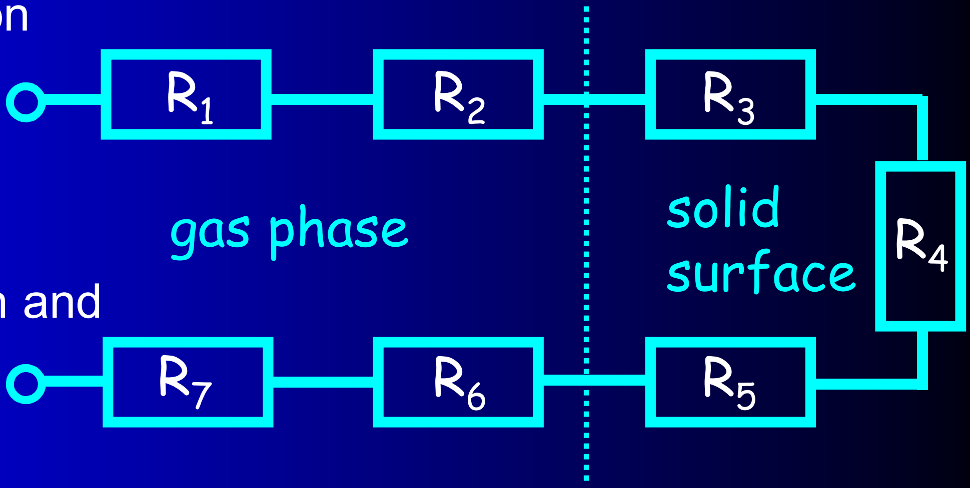
10. Plasma Enhanced Chemical Vapor Deposition

10.1 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

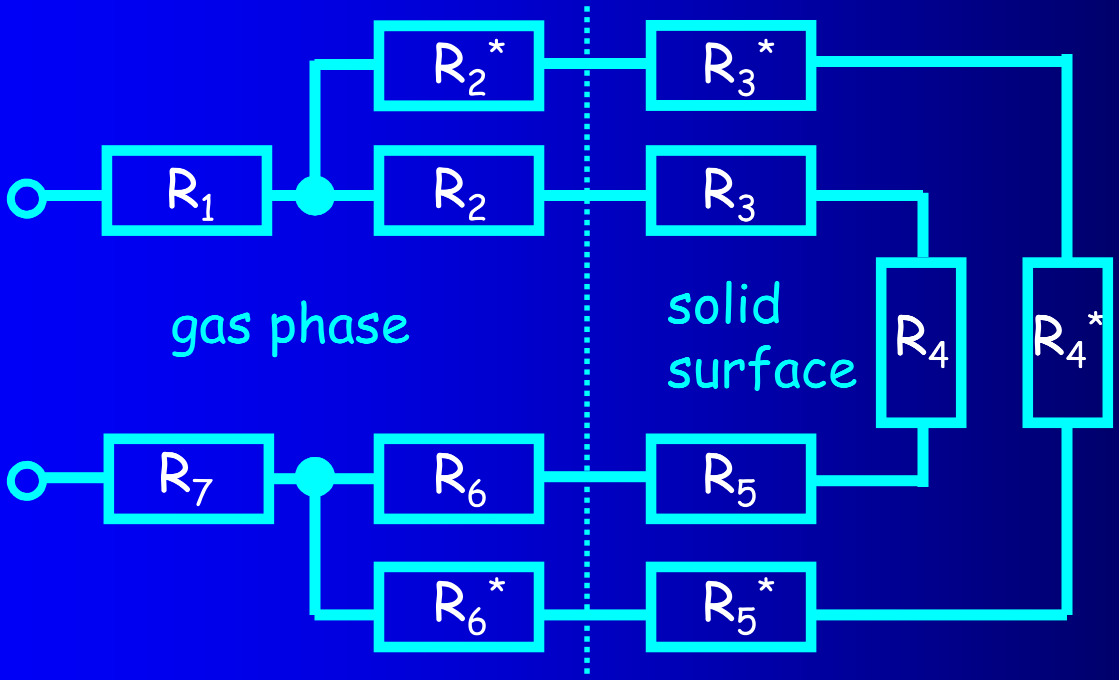
Plasma Enhanced (or Assisted) CVD (PECVD or PACVD)

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

reaction branch:

thermal $A \rightarrow B$ $3SiH_4 + 4NH_3 \rightarrow Si_3N_4 + 12H_2$

700-900°C

plasma $A + e^- \rightarrow A^* + e^-$

$A^* \rightarrow B'$ $SiH_4 + NH_3 \rightarrow SiNH + 3H_2$,

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)

10.2 PECVD of Silicon-Based Thin Films

- dielectric films for microelectronics

silicon nitride:
(final protective passivation for integrated circuit)

SiH_4+NH_3 or SiH_4+N_2

T=250-400 °C

silicon oxide:
(insulating film – el. separation)

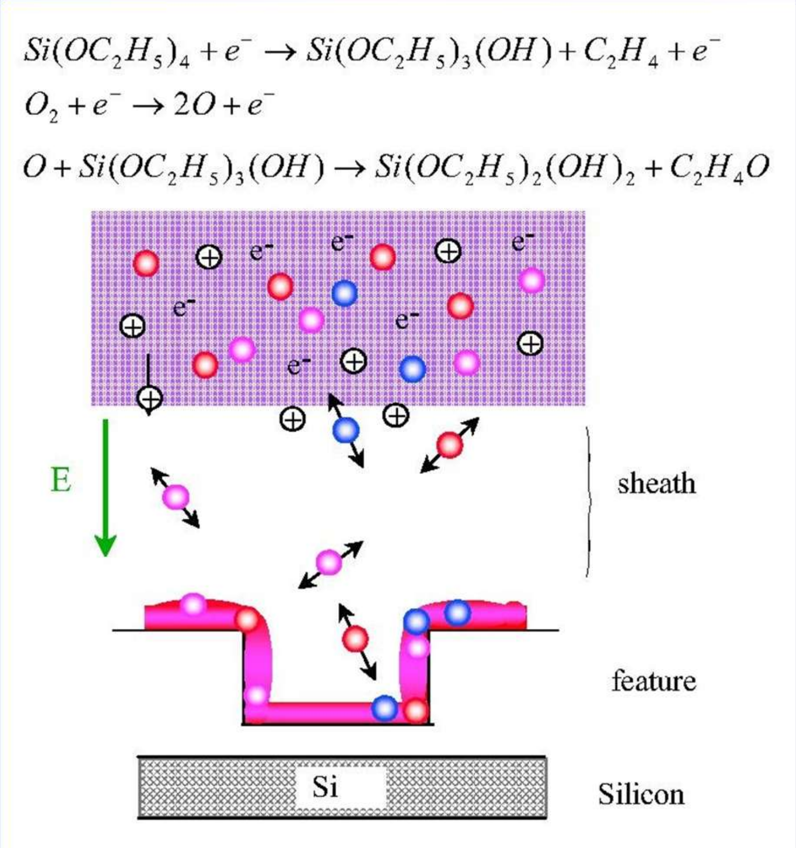
SiH_4+N_2O/NO/CO_2/O_2

T=200-400 °C

$Si(OC_2H_5)_4 + O_2$

↘

tetraetoxysilane (TEOS)



$$Si(OC_2H_5)_4 + e^- \rightarrow Si(OC_2H_5)_3(OH) + C_2H_4 + e^-$$

$$O_2 + e^- \rightarrow 2O + e^-$$

$$O + Si(OC_2H_5)_3(OH) \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_4O$$

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)

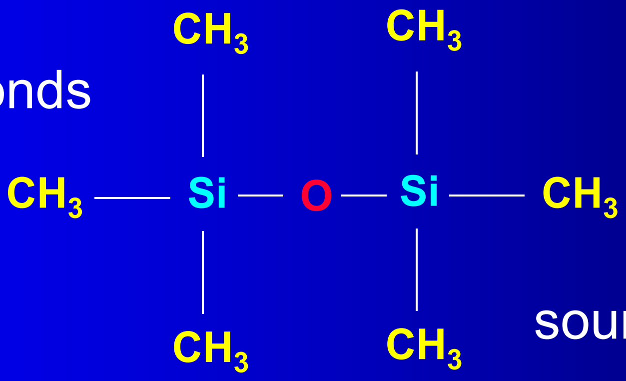
- SiO_x and $SiO_xC_yH_z$ for many other applications

  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)



$$CH_3 - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}} - O - \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{Si}}}} - CH_3$$

source of Si-O-Si bonds

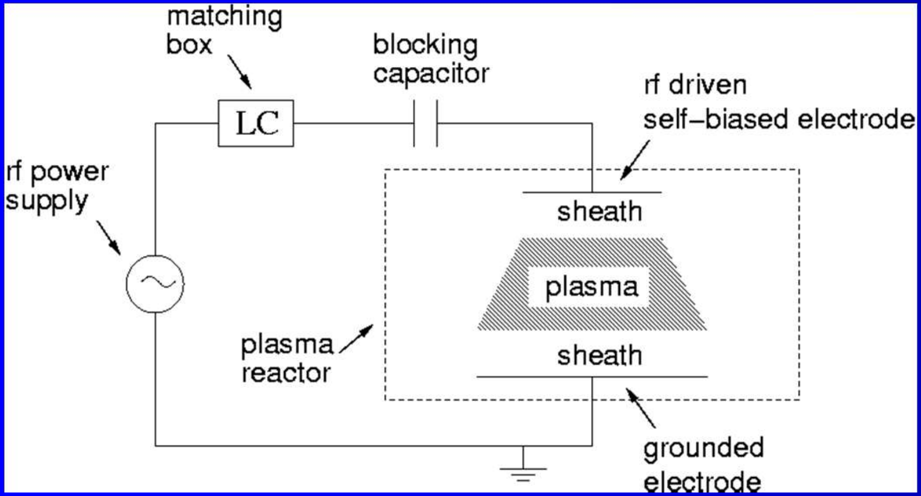
SiO_2-like films

source of CH_3 groups

$SiO_xC_yH_z$ plasma polymers

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

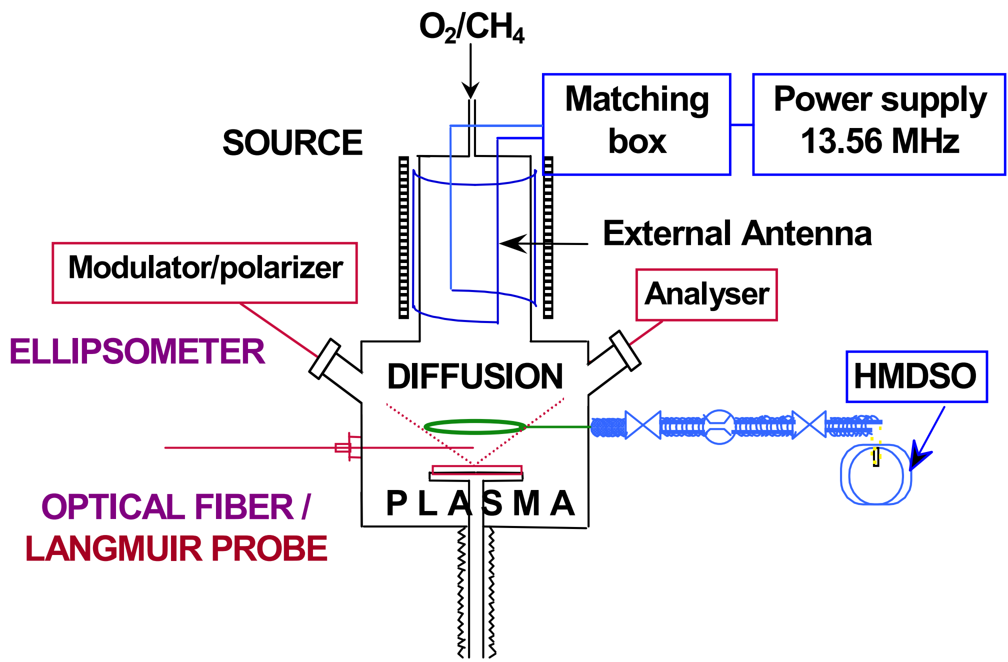
PECVD from HMDSO/O_2 in CCP and ICP (13.56 MHz)



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

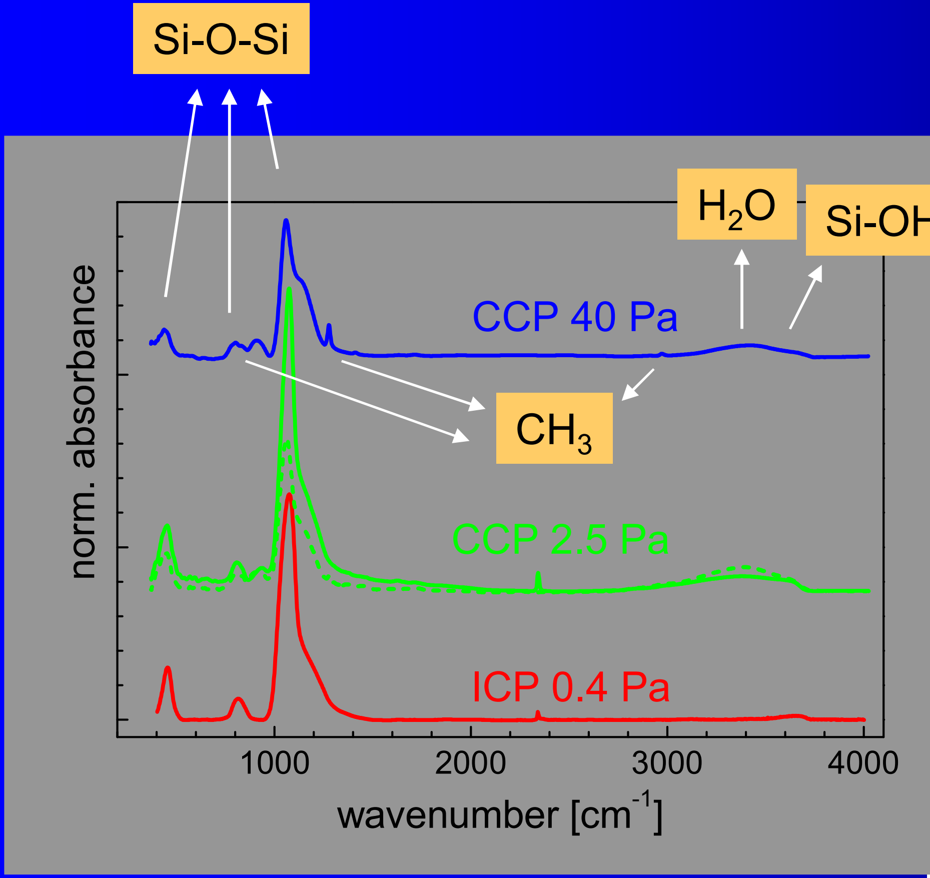


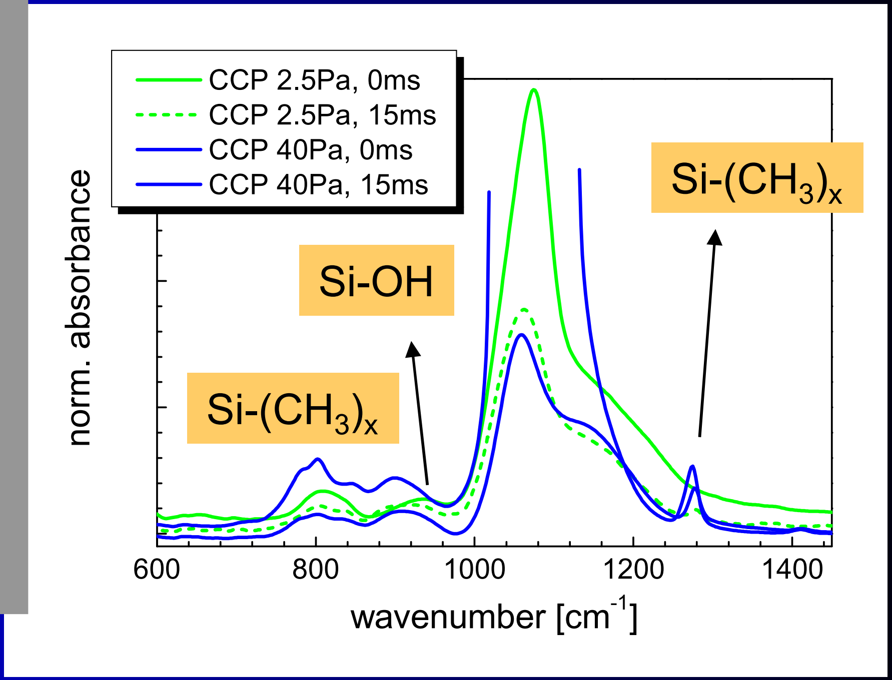
helical antenna in ICP mode:

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

Variation of film composition

5 % HMDSO in O_2





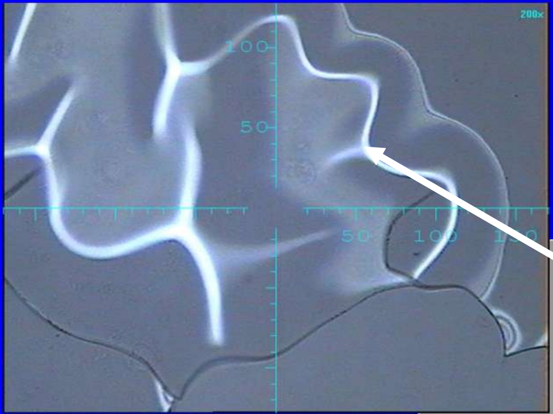
⇨ *0.4 Pa: SiO_2 structure, almost no impurities*

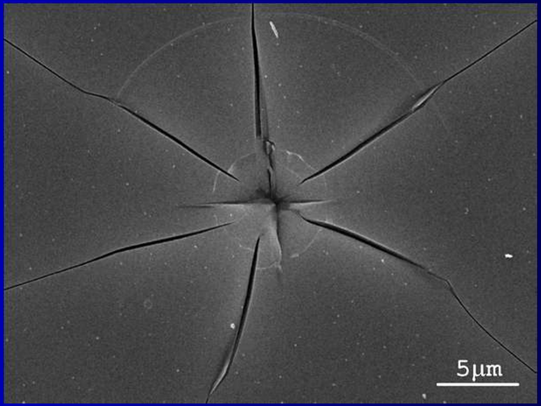
⇨ *2.5 Pa: SiO_2 structure, OH groups and H_2O*

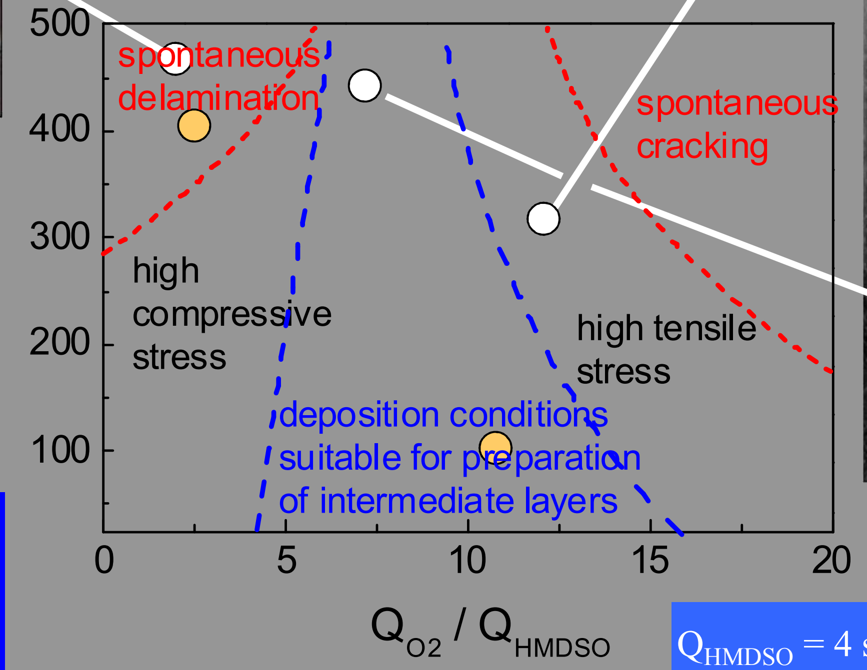
⇨ *40 Pa: organosilicon films*

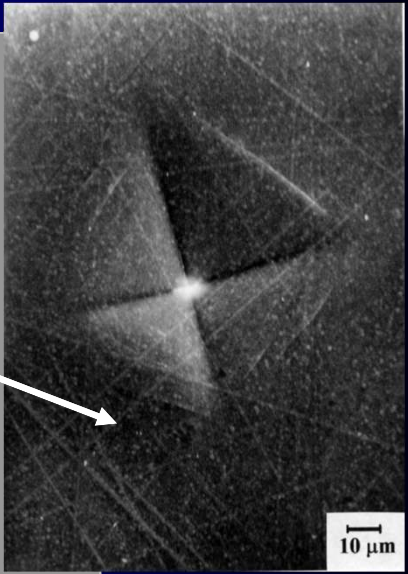
Domains of stresses

without treatment









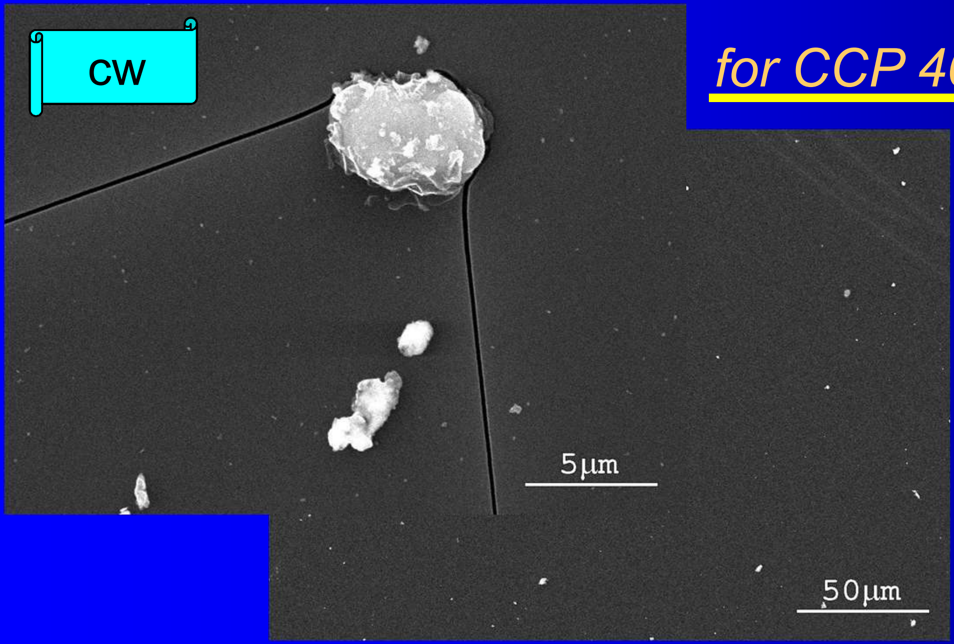
Q_{HMDSO} = 4 sccm

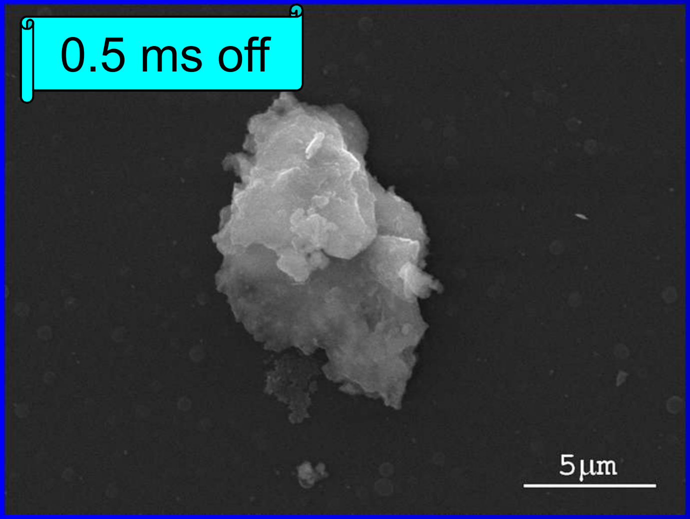
two different coatings choosen for treatment testing:

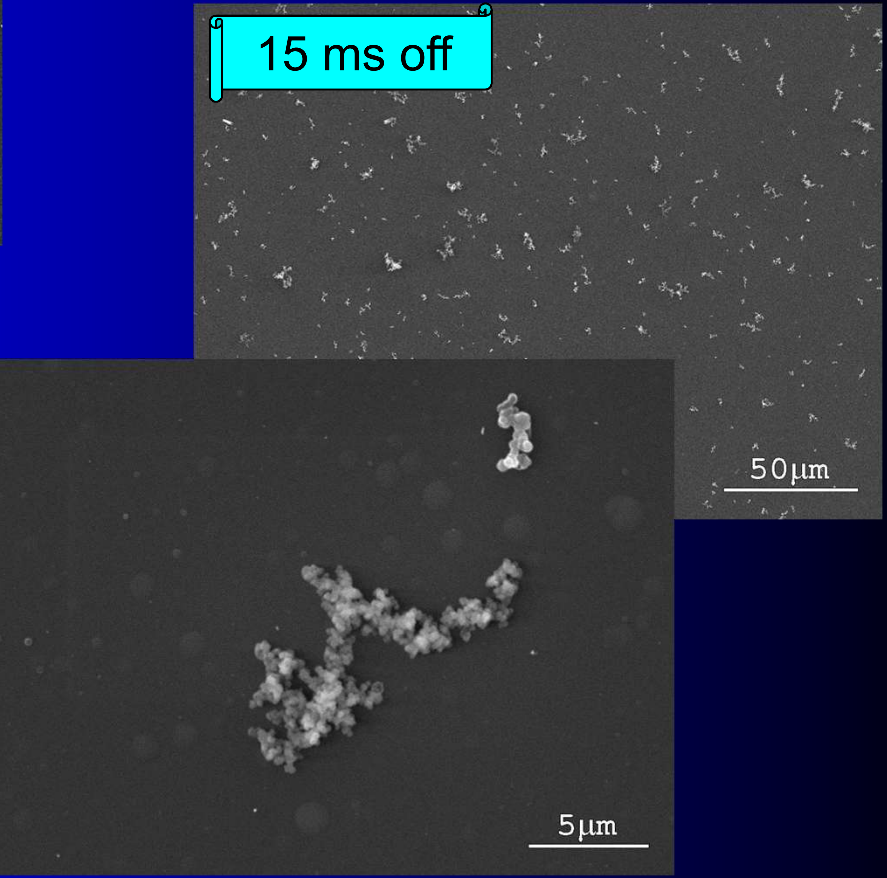
- P = 100 W, Q_{O2} = 45 sccm, d = 0.5 µm
- P = 400 W, Q_{O2} = 10 sccm, d = 1.2 µm

Film microstructure

for CCP 40 Pa


cw


0.5 ms off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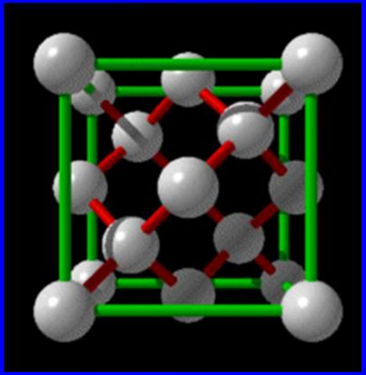
10.3 PECVD of Carbon-Based Thin FIlms

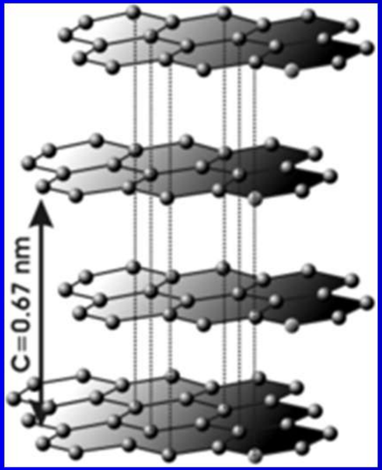
Diamond, graphite and much more

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

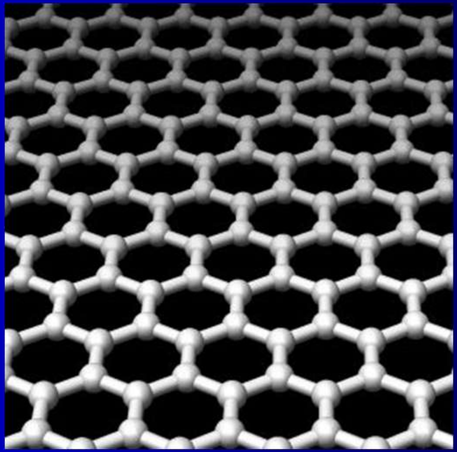
sp^3 C - diamond



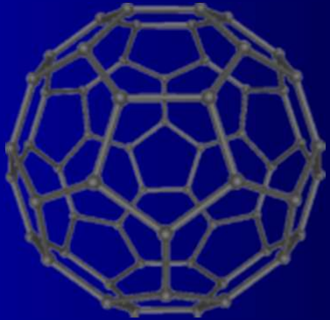
sp^2 C - graphite



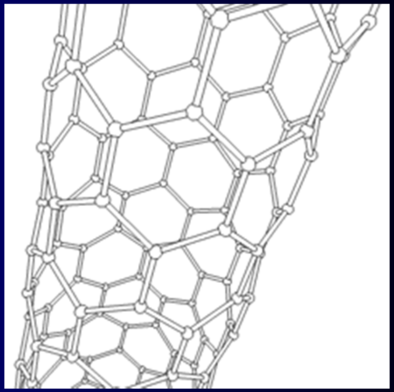
graphene



C_{60} - Buckminsterfullerene



carbon nanotube



PECVD of carbon based materials

- crystalline diamond films

0.1 - 5% $CH_4/C_2H_2/\ldots$ in H_2 T=700-1000°C

RF plasma p=0.01-4kPa, T_{gas}=1000-1500°C, P=0.5-3kW

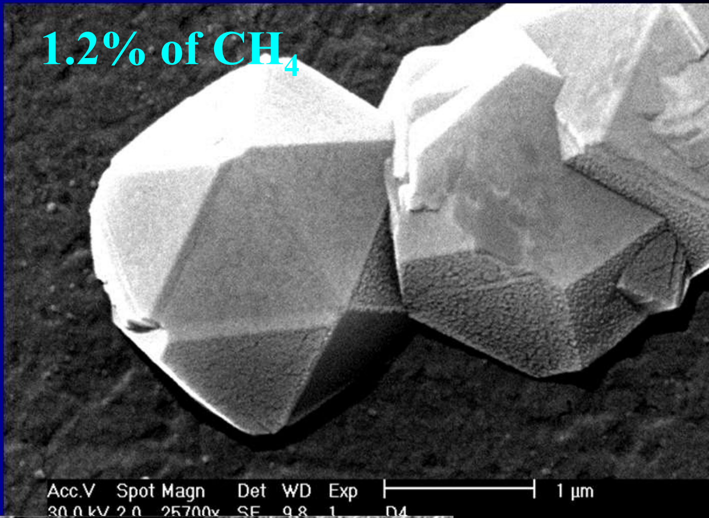
MW plasma p=2-10kPa, T_{gas}=2000-2500°C, P=0.5-2kW

- amorphous diamond like carbon (DLC) films

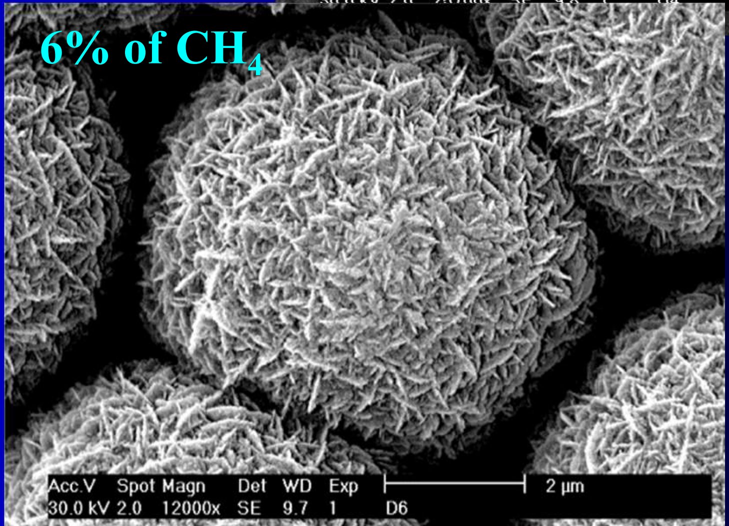
!! ion bombardment

$CH_4/C_2H_2/\ldots + (Ar/H_2)$, T < 300 °C

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

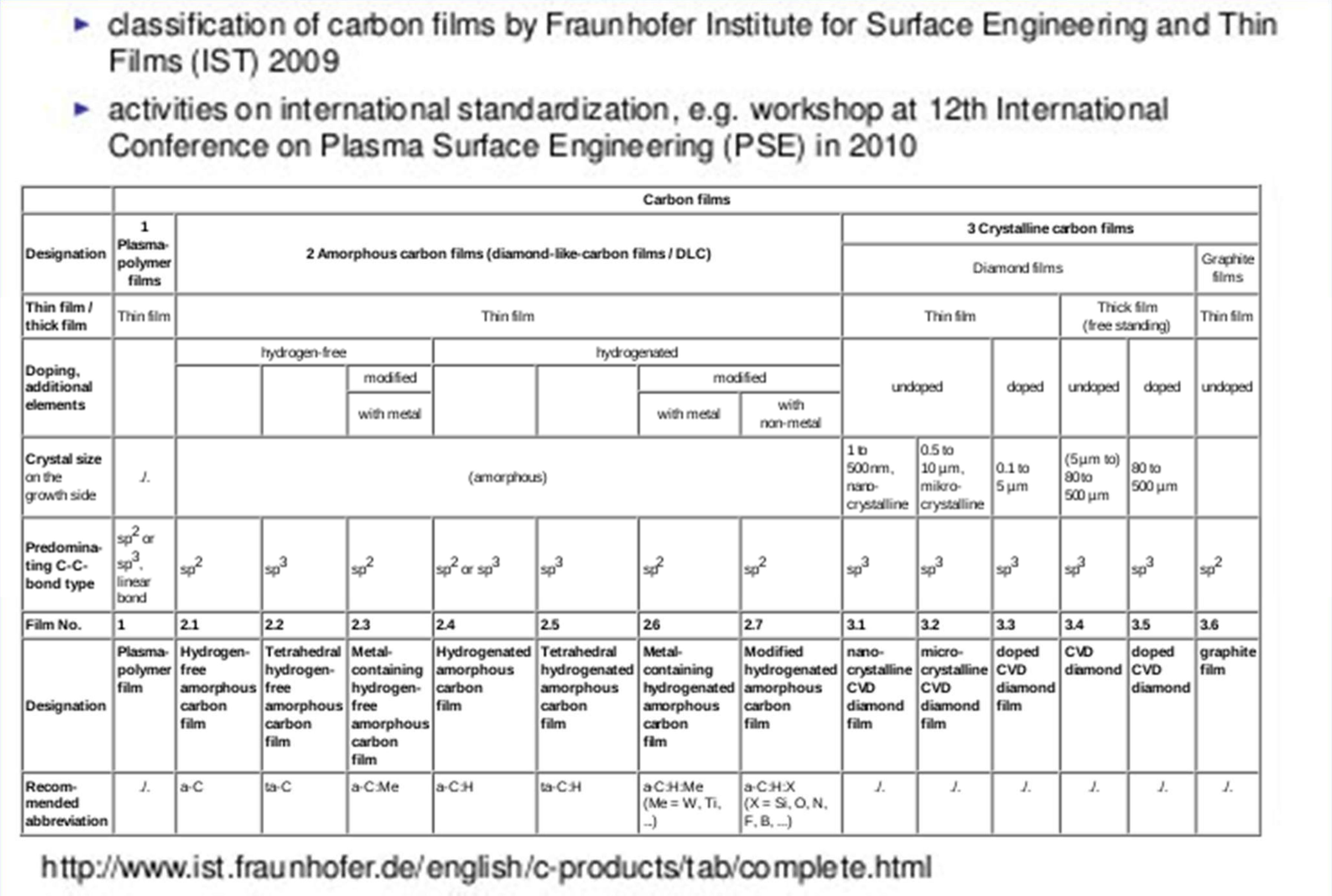


1.2% of CH_4



6% of CH_4

Classification of carbon films

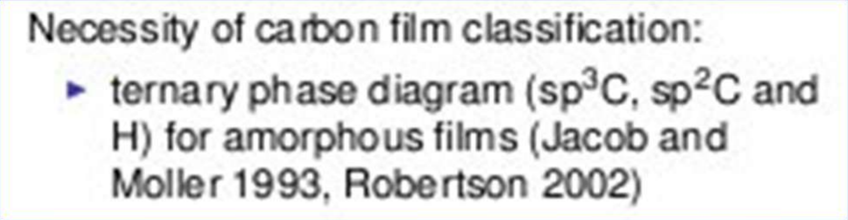


- classification of carbon films by Fraunhofer Institute for Surface Engineering and Thin Films (IST) 2009
- activities on international standardization, e.g. workshop at 12th International Conference on Plasma Surface Engineering (PSE) in 2010

	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**
Recom-mended 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, ...)	./.	./.	./.	./.	./.	./.

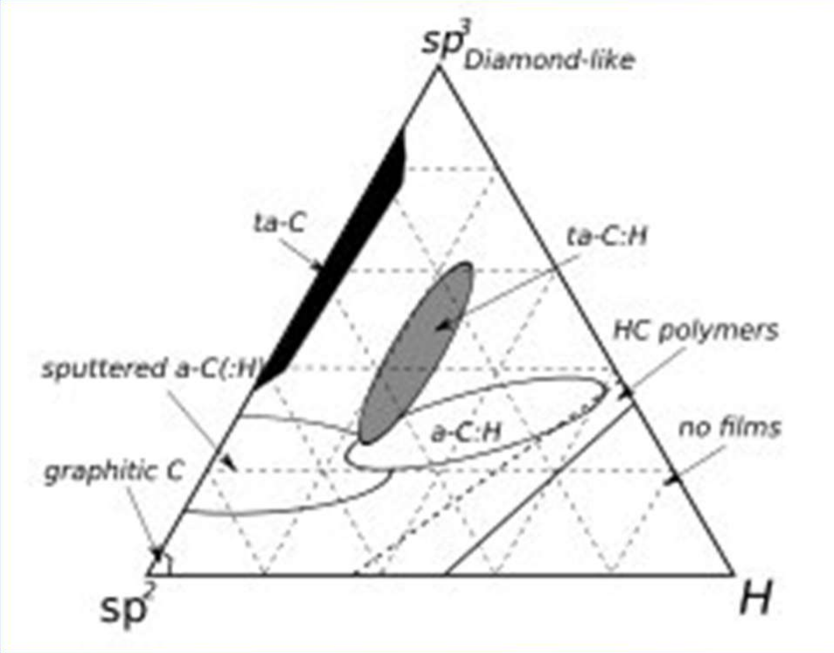
http://www.ist.fraunhofer.de/english/c-products/tab/complete.html

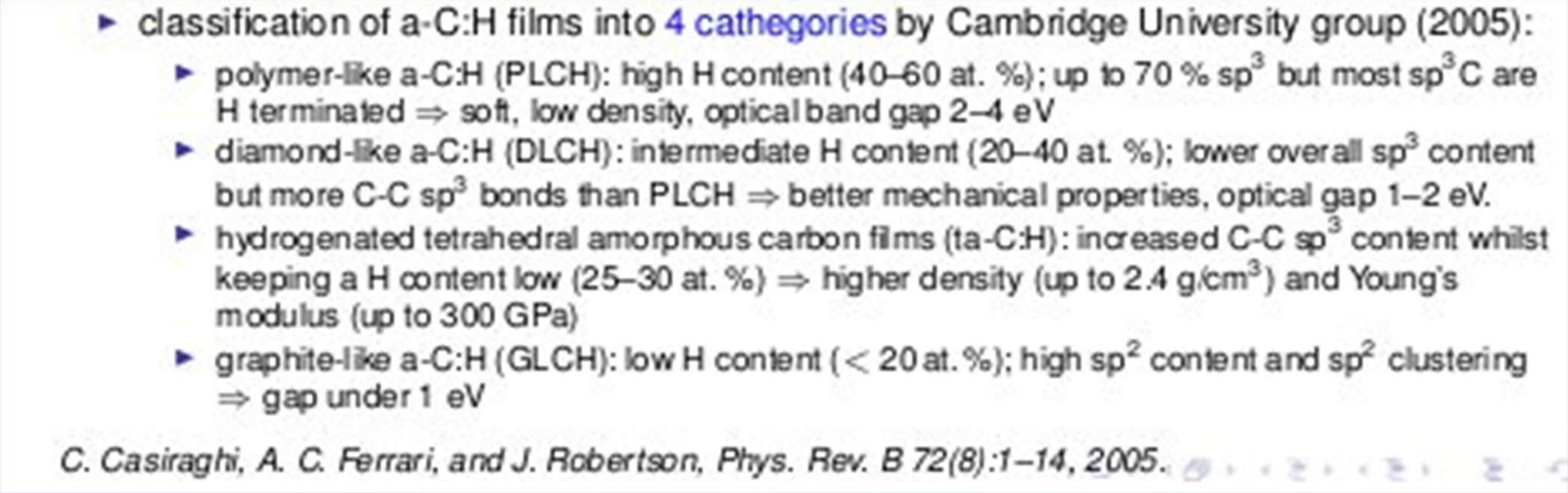
Classification of amorphous hydrogenated carbon films



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.