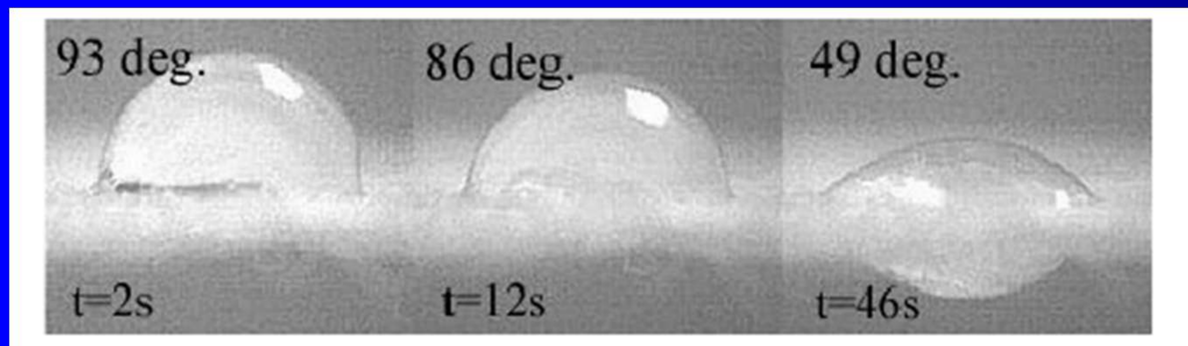
7.4 Plasma Surface Modification

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



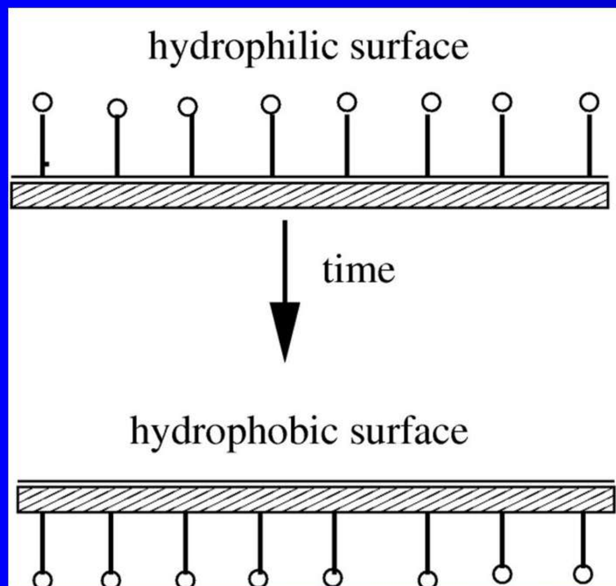
Plasma Treatment

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!

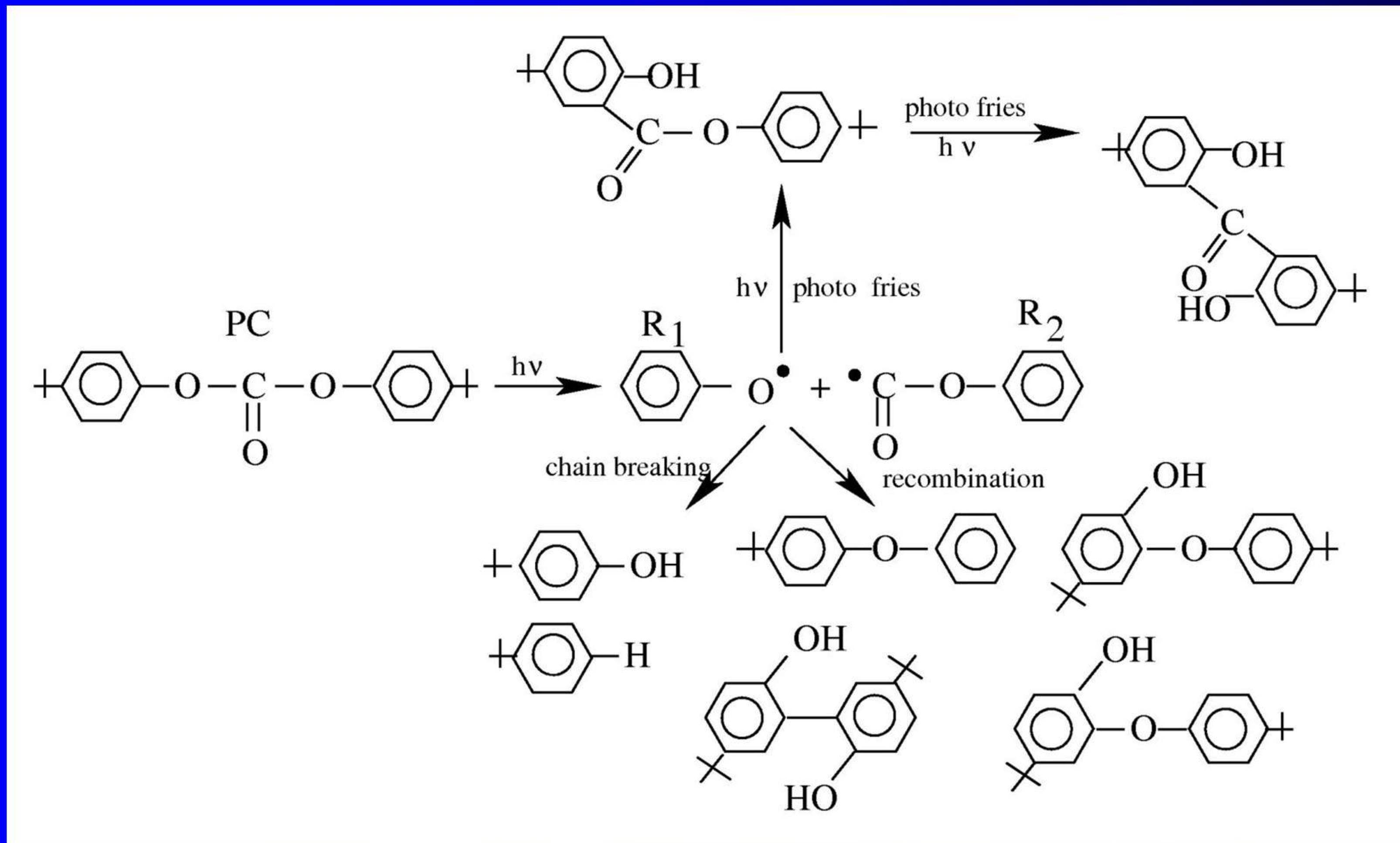
ageing of treated surfaces



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!

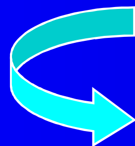
Plasma modifications of polymers in inert gas

- 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 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≡C), amide (N-C=O)
  - incorporation of oxygen and its functional groups
  - grafting of amine groups $–NH_2$

hydrophilization, biocompatibility, imobilization of biomolecules

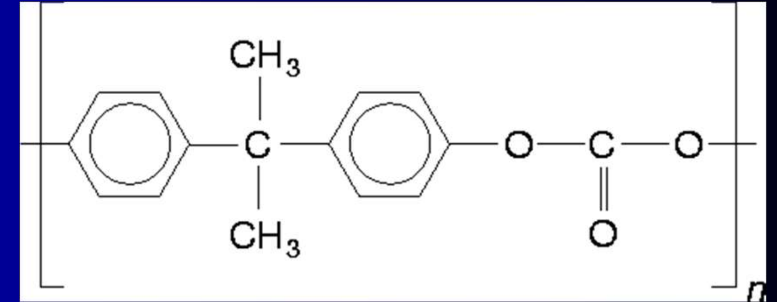
- plasma containing fluorine (SF_6, CF_4, C_2F_6 …)

  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

replace glass and metals in:

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

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

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

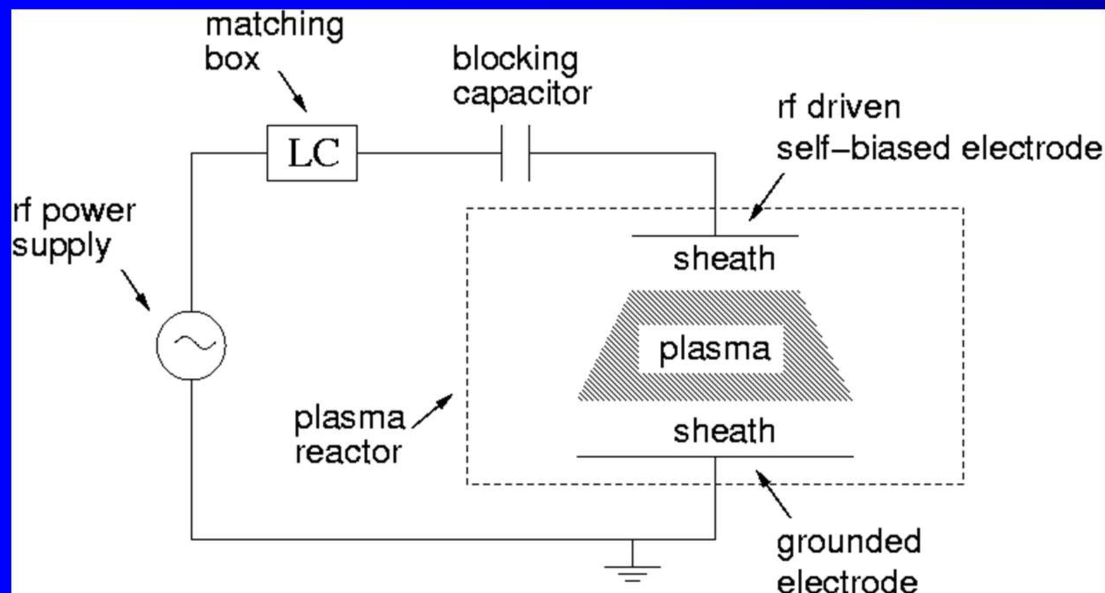
deposition of functional films (scratch resistant, reflective, ...)

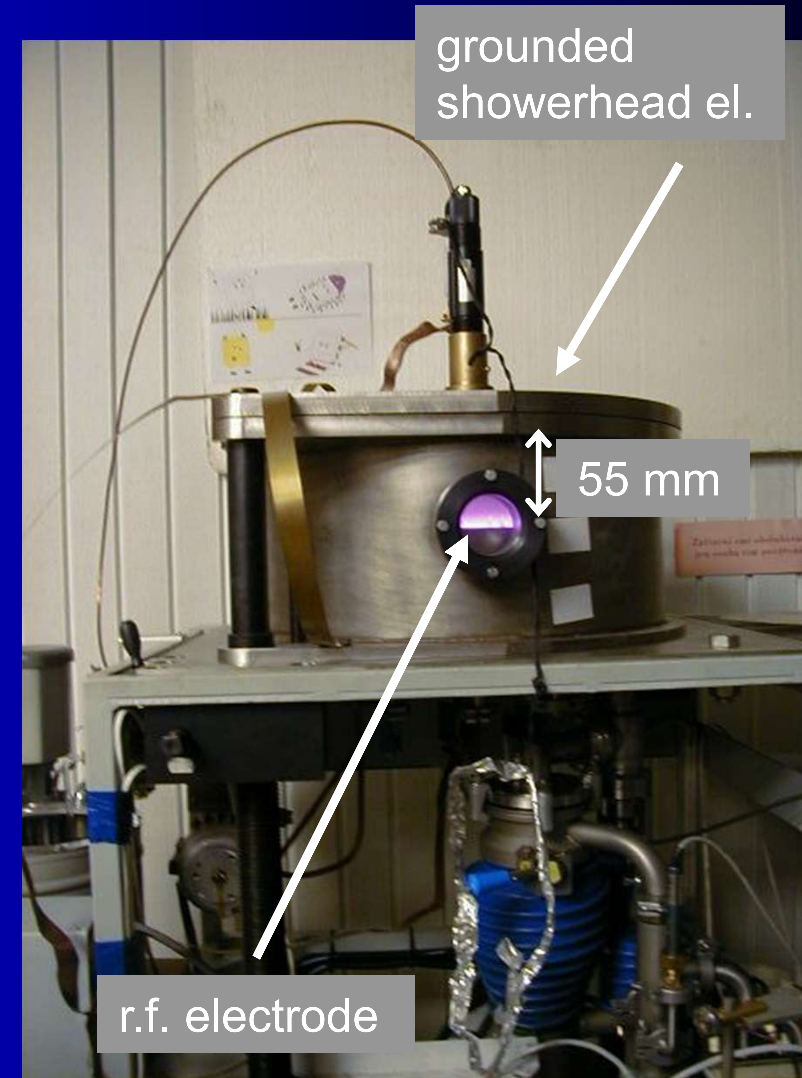
surface treatment for improved film adhesion

Plasma treatment of polycarbonate in Ar or O_2 discharges (CCP)

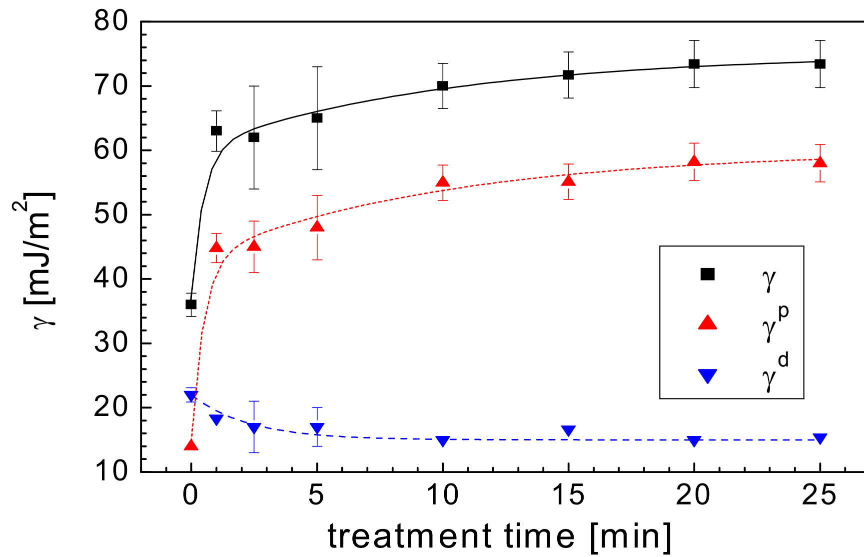
External plasma parameters:

- f = 13.56 MHz
- inner diameter of reactor 490 mm
- r.f. driven bottom electrode (420 mm)
- Ar, O_2: Q = 5.7 sccm , p = 1.5 Pa
- r.f. power P = 100 and 400 W

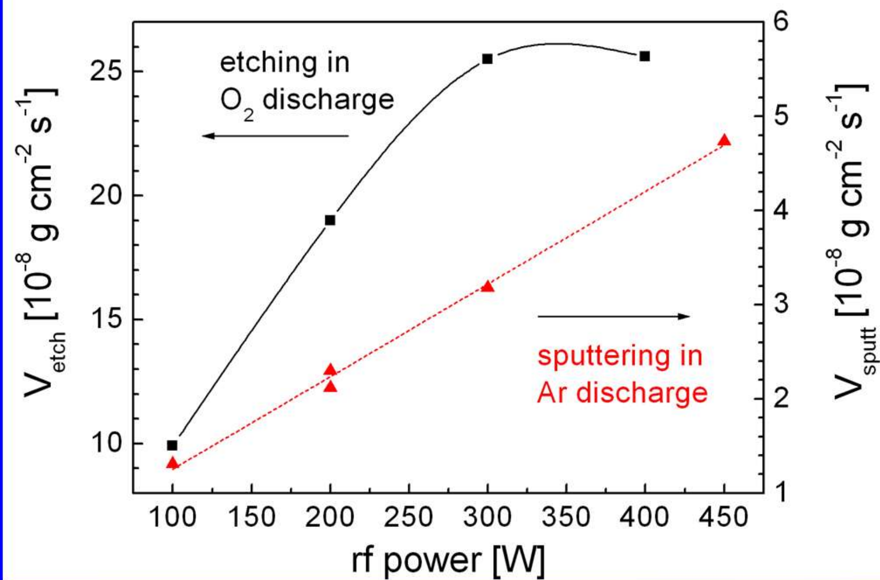


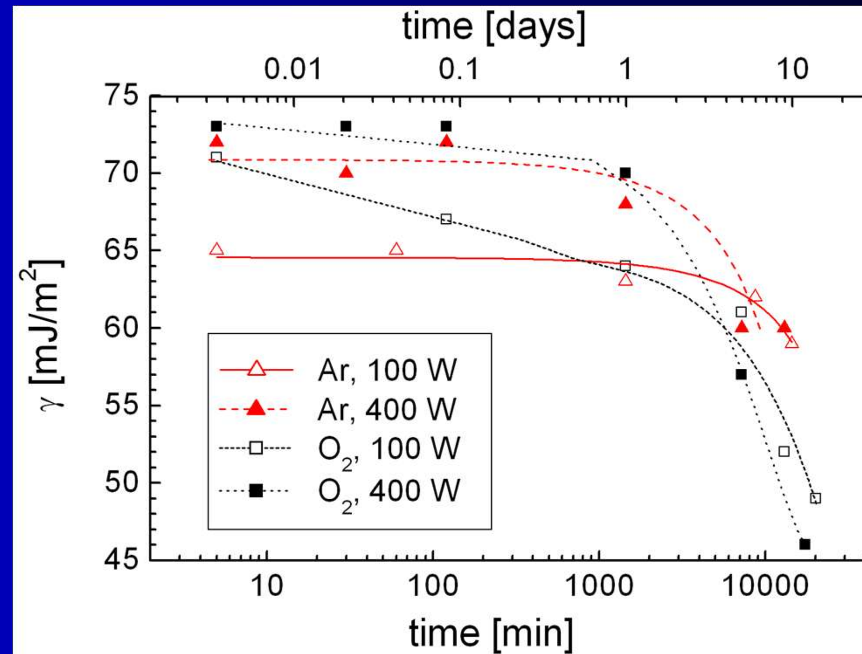


Plasma treatment of polycarbonate – etching rate and surface free energy

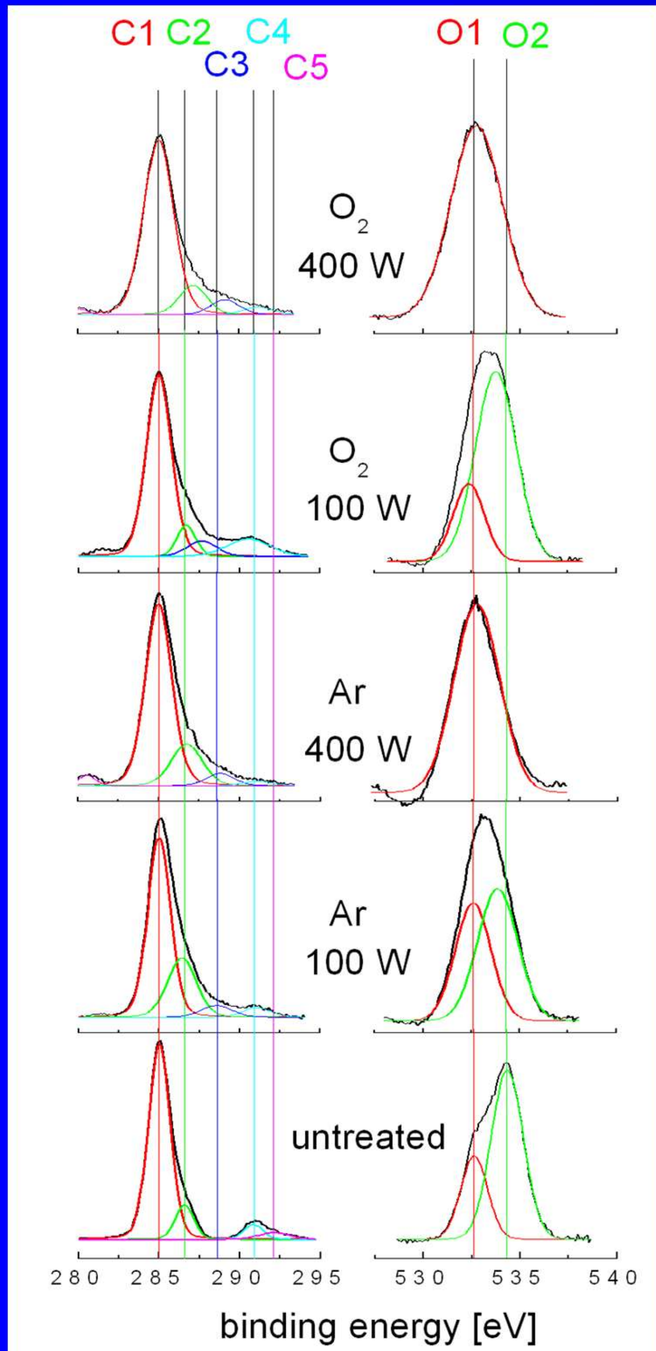


P = 100 W, U_{bias} = -115 V, Q_{ar} = 5.7 sccm, p = 1.5 Pa





Plasma treatment of polycarbonate – surface chemistry by XPS



	position [eV]	assigment
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

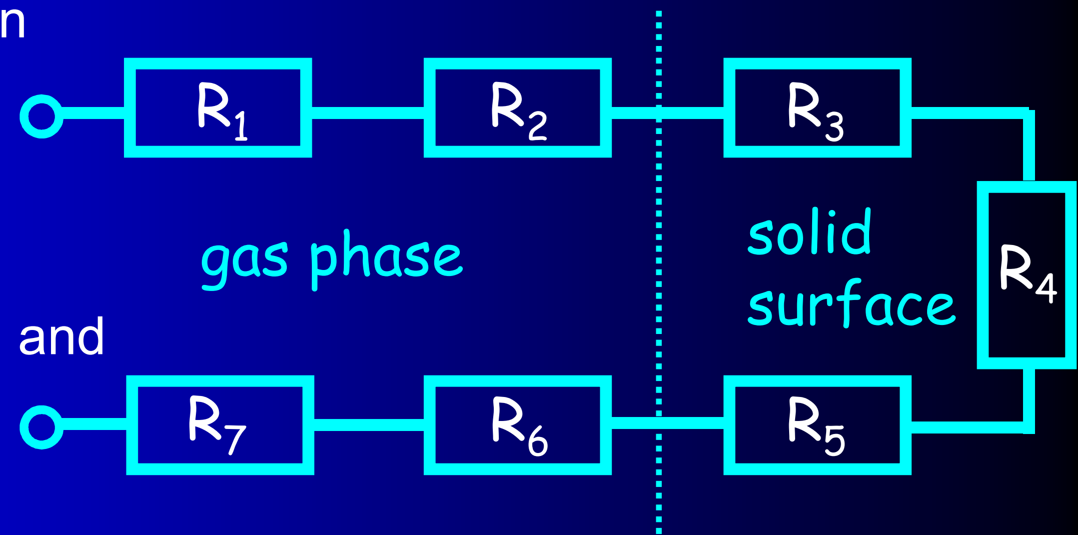
7.5 Plasma Enhanced Chemical Vapor Deposition

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 ☞ 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

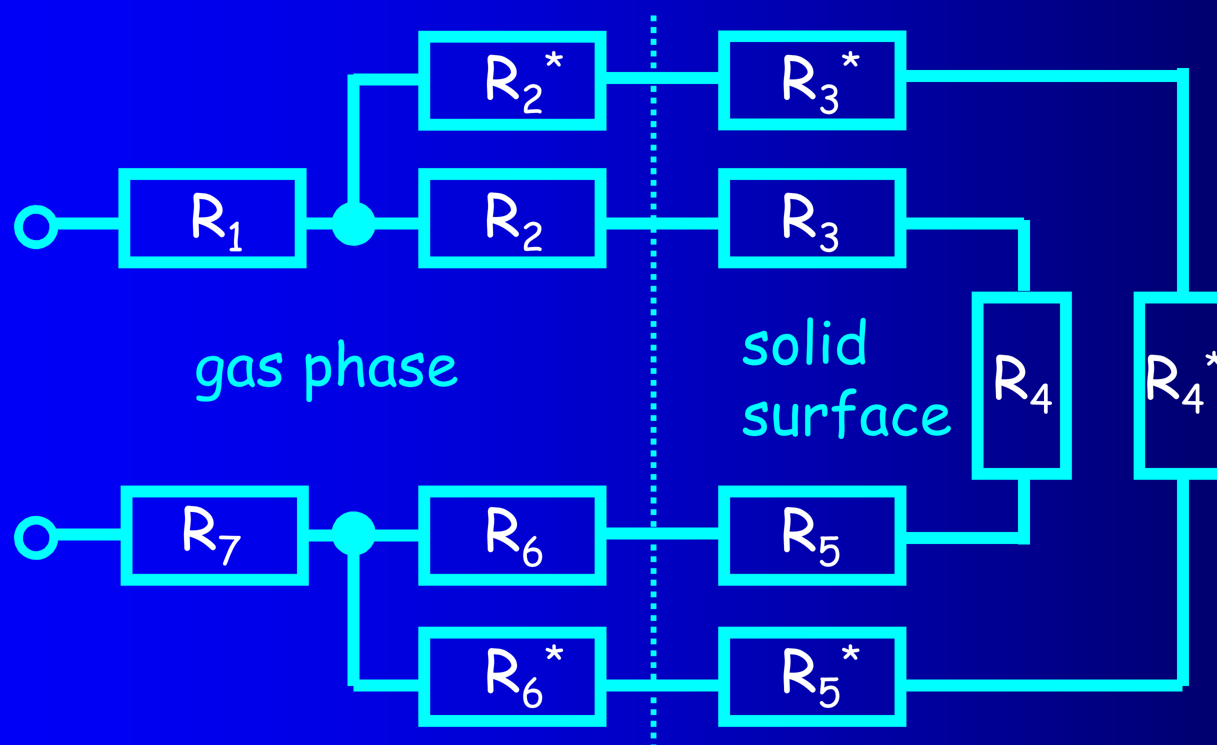
Plasma Enhanced (or Assisted) CVD (PECVD or PACVD)

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

☞ collisions of energetic electrons with heavy gas particles

☞ production of highy reactive species

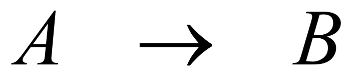
☞ more competing processes take place, deposition can be generally divided into thermal and plasma branches

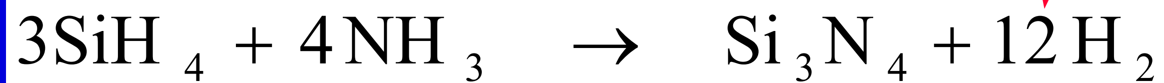


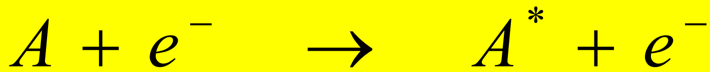
PECVD x CVD

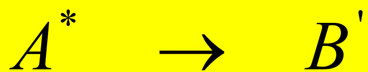
700-900°C

reaction branch:

thermal 



plasma 



250-350°C

plasma reaction branch at PECVD is much more important because:

☞ 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 electrostaticaly (charge accumulation)

7.5.2 PECVD of materials with silicon

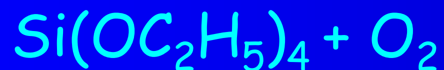
- dielectric films for microelectronics

silicon nitride:
(final protective passivation for integrated circuit)

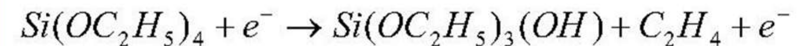
T=250-400 °C

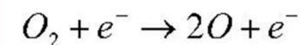
silicon oxide:
(insulating film – el. separation)

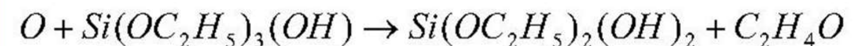
T=200-400 °C

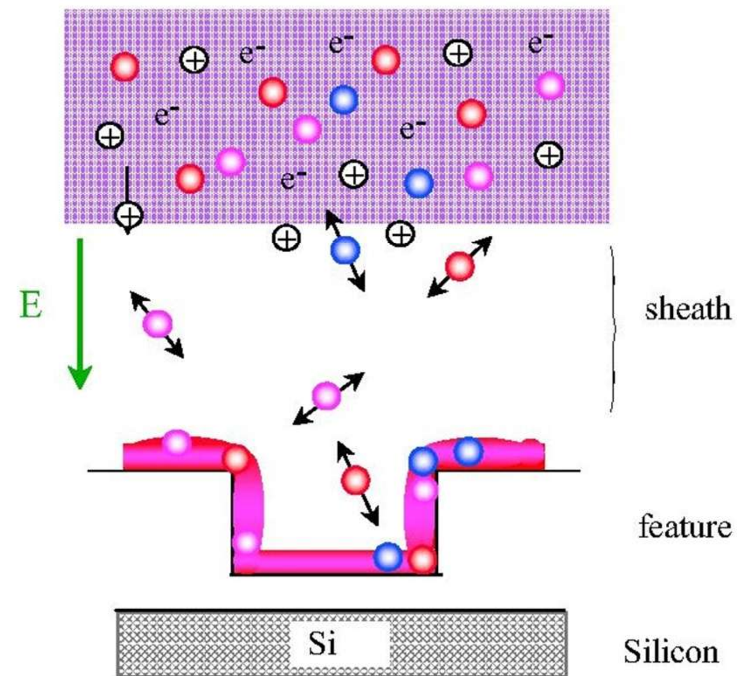


↘ tetraetoxysilane (TEOS)





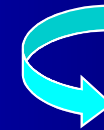




PECVD of materials with silicon

- more dielectric films for microelectronics

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



organosilicon glass (OSG)

- semiconducting films for microelectronics

  epitaxial silicon: SiH_4+H_2 T=800 °C

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

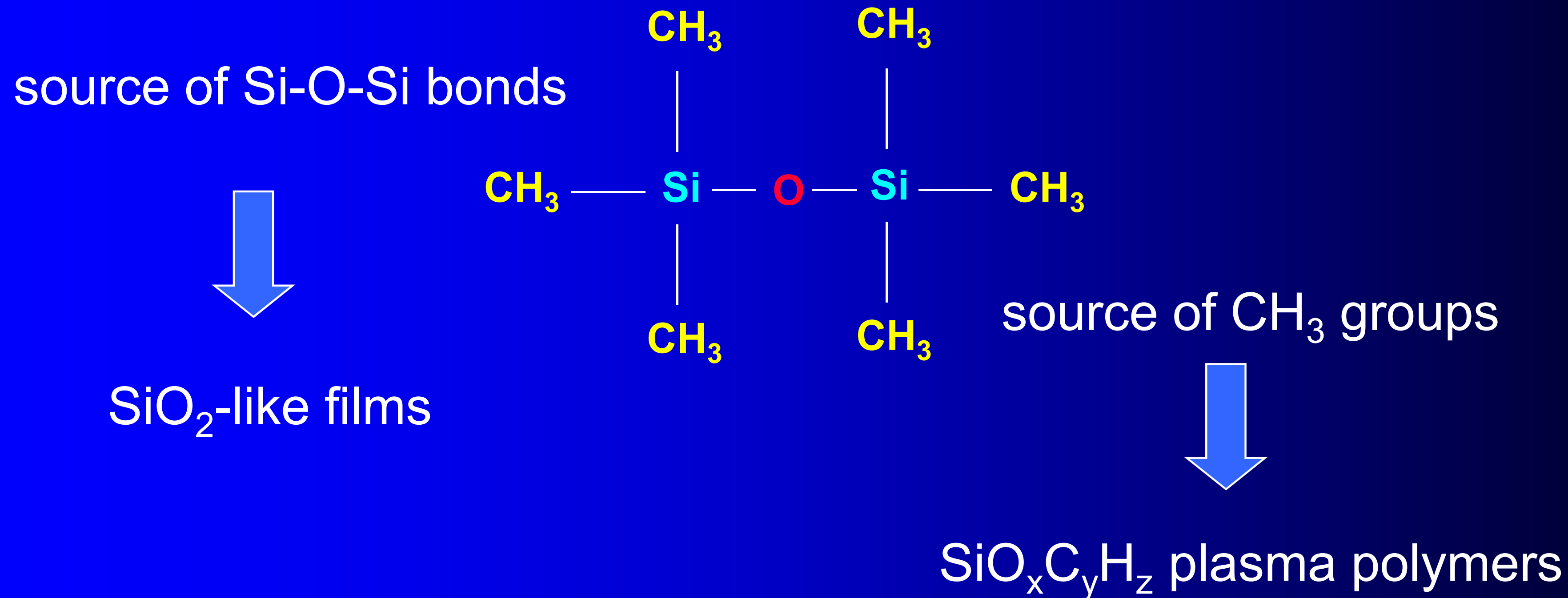
- SiO_x and $SiO_xC_yH_z$ for many other applications

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

  mixtures with organosilicons (TEOS, HMDSO, HMDSZ)

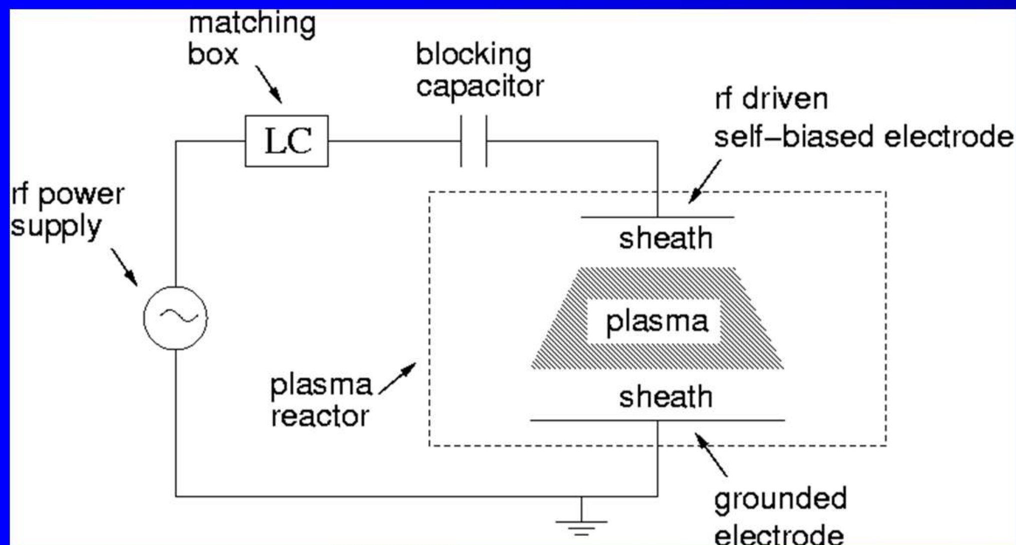
PECVD of films using HMDSO

(hexamethyldisiloxane)



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

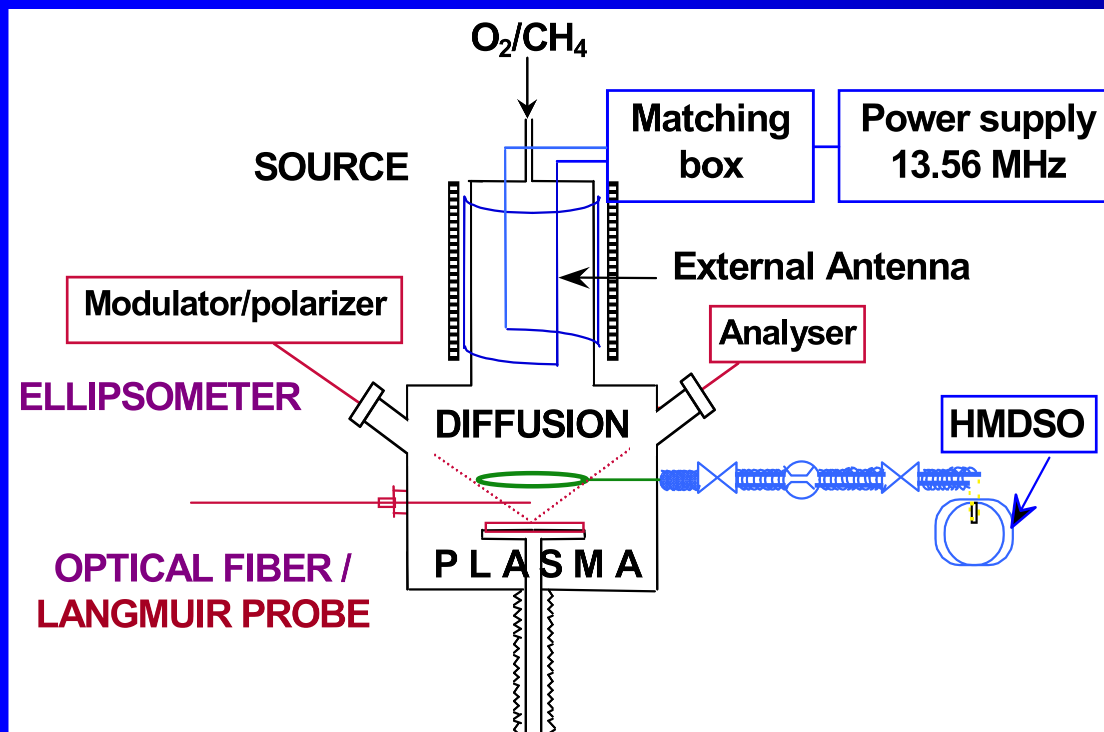
PECVD from HMDSO/O_2 in CCP and ICP (13.56 MHz)



5-100 % HMDSO in O_2

CCP:

- Q_{hmdso} = 4 sccm, Q_{o2} = 0 – 80 sccm
- pressure 1 - 40 Pa
- rf power 100 - 450 W
- dc self-bias from –20 and –335 V

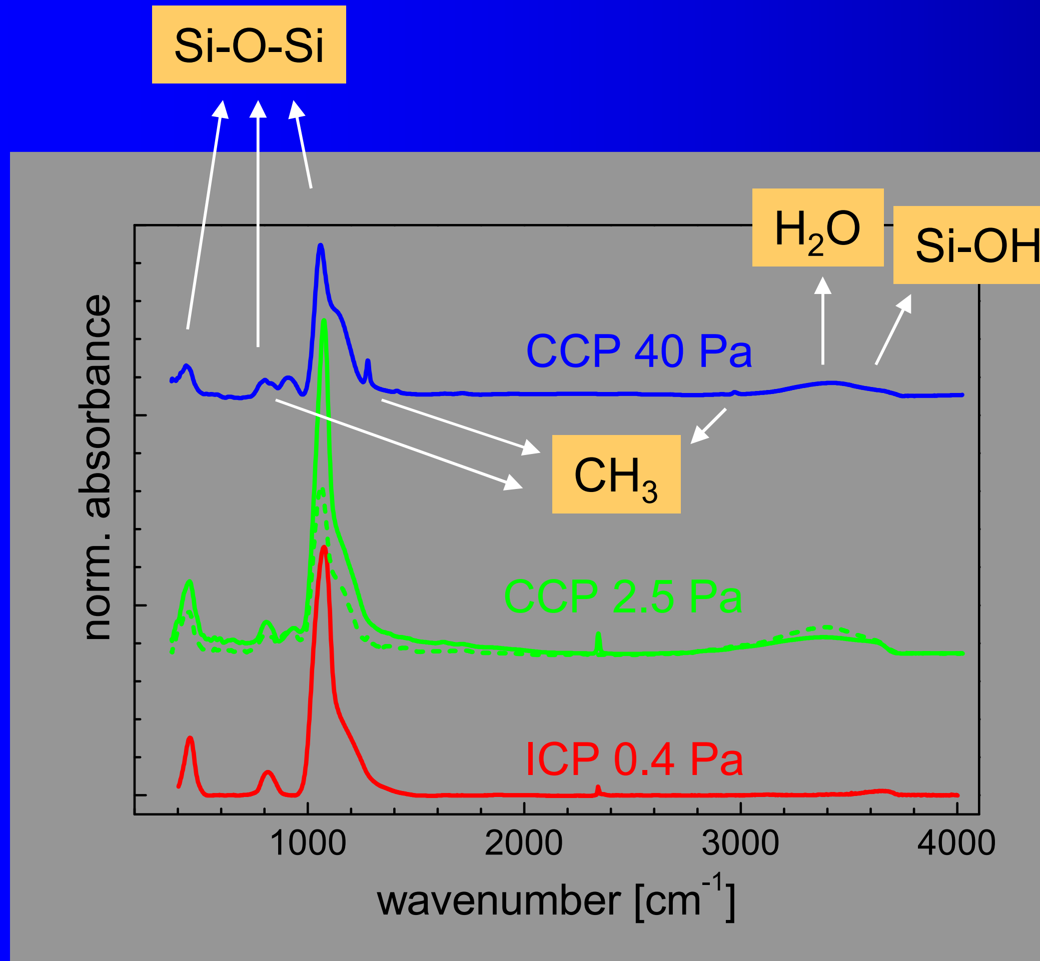


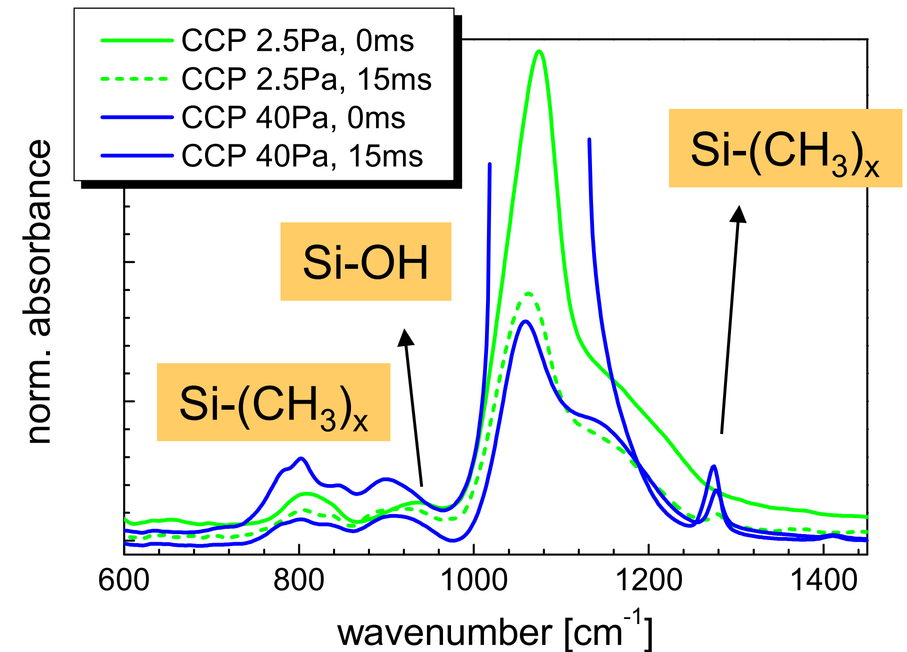
helical antenna in ICP mode:

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

Variation of film composition

5 % HMDSO in O_2

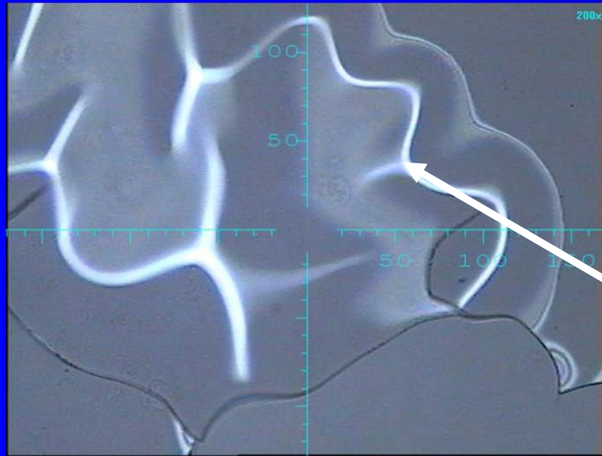


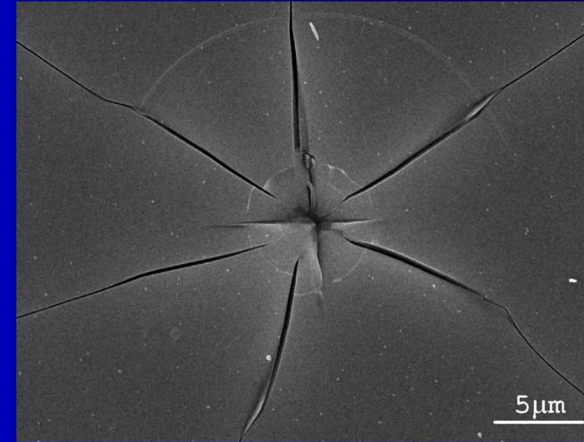


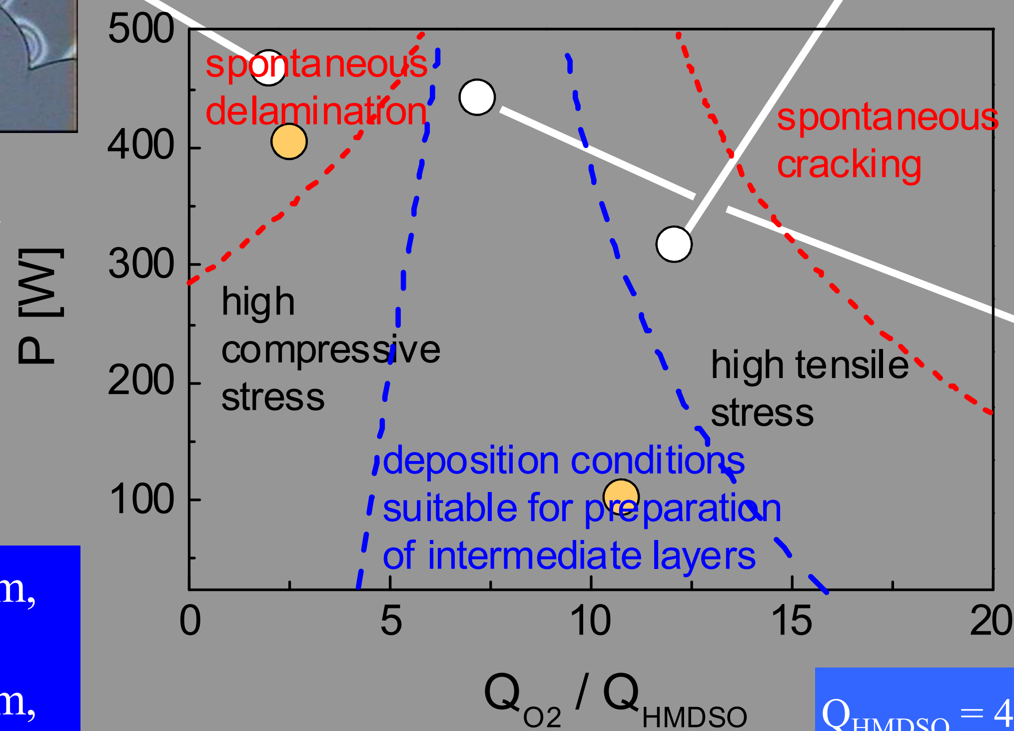
- ⇨ *0.4 Pa: SiO_2 structure, almost no impurities*
- ⇨ *2.5 Pa: SiO_2 structure, OH groups and H_2O*
- ⇨ *40 Pa: organosilicon films*

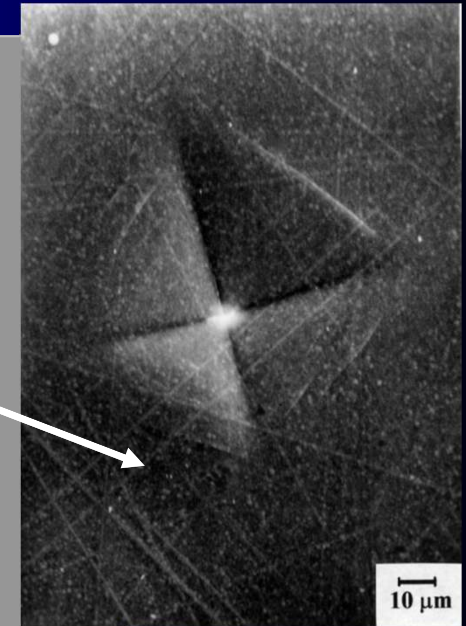
Domains of stresses

without treatment







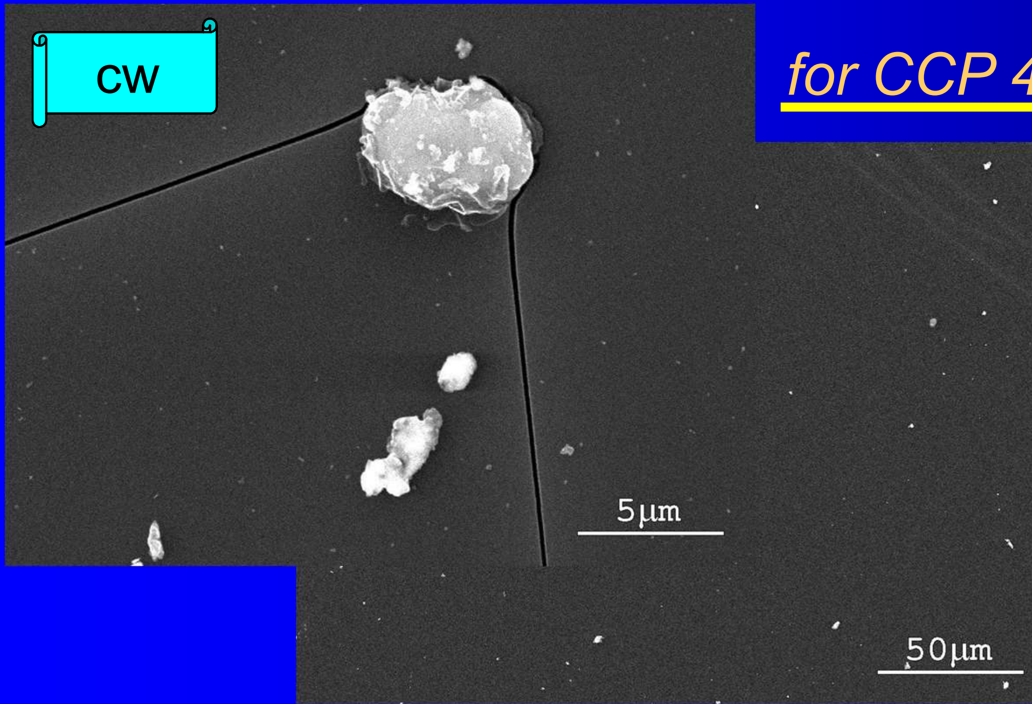


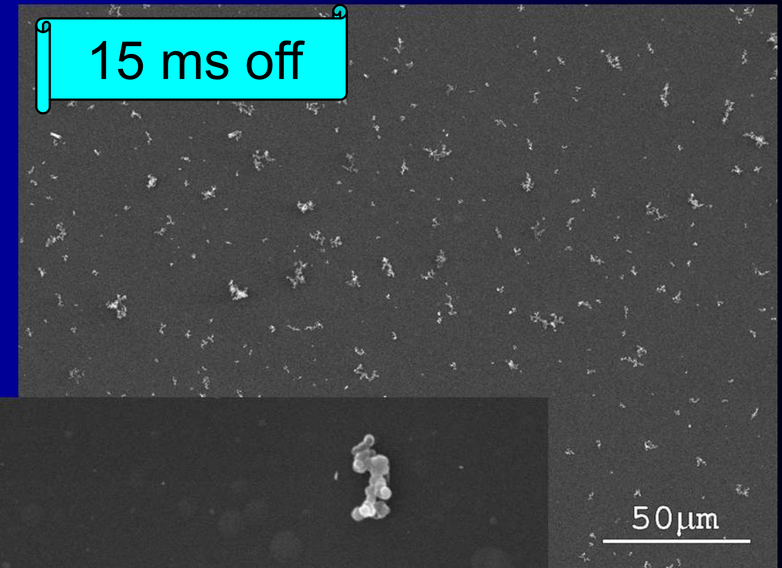
two different coatings choosen for treatment testing:

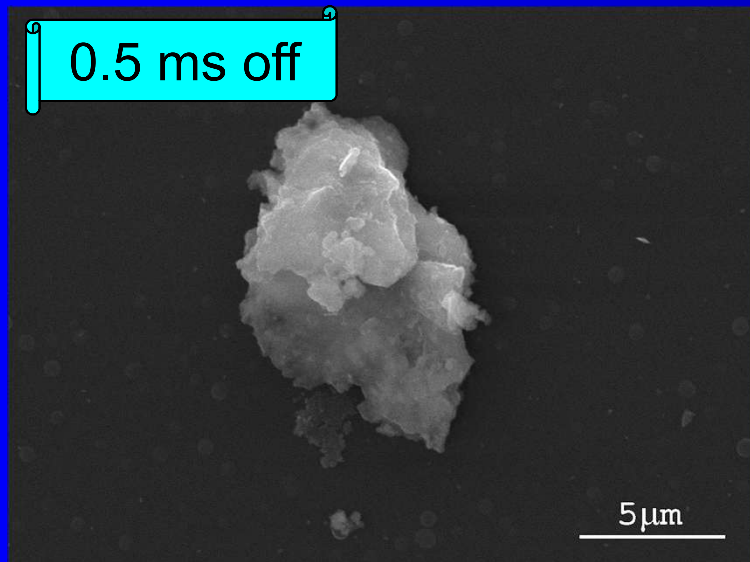
- $P = 100$ W, $Q_{O2} = 45$ sccm, $d = 0.5$ μm
- $P = 400$ W, $Q_{O2} = 10$ sccm, $d = 1.2$ μm

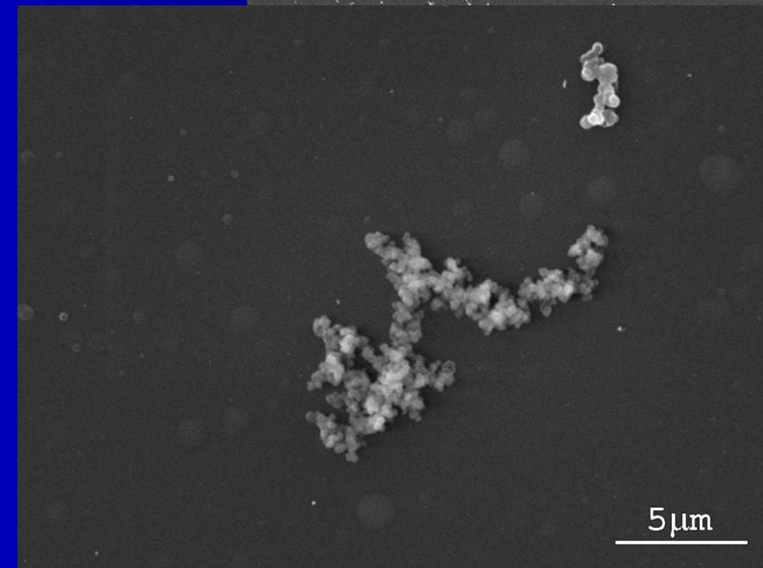
Film microstructure

for CCP 40 Pa







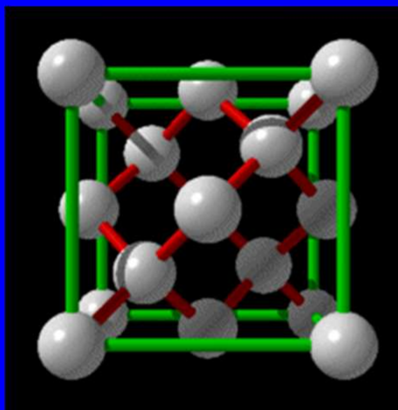


7.5.3 Carbon materials

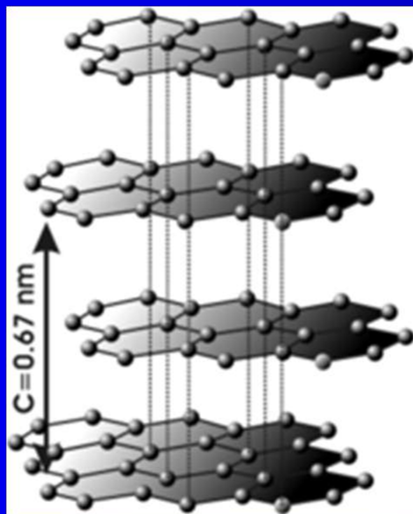
Diamond, graphite and much more

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

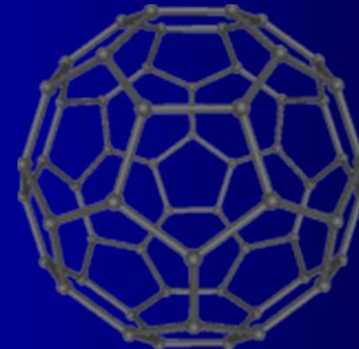
sp^3 C - diamond



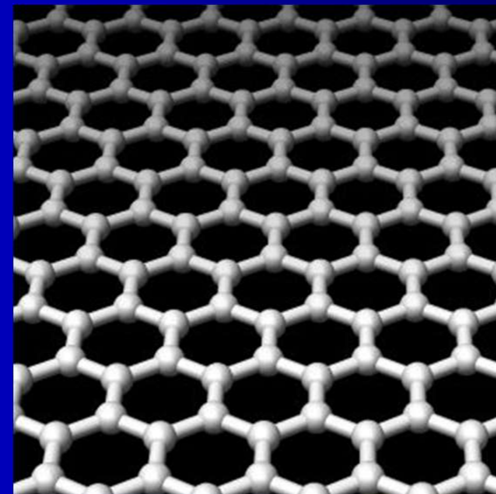
sp^2 C - graphite



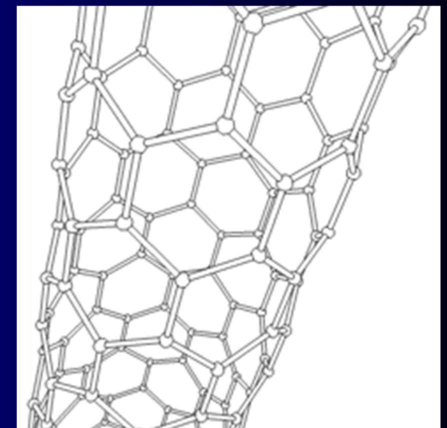
C_{60} - Buckminsterfullerene



graphene



carbon nanotube



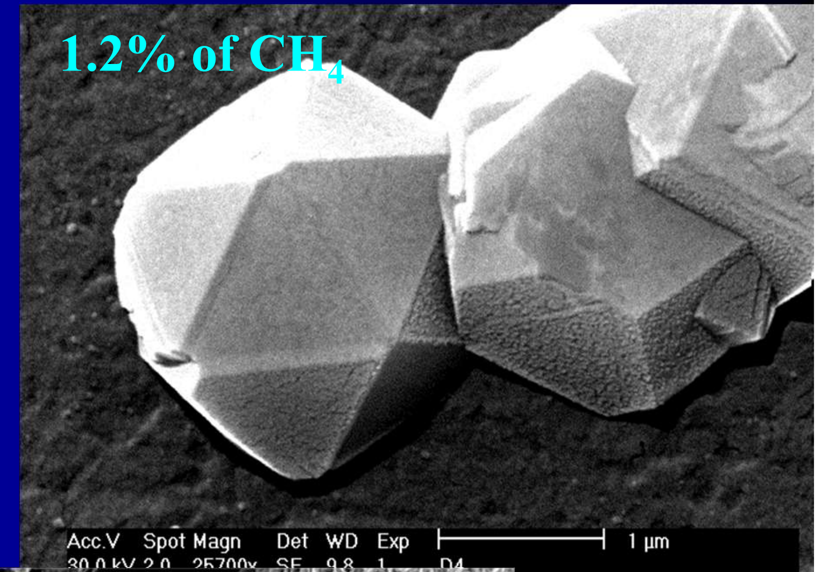
PECVD of carbon based materials

- crystalline diamond films

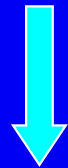
$0.1 - 5\%\ CH_4/C_2H_2/\ldots$ in H_2 $T=700\text{-}1000^oC$

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

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

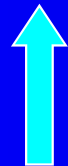


- amorphous diamond like carbon (DLC) films

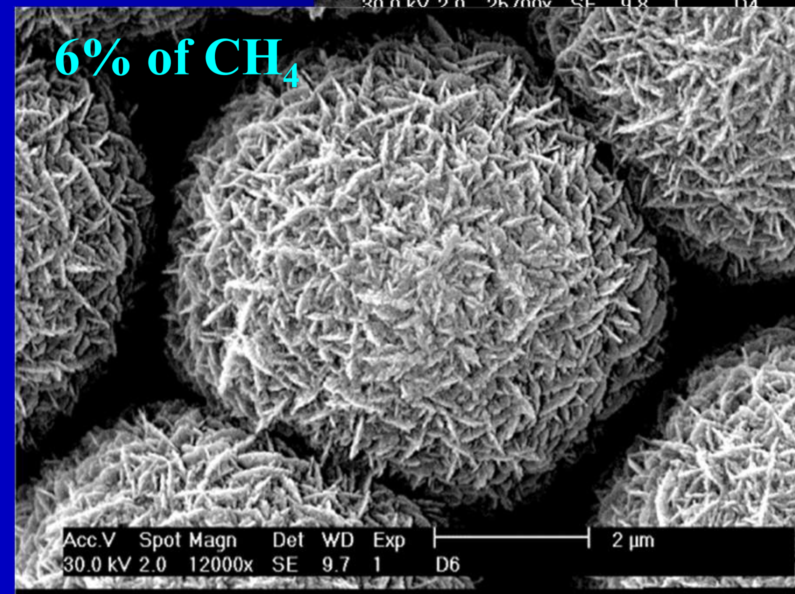


!! ion bombardment

$CH_4/C_2H_2/\ldots + (Ar/H_2)$, $T < 300\ ^oC$



- 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

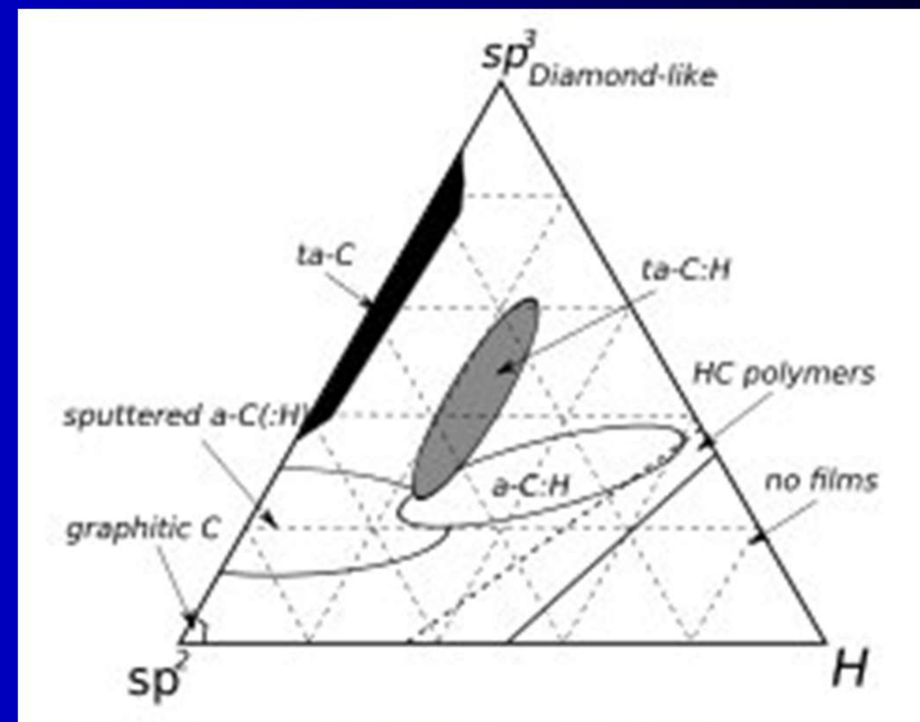
	Carbon films													
Designation	1 Plasma-polymer films	2 Amorphous carbon films (diamond-like-carbon films / DLC)							3 Crystalline carbon films					
									Diamond films					Graphite films
Thin film / thick film	Thin film	Thin film							Thin film			Thick film (free standing)		Thin film
Doping, additional elements		hydrogen-free			hydrogenated				undoped		doped	undoped	doped	undoped
				modified			modified							
				with metal			with metal	with non-metal						
Crystal size on the growth side	./.	(amorphous)							1 to 500nm, nano-crystalline	0.5 to 10 µm, mikro-crystalline	0.1 to 5 µm	(5µm 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^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	./.	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, ...)	./.	./.	./.	./.	./.	./.

http://www.ist.fraunhofer.de/english/c-products/tab/complete.html

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 cathegories 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 ⇒ 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 ⇒ 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. %) ⇒ higher density (up to 2.4 g/cm^3) 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 ⇒ gap under 1 eV

C. Casiraghi, A. C. Ferrari, and J. Robertson, Phys. Rev. B 72(8):1–14, 2005.