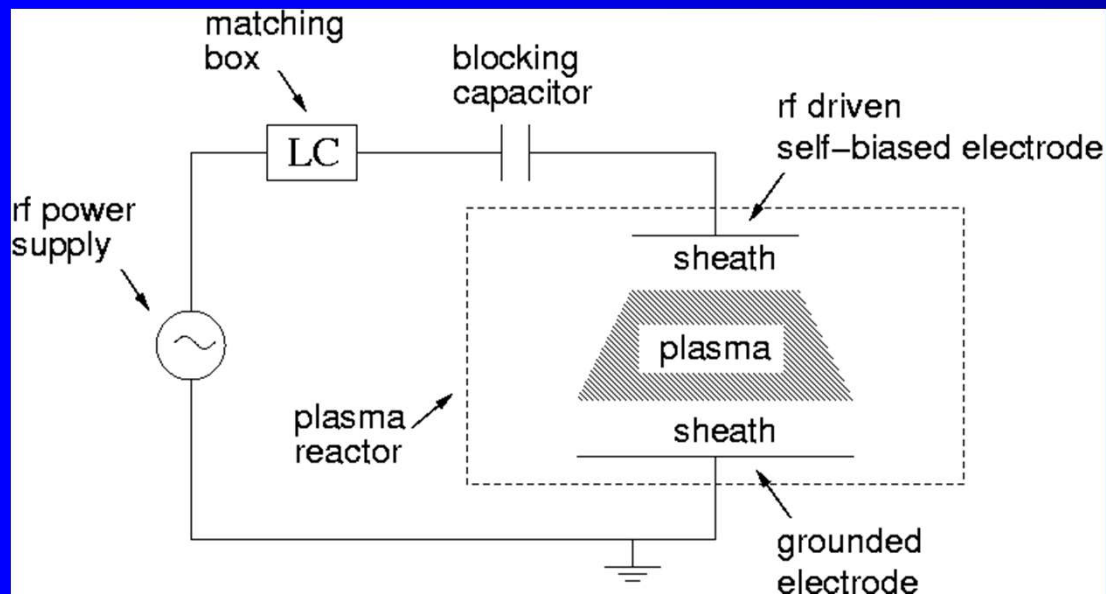
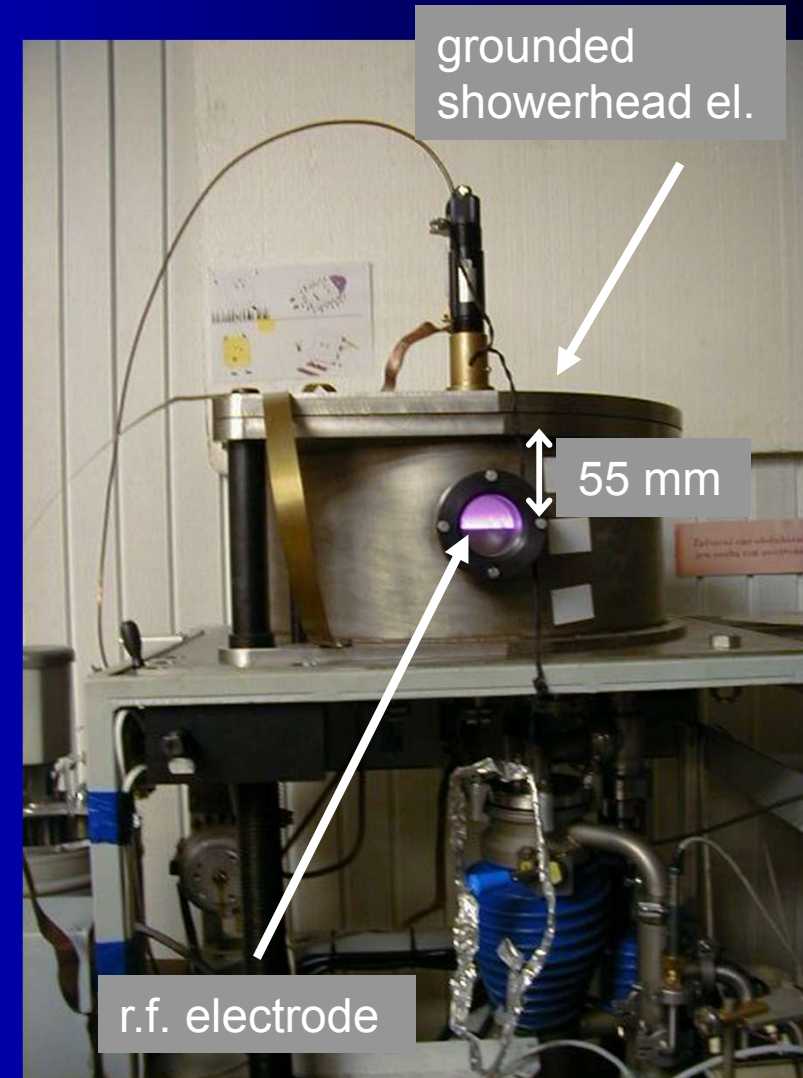
deposition of functional films (scratch resistant, reflective, ...)

surface treatment for improved film adhesion

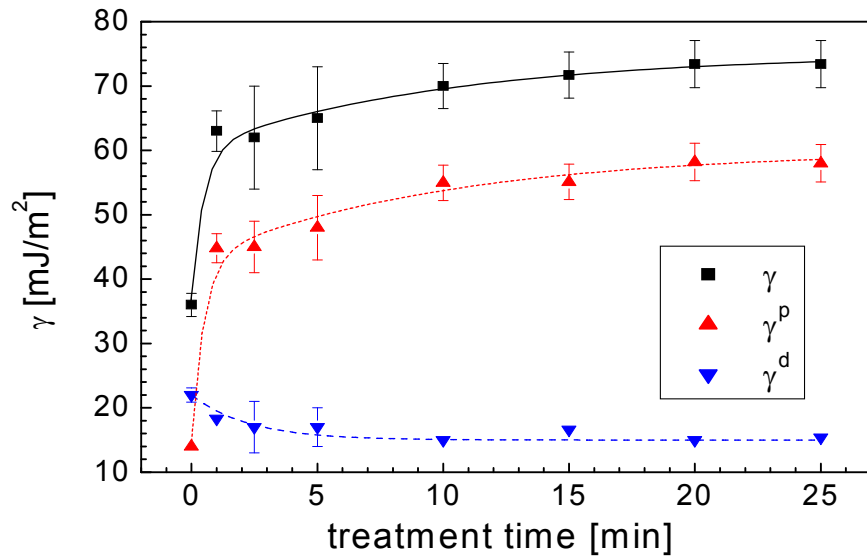
Plasma treatment of polycarbonate in Ar or O₂ discharges (CCP)

External plasma parameters:

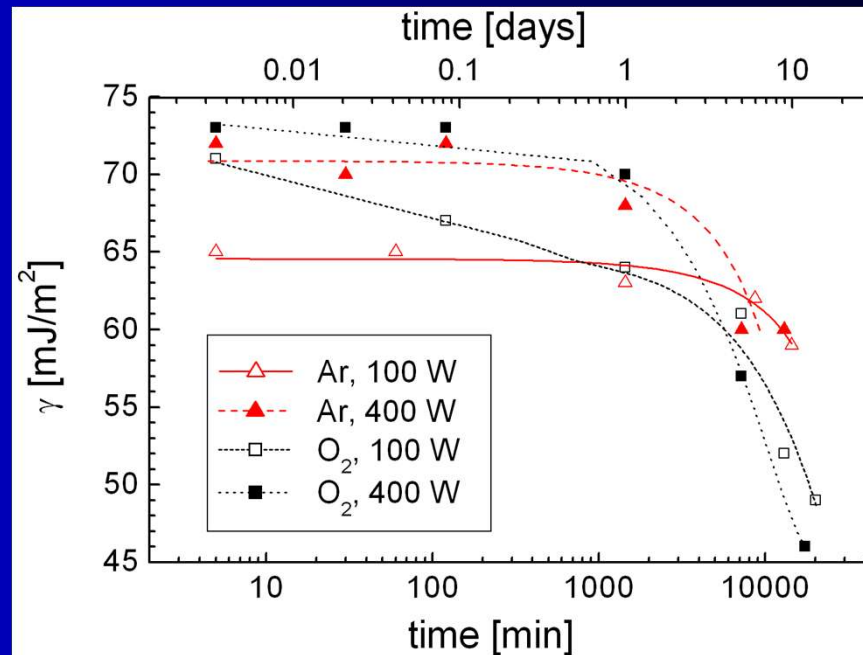
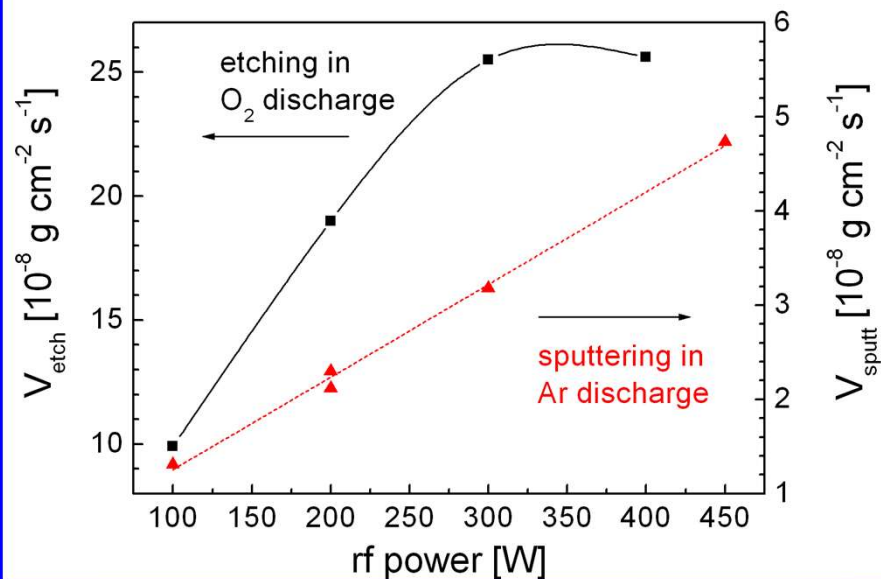
- $f = 13.56$ MHz
- inner diameter of reactor 490 mm
- r.f. driven bottom electrode (420 mm)
- Ar, O₂: $Q = 5.7$ sccm , $p = 1.5$ Pa
- r.f. power $P = 100$ and 400 W



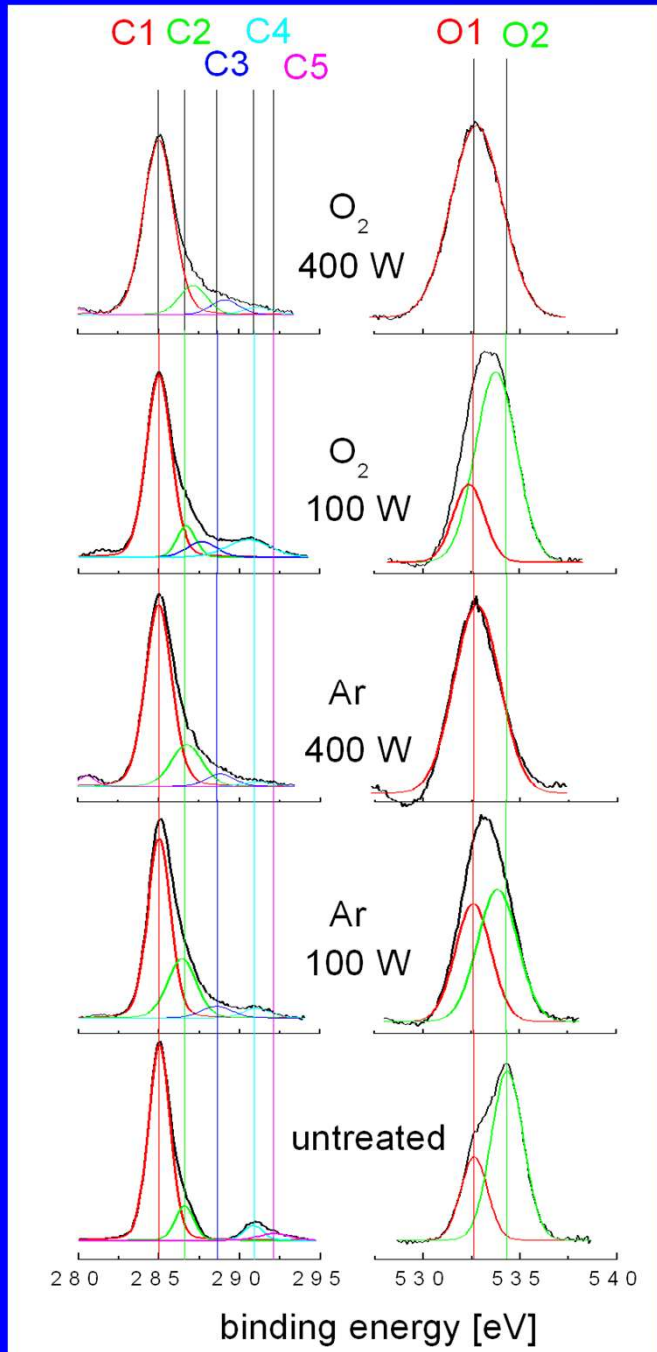
Plasma treatment of polycarbonate – etching rate and surface free energy



$P = 100 \text{ W}$, $U_{\text{bias}} = -115 \text{ V}$, $Q_{\text{ar}} = 5.7 \text{ sccm}$,
 $p = 1.5 \text{ Pa}$



Plasma treatment of polycarbonate – surface chemistry by XPS



	position [eV]	assignment
C1	285.0	C-C, C-H
C2	286.6	C-O
C3	288/289	C-C(=O)-C / O-C(=O)-O
C4	290.9	C-C(=O)-O
C5	292.1	shake up

gas	power [W]	C [at. %]	O [at. %]	Si [at. %]	N [at. %]
untreated		84.3	15.7	0	0
Ar	100	76.4	20.3	0.4	2.2
Ar	400	76.0	19.9	1.3	2.8
O ₂	100	74.0	24.0	0.4	1.7
O ₂	400	72.6	24.7	1.6	1.2

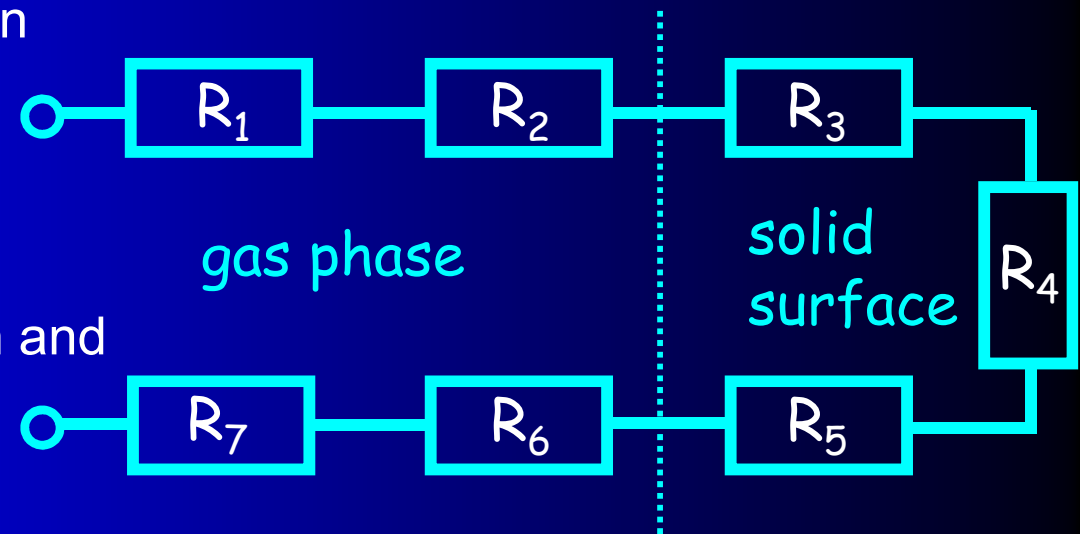
7.5 Plasma Enhanced Chemical Vapor Deposition

7.5.1 Introduction to PECVD

Chemical Vapor Deposition (CVD)

thermally driven chemical deposition from gas phase:

1. transport of reactants to the deposition space
2. diffusion of reactants to the substrate surface
3. adsorption of reactants
4. phys.-chem. processes \rightarrow film growth and by-products
5. desorption of by-products
6. diffusion of by-products in gas flow
7. transport of by-products from deposition space

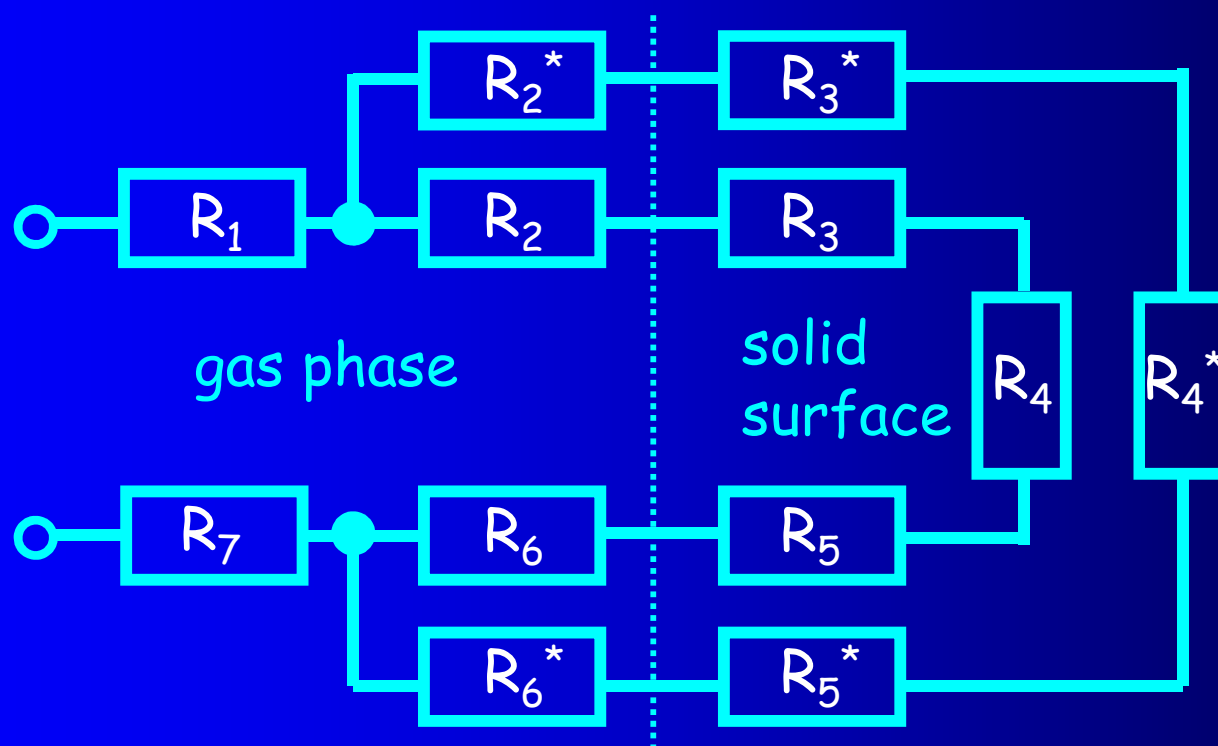


Low Pressure CVD (LPCVD) is often used in microelectronics or in applications requiring excellent control over impurities

Plasma Enhanced (or Assisted) CVD (PECVD or PACVD)

CVD method in which discharge is ignited in the gas mixture:

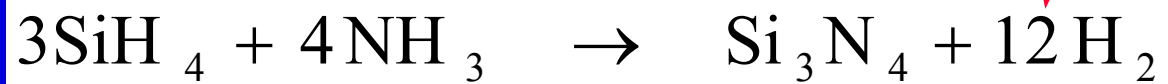
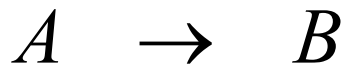
- ☞ collisions of energetic electrons with heavy gas particles
- ☞ production of highly reactive species
- ☞ more competing processes take place, deposition can be generally divided into thermal and plasma branches



PECVD x CVD

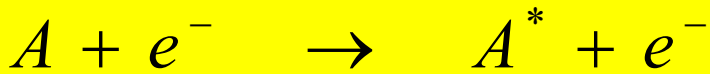
reaction branch:

thermal



700-900°C

plasma



plasma reaction branch at PECVD is much more important because:

250-350°C

- ☞ sticking coefficient is much higher for reactive radicals and activated surface
- ☞ activation energies of chemical reactions are lower for excited reactants

PECVD - lower deposition temperature, novel reaction schemes leading to new materials, replacement of toxic and dangerous reactants but

high complexity of chemical reactions and processes, worse selectivity and reaction control, possibility of damages by energetic ions, UV radiation or electrostatically (charge accumulation)

7.5.2 PECVD of materials with silicon

○ dielectric films for microelectronics

silicon nitride:

(final protective passivation for integrated circuit)



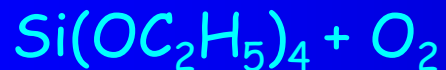
T=250-400 °C

silicon oxide:

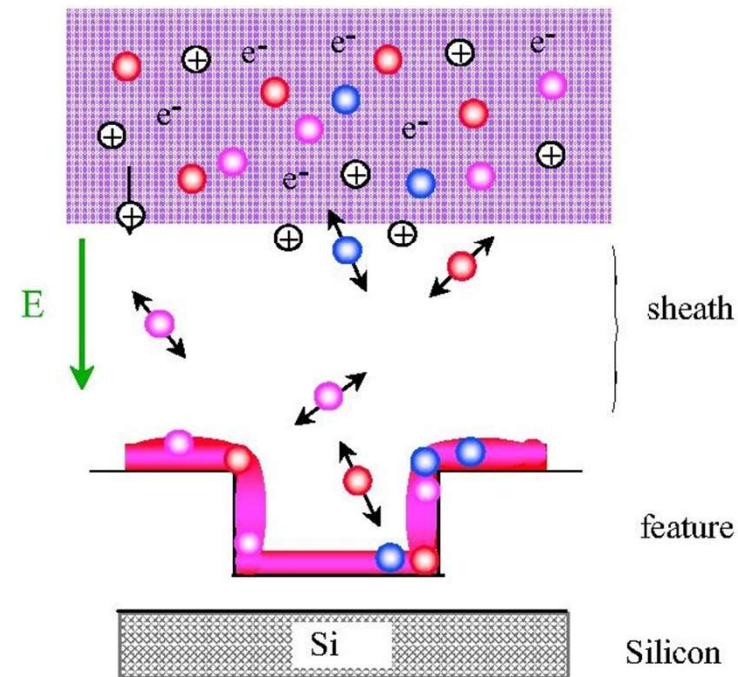
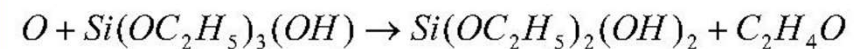
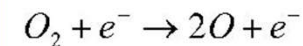
(insulating film - el. separation)



T=200-400 °C



tetraethoxysilane (TEOS)



PECVD of materials with silicon

- more dielectric films for microelectronics

low-k dielectrics: organosilicons + O_2 /... + ...
(el. separation for ULSI)



organosilicon glass
(OSG)

- semiconducting films for microelectronics

epitaxial silicon: $SiH_4 + H_2$ $T=800\text{ }^\circ C$

polycrystalline silicon: $SiH_4/SiH_2Cl_2 + H_2/Ar$ $T=450-700\text{ }^\circ C$
(gate electrode, connections in
MOS i.c., solar energy pannels)

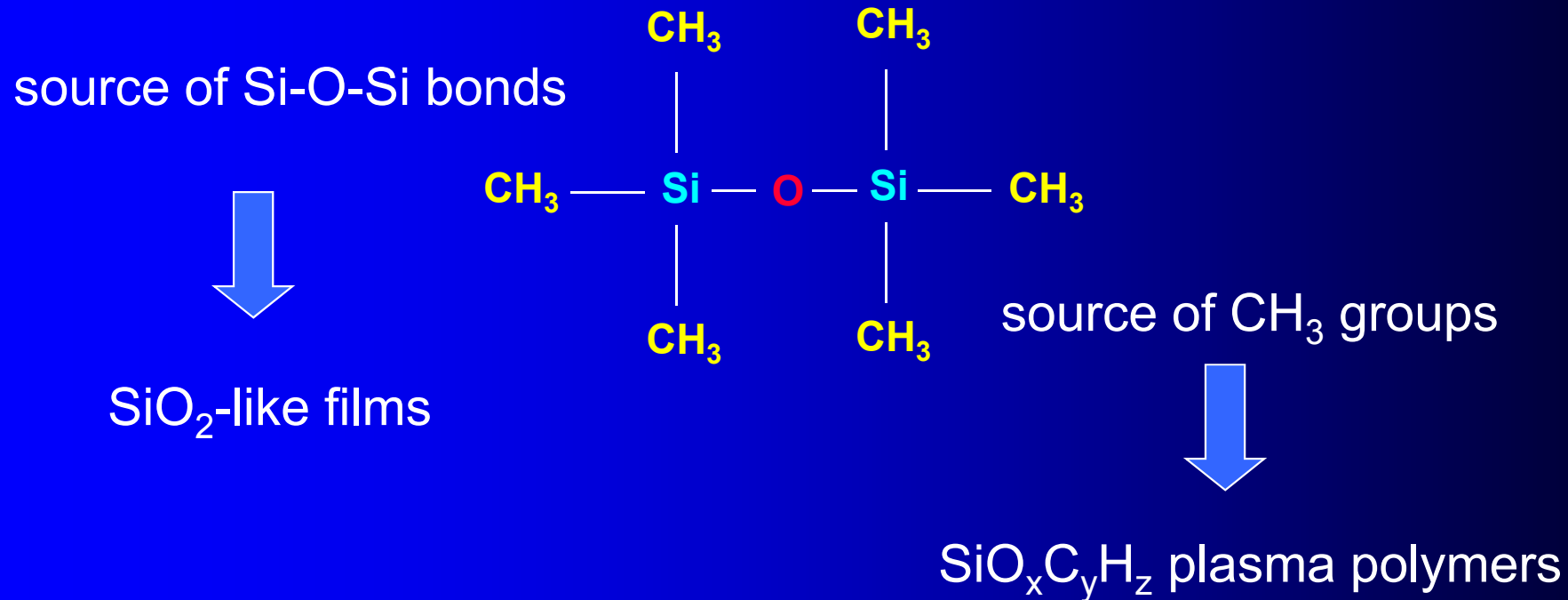
- SiO_x and $SiO_xC_yH_z$ for many other applications

scratch resistant films for plastics, anticorrosion films for metals,
barrier films for packaging and pharmacy,
biocompatible films

mixtures with organosilicons (TEOS, HMDSO, HMDSZ)

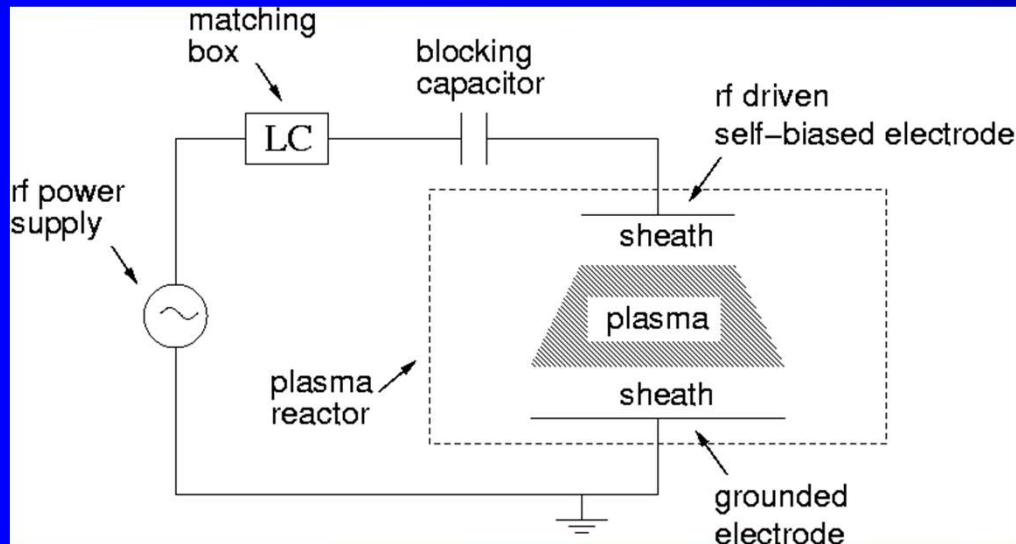
PECVD of films using HMDSO

(hexamethyldisiloxane)



- concentration of HMDSO in the gas feed, especially oxygen
- power
- bias voltage / ion energy
- pressure
- pulsing

PECVD from HMDSO/O₂ in CCP and ICP (13.56 MHz)

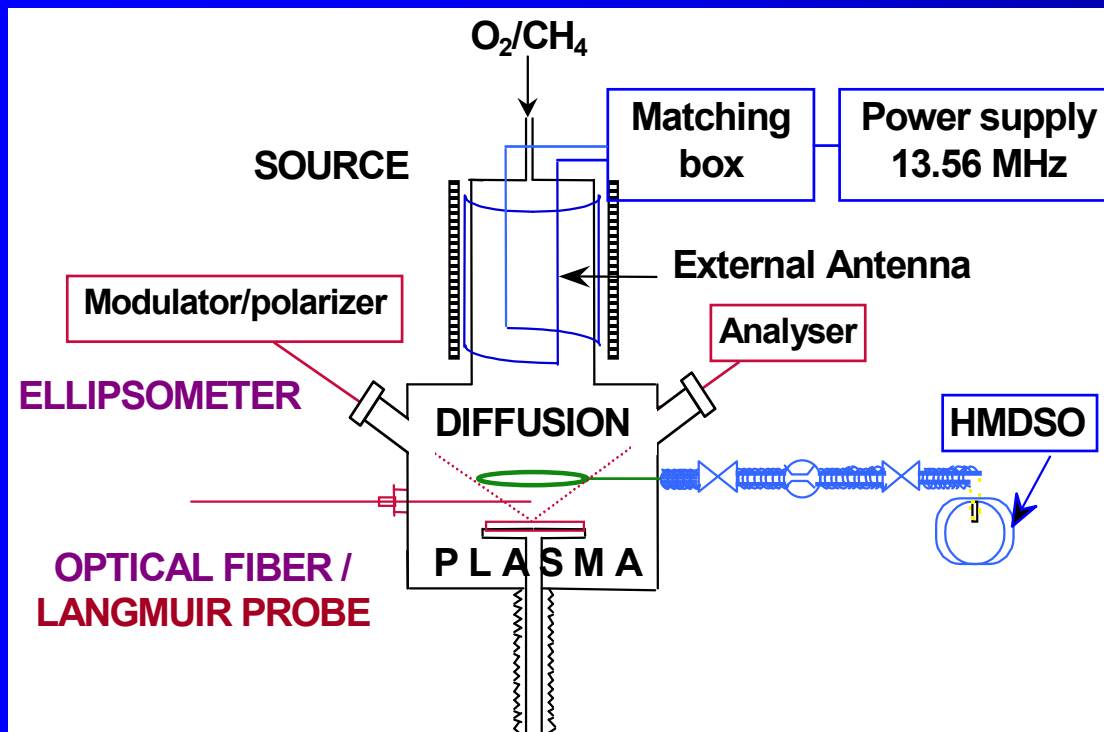


5-100 % HMDSO in O₂



CCP:

- $Q_{\text{hmdso}} = 4 \text{ sccm}$, $Q_{\text{o}_2} = 0 - 80 \text{ sccm}$
- pressure 1 - 40 Pa
- rf power 100 - 450 W
- dc self-bias from -20 and -335 V

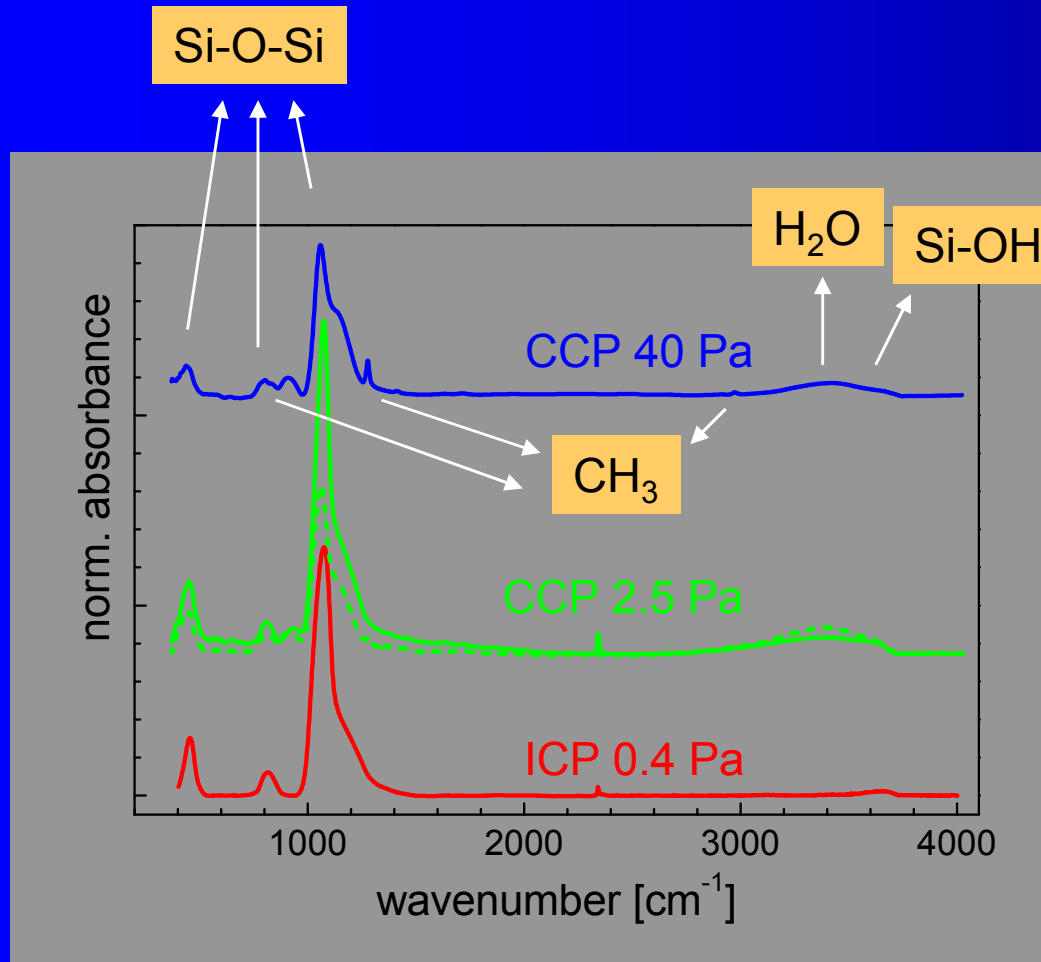


helical antenna in ICP mode:

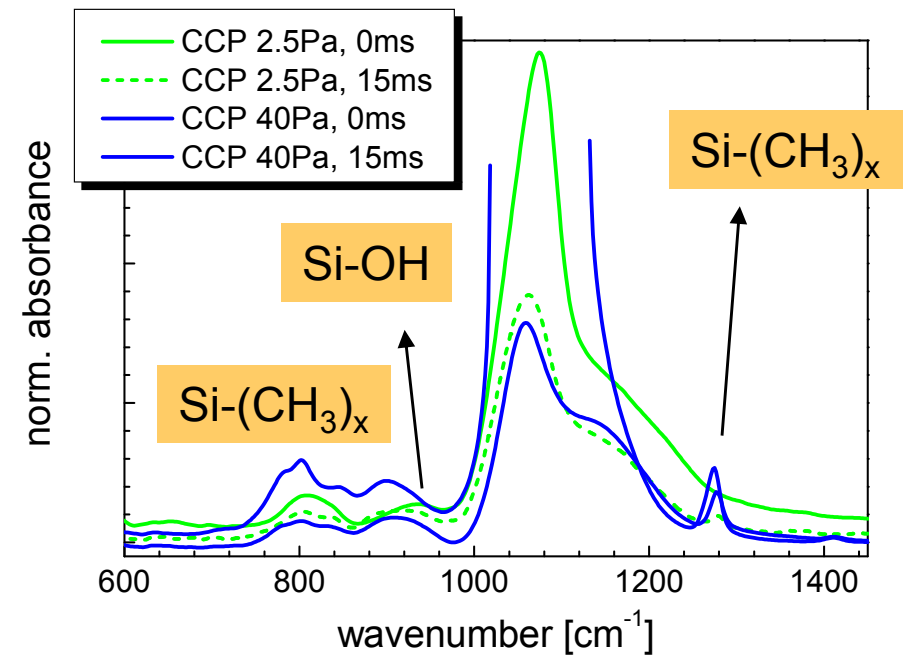
- pressure 0.4 Pa
- rf power 300 W
- substrate at ground



Variation of film composition



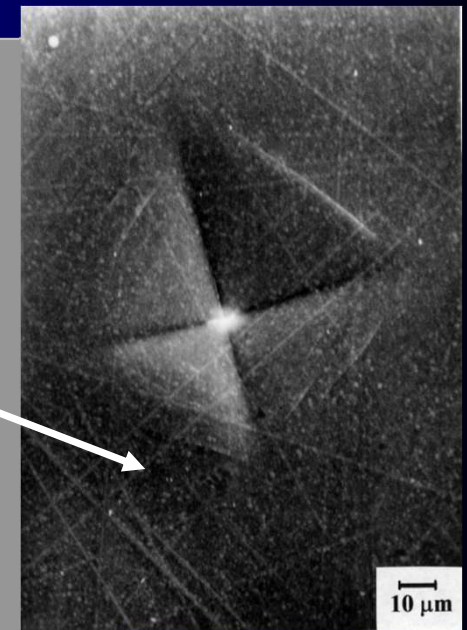
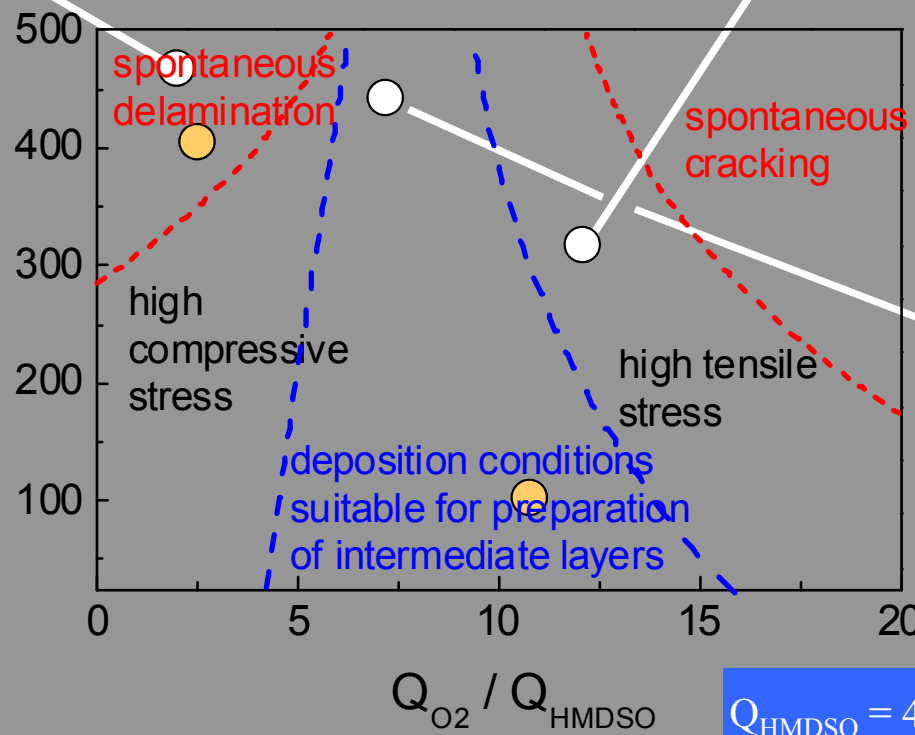
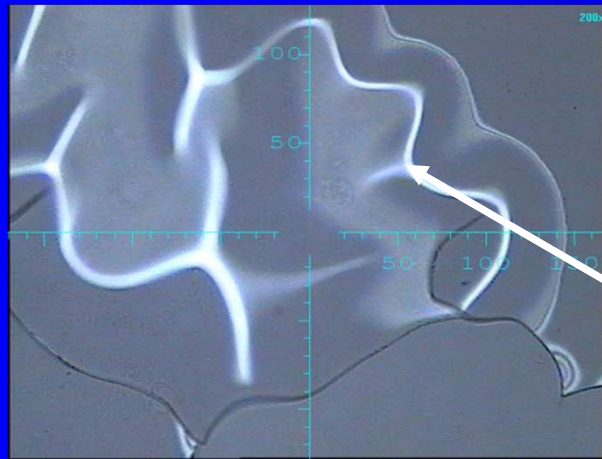
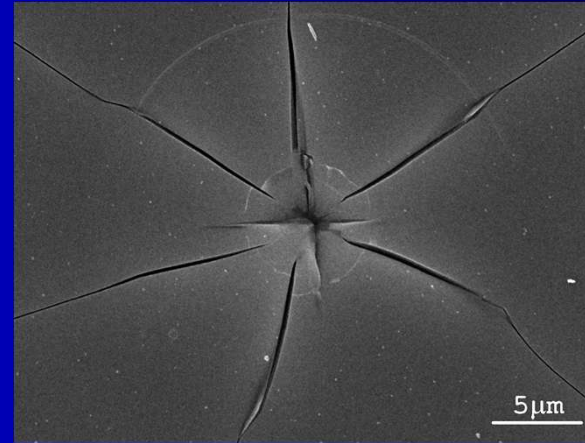
5 % HMDSO in O₂



- ⇒ 0.4 Pa: SiO₂ structure, almost no impurities
- ⇒ 2.5 Pa: SiO₂ structure, OH groups and H₂O
- ⇒ 40 Pa: organosilicon films

Domains of stresses

without treatment

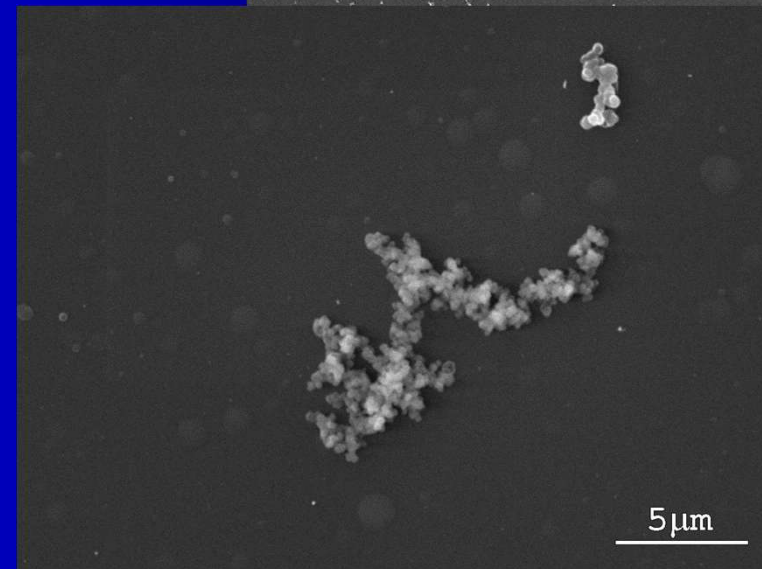
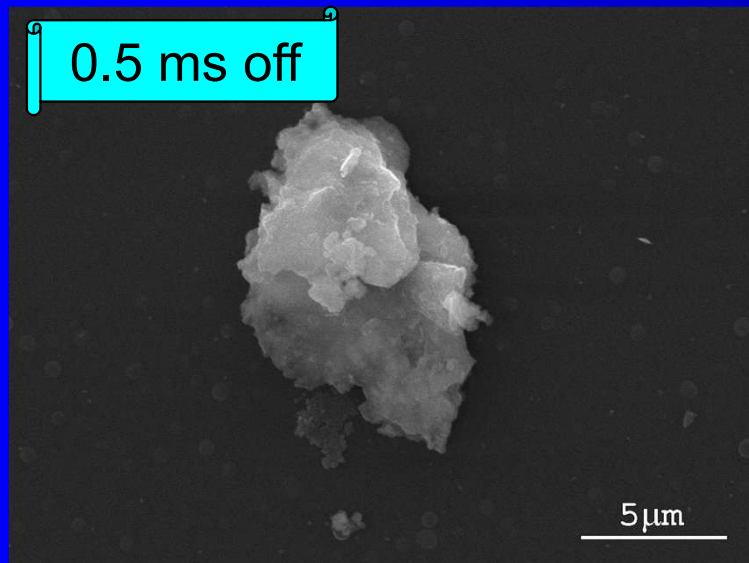
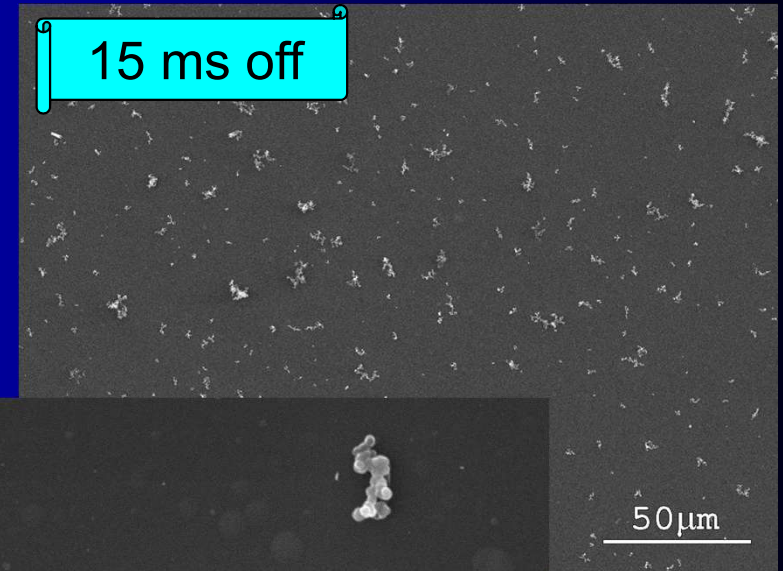
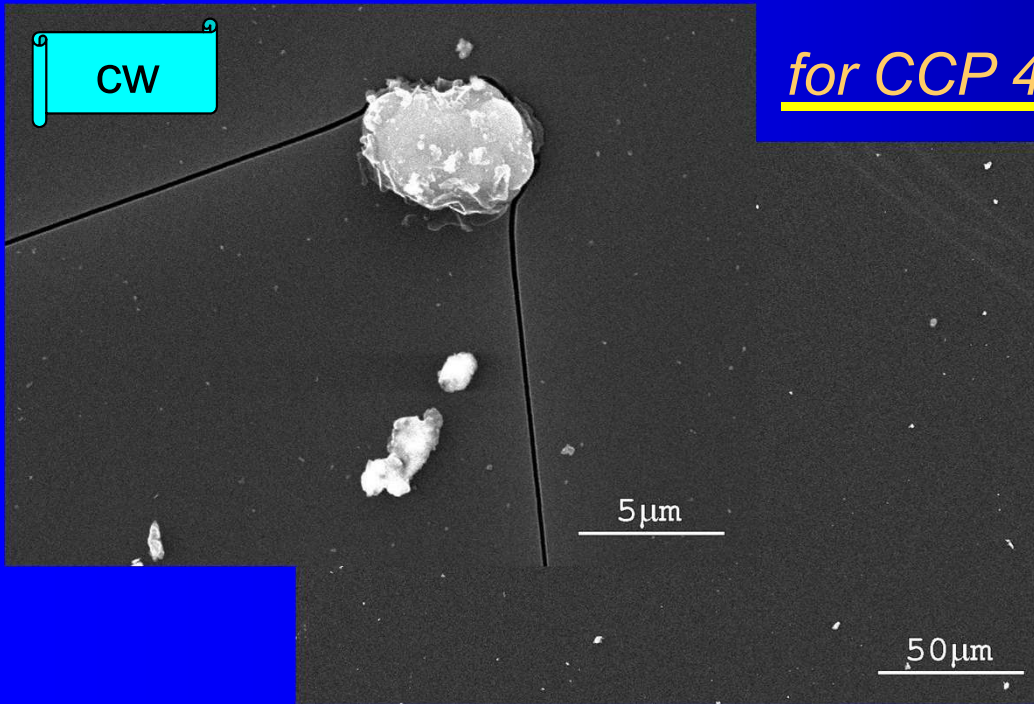


two different coatings chosen for treatment testing:

- $P = 100$ W, $Q_{O_2} = 45$ sccm, $d = 0.5$ μ m
- $P = 400$ W, $Q_{O_2} = 10$ sccm, $d = 1.2$ μ m

Film microstructure

for CCP 40 Pa



7.5.3 Carbon materials

Diamond, graphite and much more

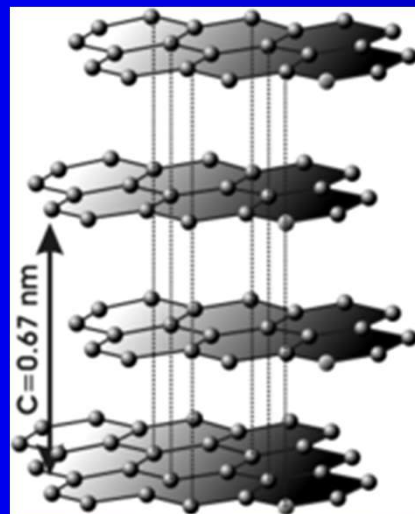
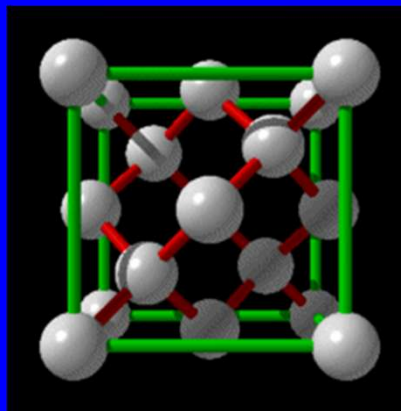
Besides well known materials such as crystalline diamond or graphite carbon can form many other interesting nanomaterials such as fullerenes, carbon nanotubes, graphene.



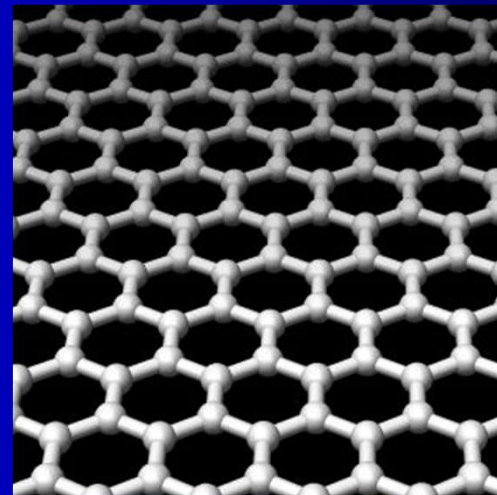
sp^3 C - diamond



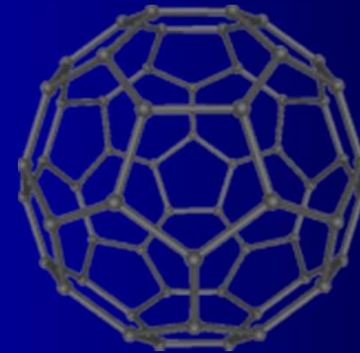
sp^2 C - graphite



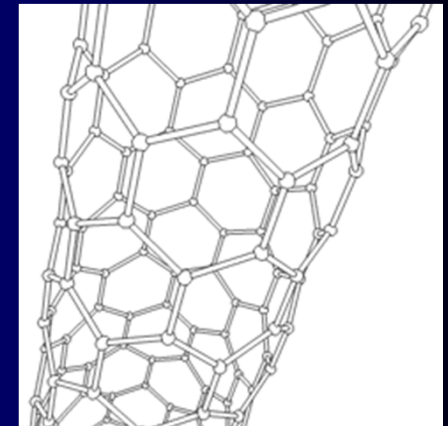
graphene



C_{60} - Buckminsterfullerene



carbon
nanotube



PECVD of carbon based materials

○ crystalline diamond films

0.1 - 5% $\text{CH}_4/\text{C}_2\text{H}_2/\dots$ in H_2 $T=700-1000^\circ\text{C}$

RF plasma $p=0.01-4\text{kPa}$, $T_{\text{gas}}=1000-1500^\circ\text{C}$, $P=0.5-3\text{kW}$

MW plasma $p=2-10\text{kPa}$, $T_{\text{gas}}=2000-2500^\circ\text{C}$, $P=0.5-2\text{kW}$

○ amorphous diamond like carbon (DLC) films

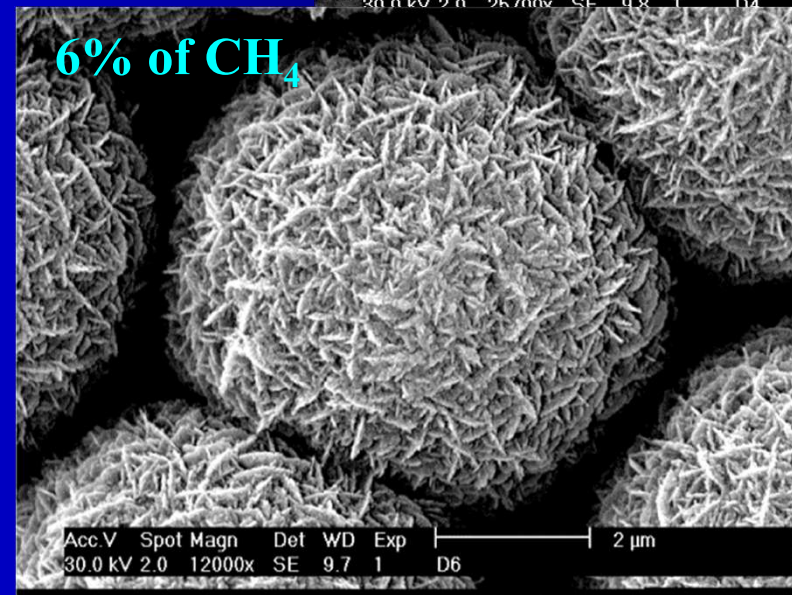
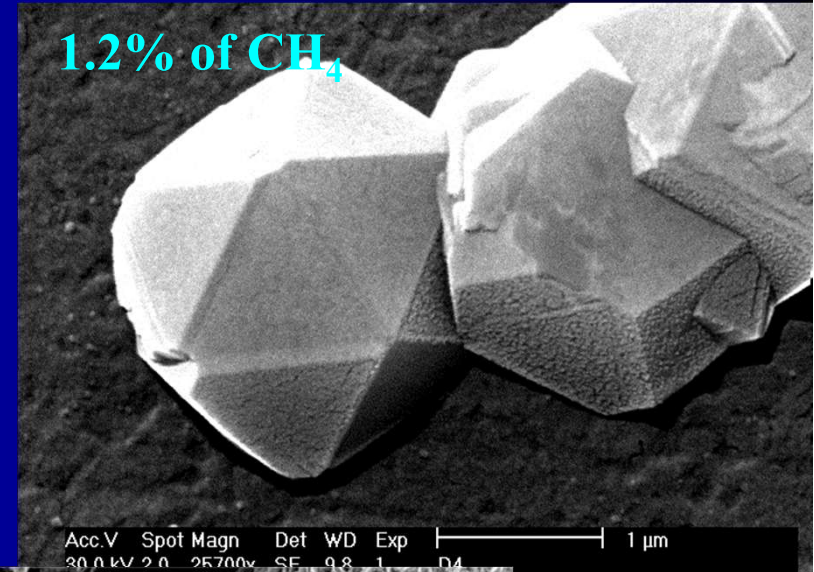


!! ion bombardment

$\text{CH}_4/\text{C}_2\text{H}_2/\dots + (\text{Ar}/\text{H}_2)$, $T < 300^\circ\text{C}$



○ polymer hydrogenated carbon films (a-C:H)



Classification of carbon films

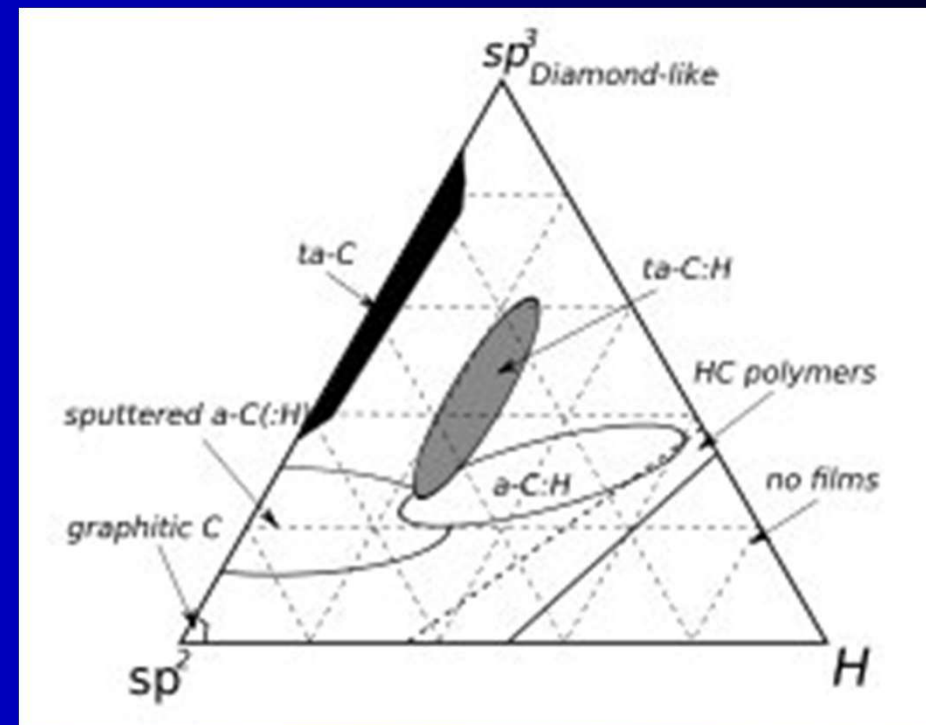
- ▶ classification of carbon films by Fraunhofer Institute for Surface Engineering and Thin Films (IST) 2009
- ▶ activities on international standardization, e.g. workshop at 12th International Conference on Plasma Surface Engineering (PSE) in 2010

Carbon films															
Designation	1 Plasma-polymer films	2 Amorphous carbon films (diamond-like-carbon films / DLC)							3 Crystalline carbon films						
									Diamond films				Graphite films		
Thin film / thick film	Thin film	Thin film							Thin film			Thick film (free standing)		Thin film	
Doping, additional elements	hydrogen-free			hydrogenated				undoped	doped	undoped	doped	undoped	doped	undoped	
			modified with metal			modified with metal	with non-metal								
Crystal size on the growth side	<i>J.</i>	(amorphous)							1 to 500 nm, nano-crystalline	0.5 to 10 μm, mikro-crystalline	0.1 to 5 μm	(5 μm to 80 to 500 μm)	80 to 500 μm		
Predominating C-C-bond type	sp^2 or sp^3 , linear bond	sp^2	sp^3	sp^2	sp^2 or sp^3	sp^3	sp^2	sp^2	sp^3	sp^3	sp^3	sp^3	sp^3	sp^3	sp^2
Film No.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3.1	3.2	3.3	3.4	3.5	3.6	
Designation	Plasma-polymer film	Hydrogen-free amorphous carbon film	Tetrahedral hydrogen-free amorphous carbon film	Metal-containing hydrogen-free amorphous carbon film	Hydrogenated amorphous carbon film	Tetrahedral hydrogenated amorphous carbon film	Metal-containing hydrogenated amorphous carbon film	Modified hydrogenated amorphous carbon film	nano-crystalline CVD diamond film	micro-crystalline CVD diamond film	doped CVD diamond film	CVD diamond	doped CVD diamond	graphite film	
Recommended abbreviation	<i>J.</i>	a-C	ta-C	a-C:Me	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti, ...)	a-C:H:X (X = Si, O, N, F, B, ...)	<i>J.</i>	<i>J.</i>	<i>J.</i>	<i>J.</i>	<i>J.</i>	<i>J.</i>	

Classification of amorphous hydrogenated carbon films

Necessity of carbon film classification:

- ▶ ternary phase diagram (sp^3C , sp^2C and H) for amorphous films (Jacob and Moller 1993, Robertson 2002)



- ▶ classification of a-C:H films into 4 categories by Cambridge University group (2005):
 - ▶ polymer-like a-C:H (PLCH): high H content (40–60 at. %); up to 70 % sp^3 but most sp^3C are H terminated \Rightarrow soft, low density, optical band gap 2–4 eV
 - ▶ diamond-like a-C:H (DLCH): intermediate H content (20–40 at. %); lower overall sp^3 content but more C-C sp^3 bonds than PLCH \Rightarrow better mechanical properties, optical gap 1–2 eV.
 - ▶ hydrogenated tetrahedral amorphous carbon films (ta-C:H): increased C-C sp^3 content whilst keeping a H content low (25–30 at. %) \Rightarrow higher density (up to 2.4 g/cm³) and Young's modulus (up to 300 GPa)
 - ▶ graphite-like a-C:H (GLCH): low H content (< 20 at. %); high sp^2 content and sp^2 clustering \Rightarrow gap under 1 eV

Methods for synthesis of carbon nanotubes (CNTs)

○ arc discharge deposition

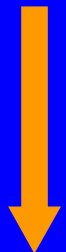
large quantities of CNTs but the purity is usually about 30%; not suitable for direct synthesis of supported aligned CNTs

○ laser ablation of graphite

costly apparatus not amenable for scaleup; small quantities of high-quality SWNTs in 70-90% purity

○ chemical vapor deposition (CVD)

(energy source)

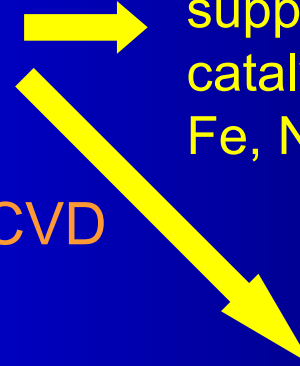


thermal CVD

plasma enhanced CVD (PECVD)

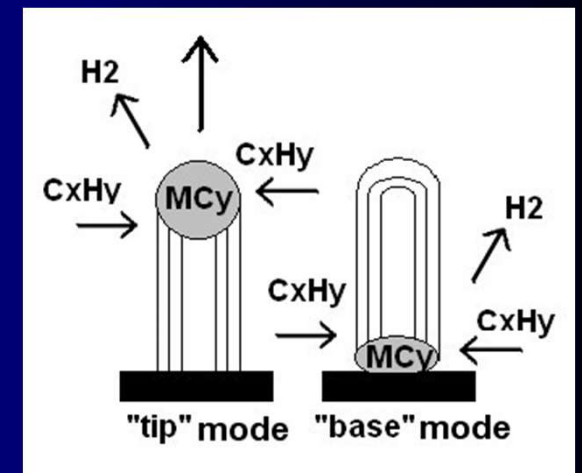


supported catalyst:
Fe, Ni, Co ...

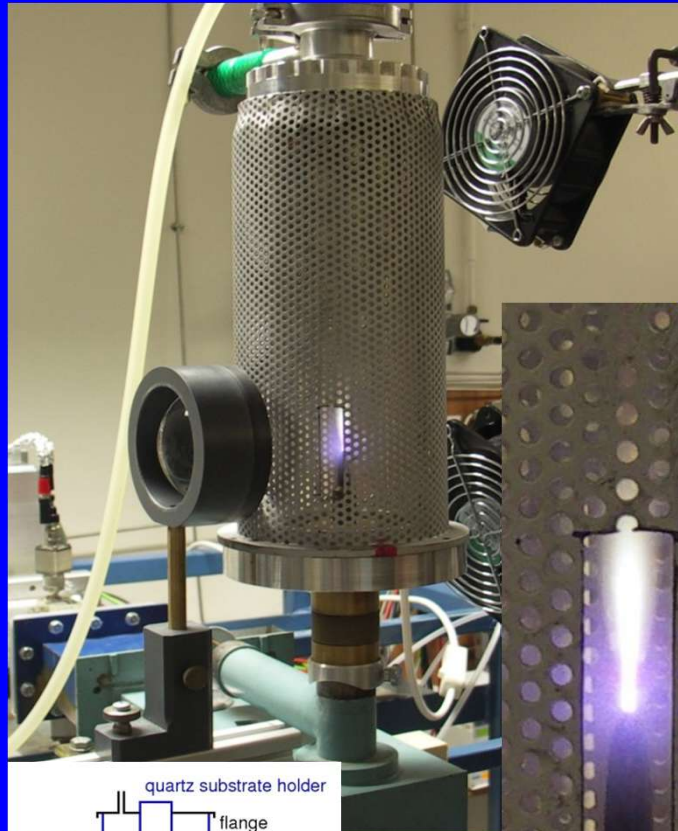


reactants: hydrocarbons or CO mixed with H_2 , NH_3 , N_2 ...

floating catalyst: $Fe(C_5H_5)_2$, $Fe(CO)_5$

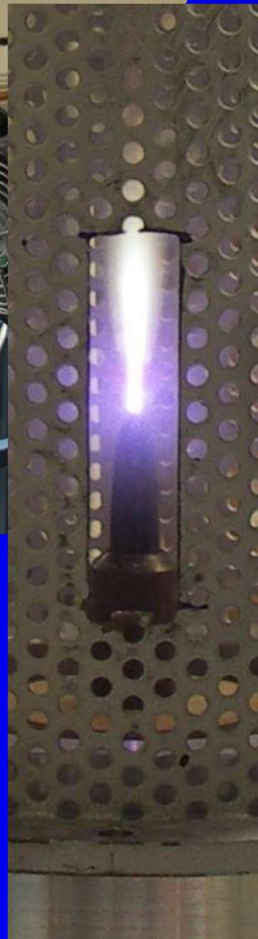
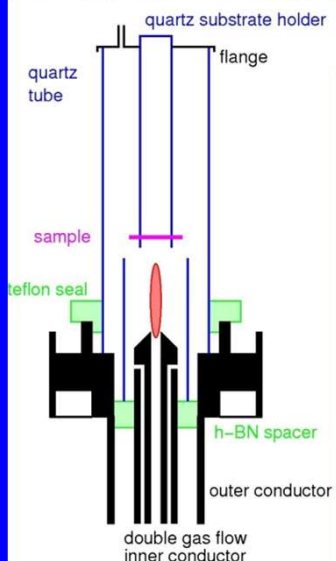
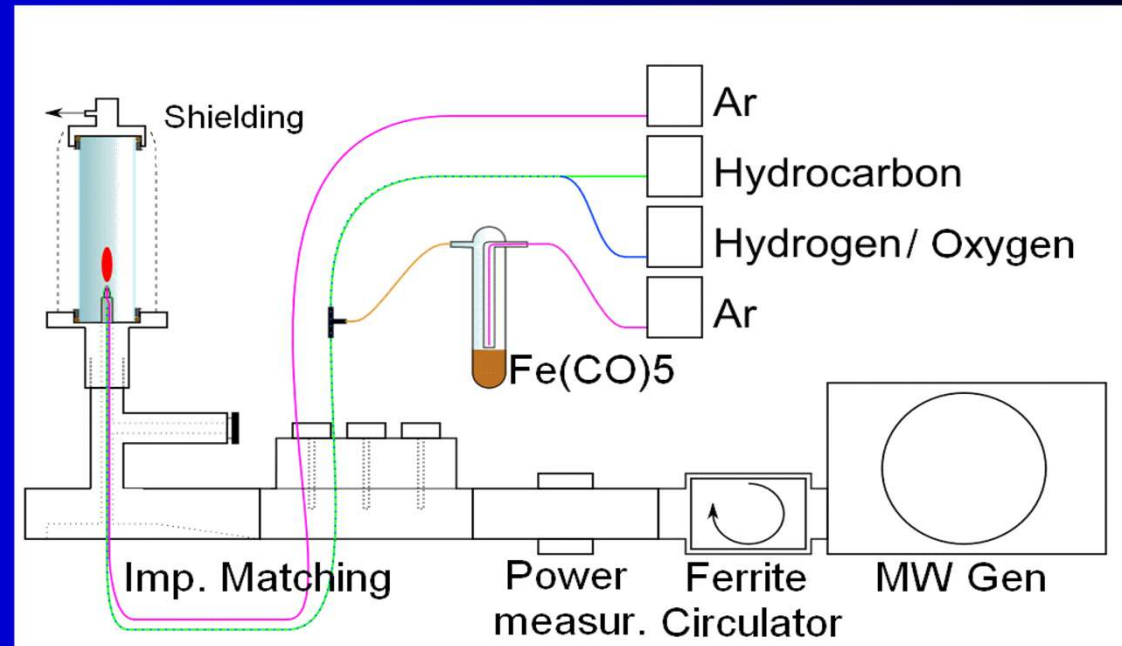


Microwave Plasma Torch at Atmospheric Pressure



Studied for the synthesis of

- carbon nanotubes (CNTs) using CH_4
- iron-based nanoparticles (Fe-NPs) using $\text{Fe}(\text{CO})_5$



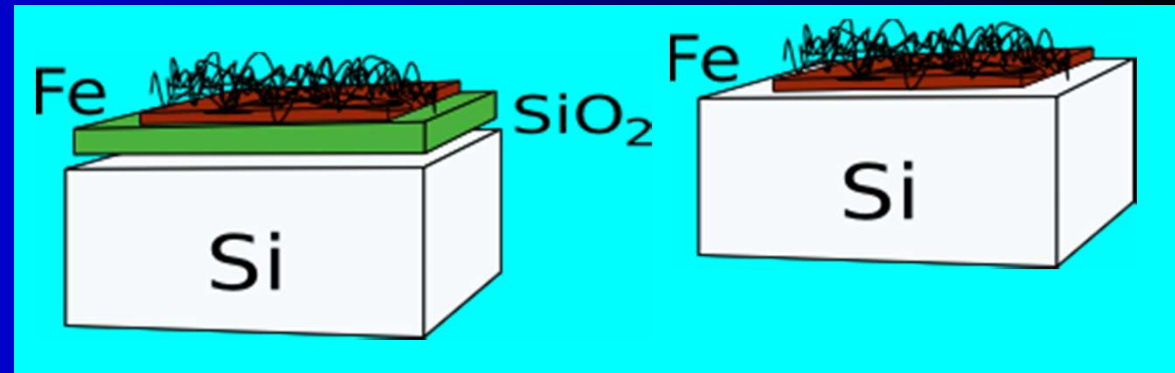
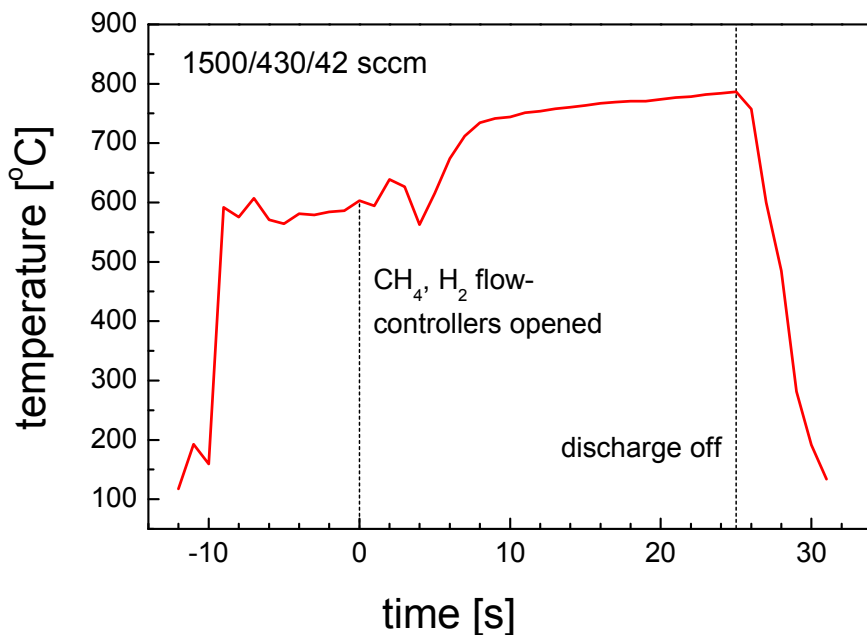
frequency 2.45 GHz, power 100 – 400 W
dual gas flow:

- central channel – Ar (500 – 1500 sccm)
- side channel – CH_4 , H_2 , Ar + $\text{Fe}(\text{CO})_5$

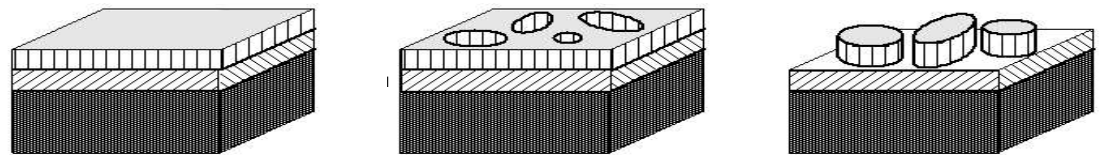
Surface Bound Deposition of CNTs

- mw power: 400 W
- Ar: 1500 sccm
- H₂: 285-430 sccm
- CH₄: 25-42 sccm

- Si substrate with
 - Fe catalytic layer, 5-15 nm
 - (- SiO₂ film, 200 nm)



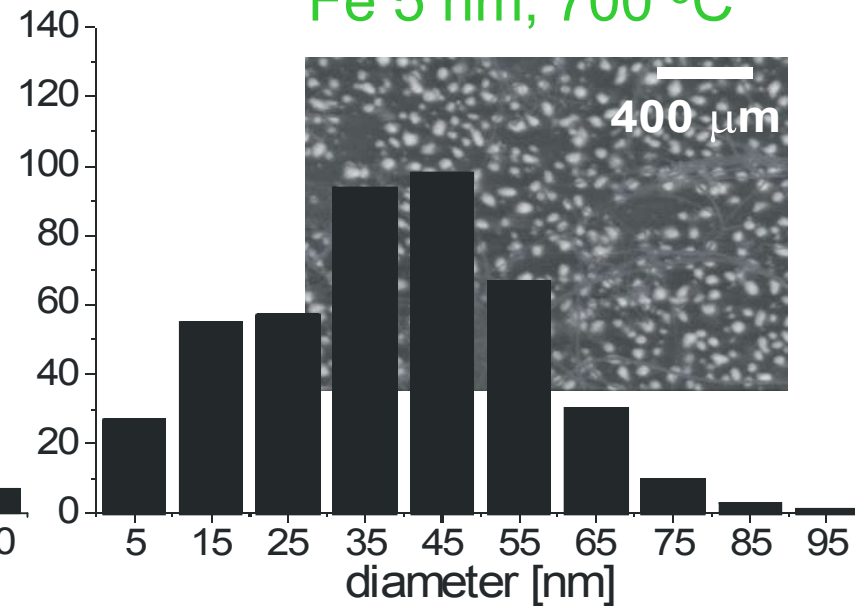
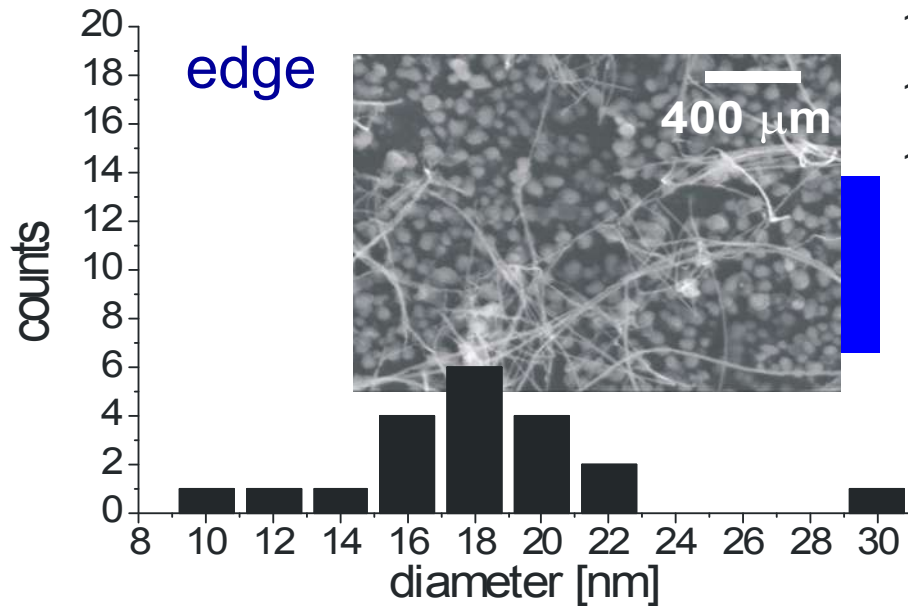
Nanostructuring of catalytical film is not necessary for torch deposition of CNTs. It takes place at the very beginning (few s) of deposition.



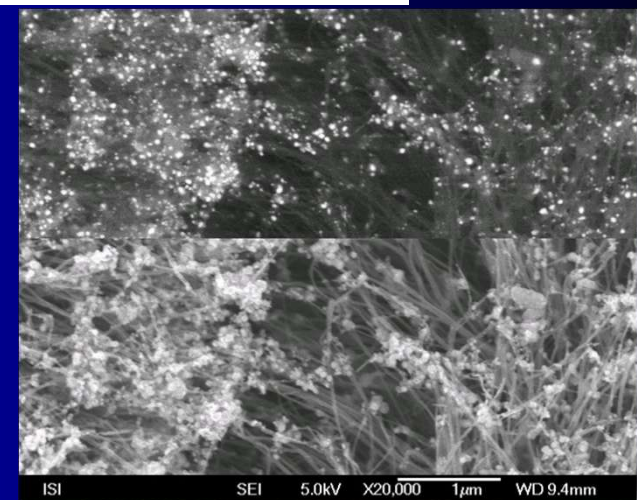
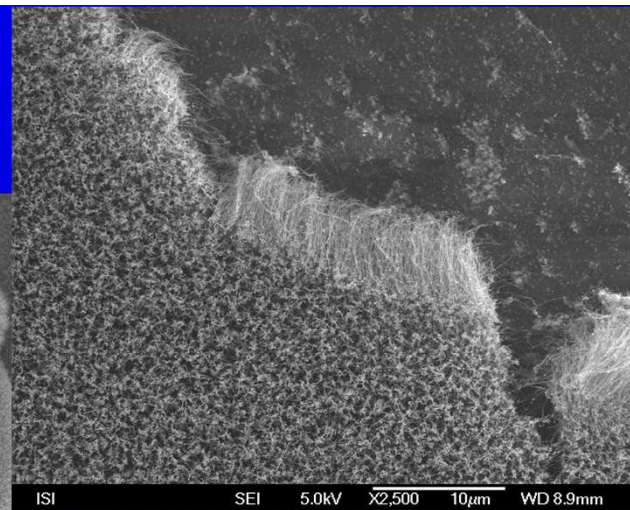
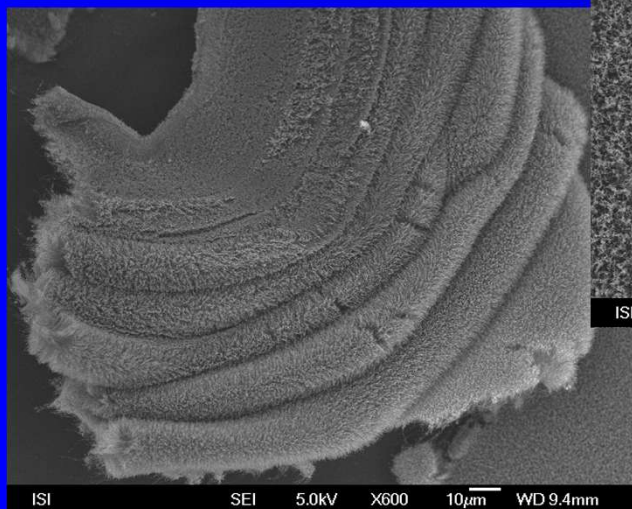
Type of CNTs Growth

1500/430/42sccm of Ar/H₂/CH₄

Fe 5 nm, 700 °C

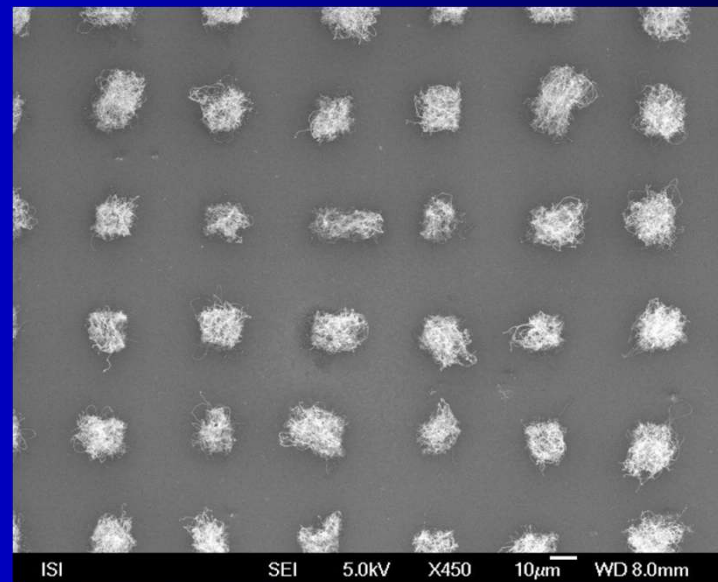
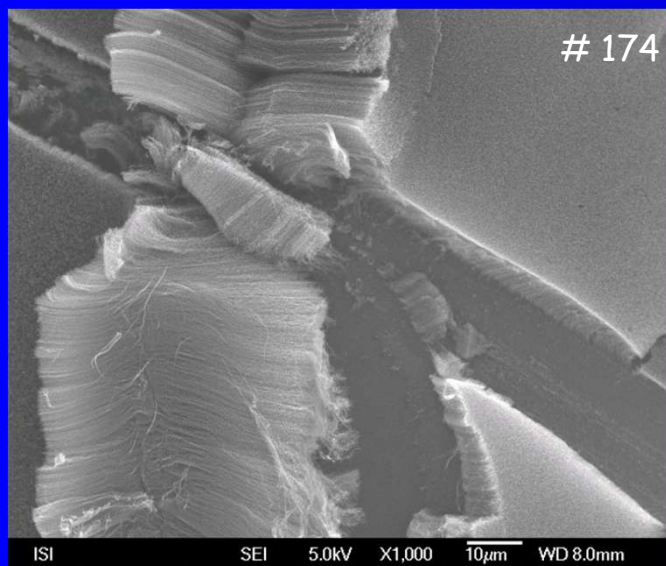


central area

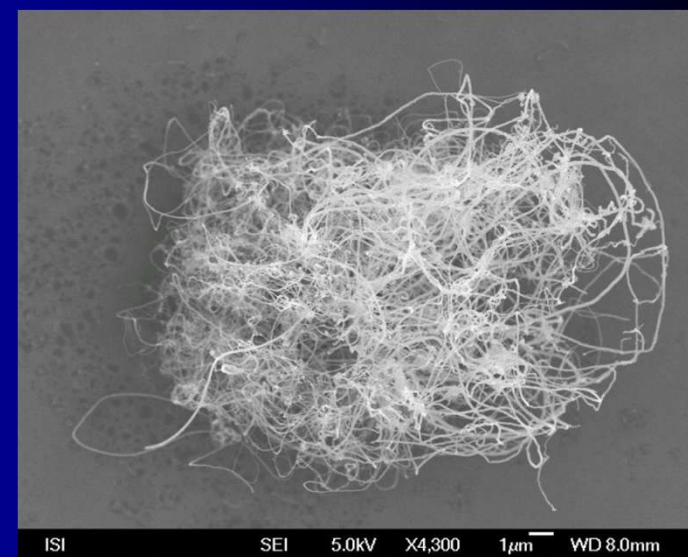
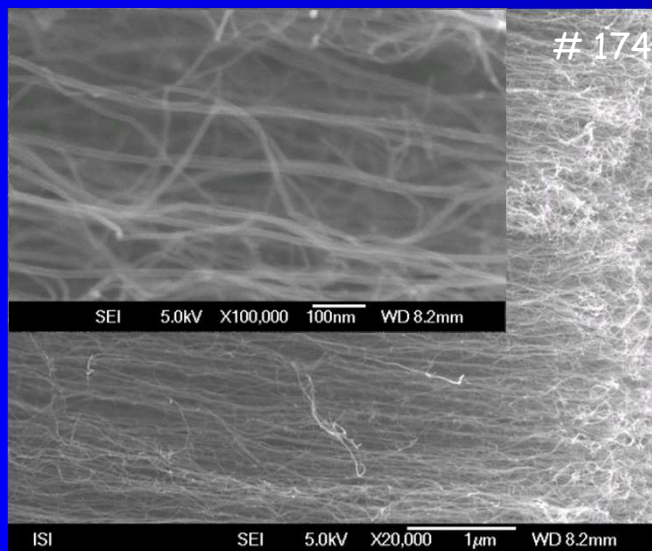


L. Zajickova et al. Plasma Process. Polym. 2007, 4, S245–S249

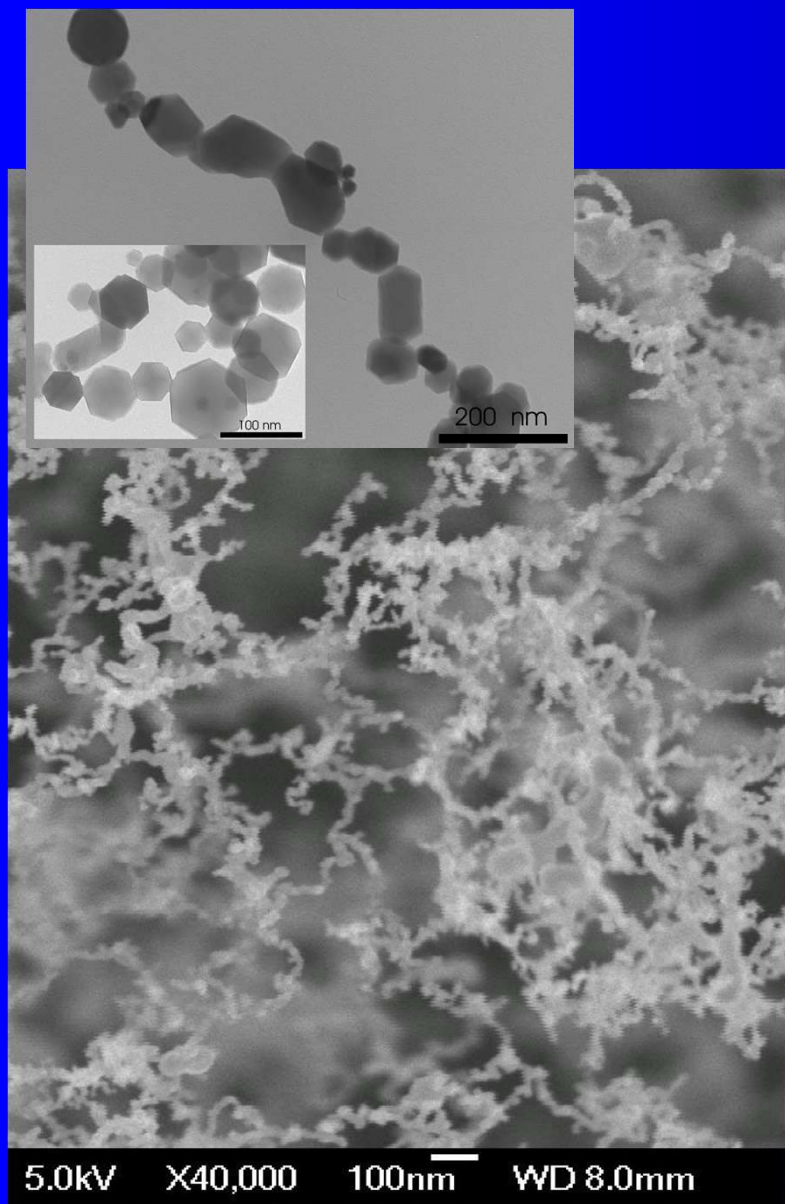
CNTs without Barrier SiO₂



1500/430/42 sccm
700 °C, 45 s,
15 nm Fe on Si



Iron Oxide NPs



phase	type of magnetism	M_s (300K) (A.m ² /kg)	applications
α -Fe ₂ O ₃	weakly ferromagnetic or antiferromagnetic	0.3	photo-chemistry
γ -Fe ₂ O ₃	ferrimagnetic ⇓	60-80	MRI, ferrofluids, drug delivery, cancer treatment, data storage
Fe ₃ O ₄	ferromagnetic	90-100	
ϵ -Fe ₂ O ₃	ferrimagnetic ⇓	20 hysteresis	high density data storage

single domain crystals (superparamagnetic)
- below approx. 14 nm