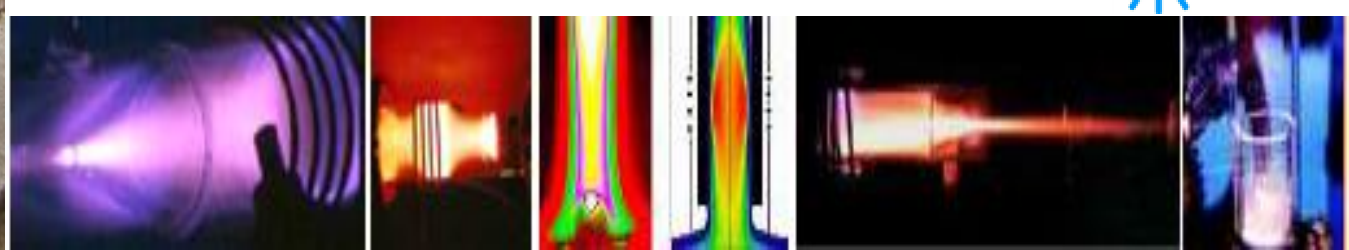
Modification de surface par procédés plasmas

Dr C. GUYON
Prof. M. TATOULIAN

Laboratory of Plasma chemical engineering
11 rue Pierre et Marie Curie –Chimie ParisTech - Paris
(Dir: Prof. Michael Tatoulian)

Cedric-guyon@chimie-paristech.fr
Michael-tatoulian@chimie-paristech.fr



Brief History of Plasma Physics…

1879

W. Crookes defines the state of a ionized gas as "… a world where matter may exist in a 4th state …".

Irving Langmuir (1881-1957)

1927

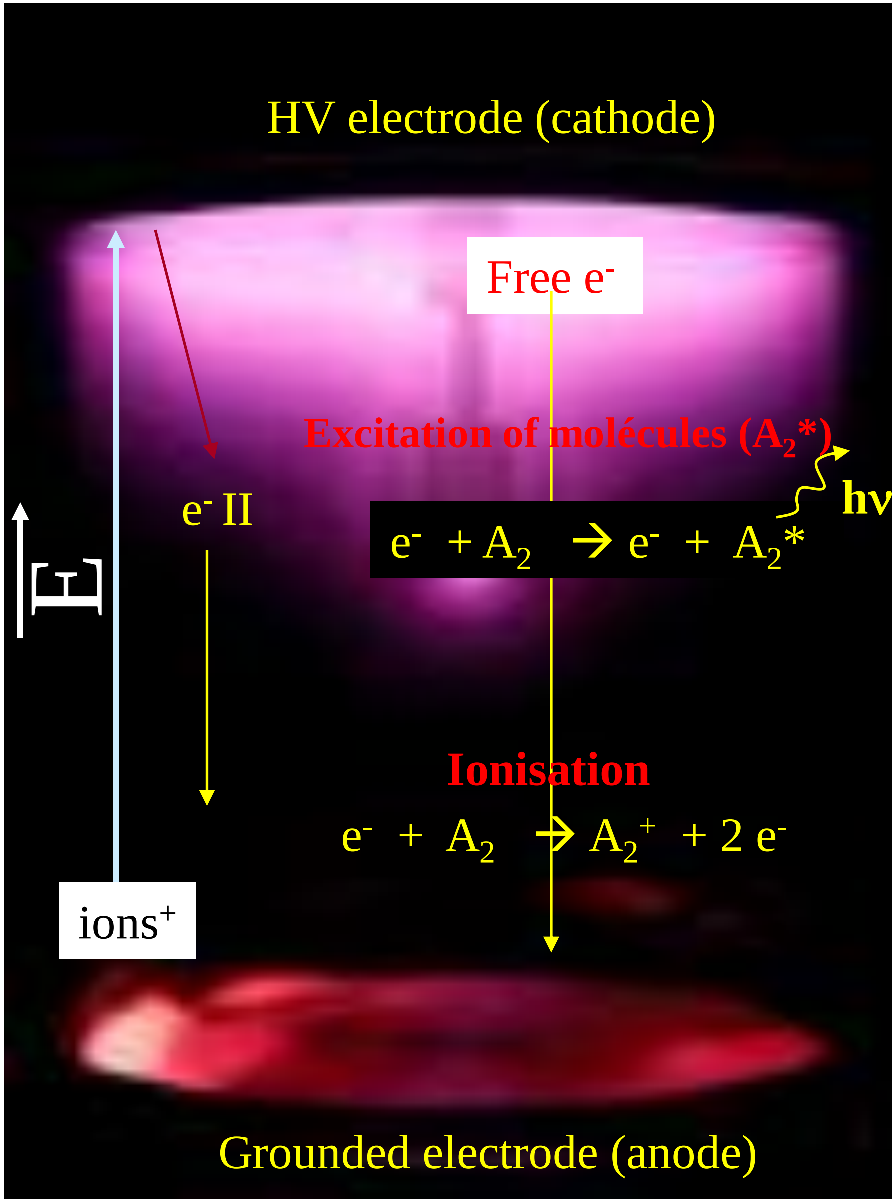
Irving Langmuir first used this term to describe an ionized gas in 1927--Langmuir was reminded of the way blood plasma carries red and white corpuscles by the way an electrified fluid carries electrons and ions

Nobel Laureate in Chemistry in 1932... for his discoveries and investigations in surface chemistry ...

Definition of Plasma …

Langmuir uses the word Plasma to define a neutral partially or fully ionized gas, containing neutral (atoms, molecules, radicals) and charged (ions, electrons) species.

GENERATION OF A PLASMA



AN ELECTRIC FIELD IS IMPOSED TO A GAS

ELECTRONS AND OTHER CHARGED SPECIES ARE ACCELERATED AND GAIN ENERGY

COLLISIONS AND ENERGY EXCHANGE PROCESSES OCCUR,
MORE IONS AND ELECTRONS ARE FORMED,
THE IONIZATION DEGREE INCREASES,
MOLECULES ARE FRAGMENTED,
HOMOGENEOUS AND HETEROGENEOUS REACTIONS OCCUR

THE PLASMA IS SUSTAINED BY A BALANCE BETWEEN PRODUCTION (ionizations) AND LOSS (recombinations) OF CHARGED SPECIES

Reactive species :
Ions, electrons, radicals,
Excited species, photons...

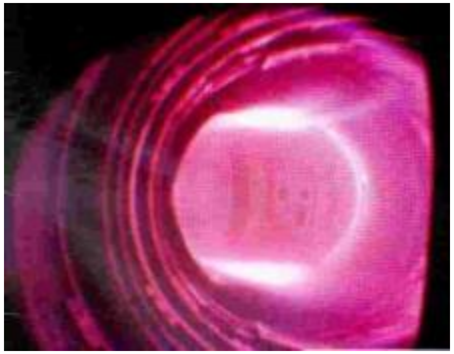
Three classes of plasmas…

« Hot plasmas »

Millions of degrees

Sun

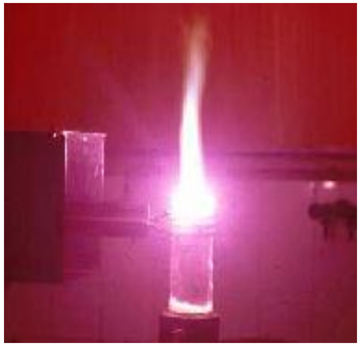
Tokamak

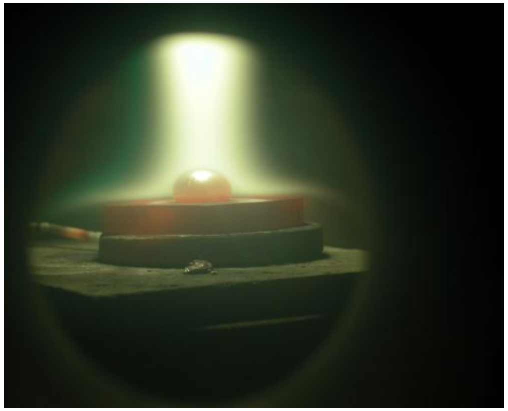


→ITER: International Thermonuclear Experimental Reactor

« Thermal plasmas »

Few thousands of degrees





Welding, Metallurgy,
Plasma spray deposition,
ICP spectroscopy,
Waste abatment

« Cold plasma »

Few hundreds of degrees

→Surface treatment of thermosensitive materials

Brief History of Plasma processing…

70's

•First plasma etching processes

•Plasma processes started to be applied for surface modification of materials, in the field of microelectronics and semiconductors

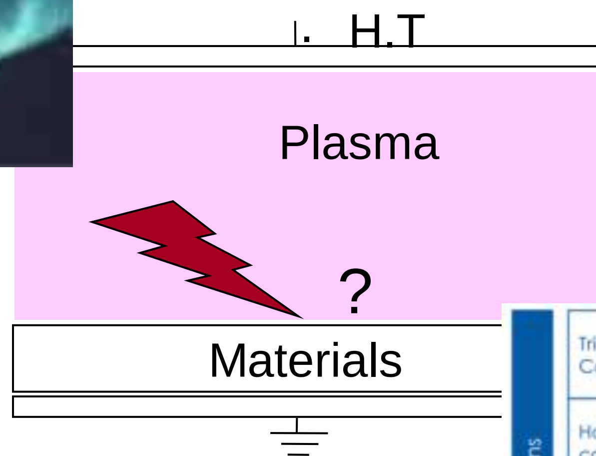
80's

• deposition processes for semiconductor thin films for solar cells (α-Si:H)

90's

•Polymers, textiles, packaging, biomaterials, paper, ceramics, metals, MEMS, composites, etc. fully exploit plasmas

Consider PLASMA a tool to engineer materials

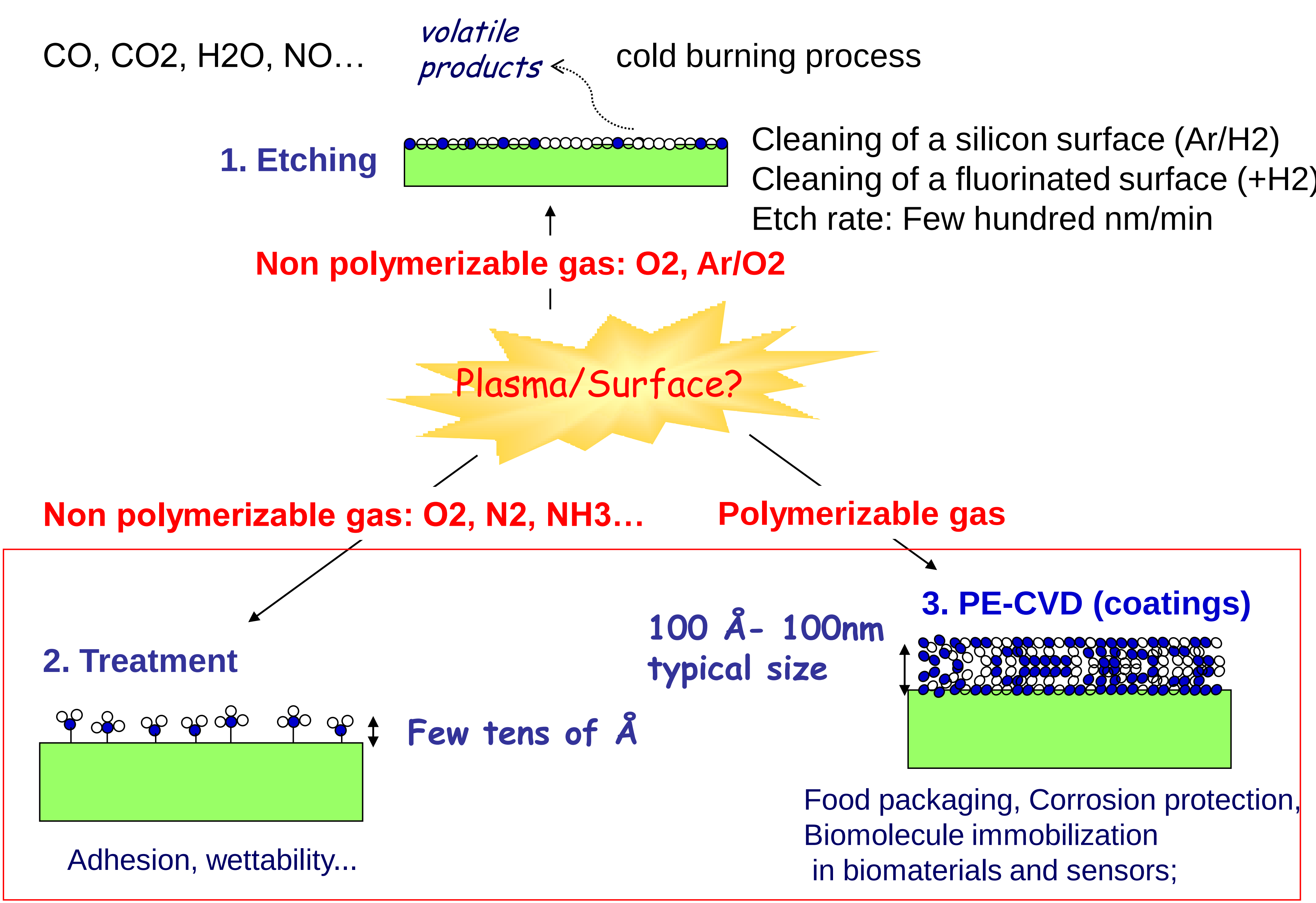


Plasma/surface Interaction ?

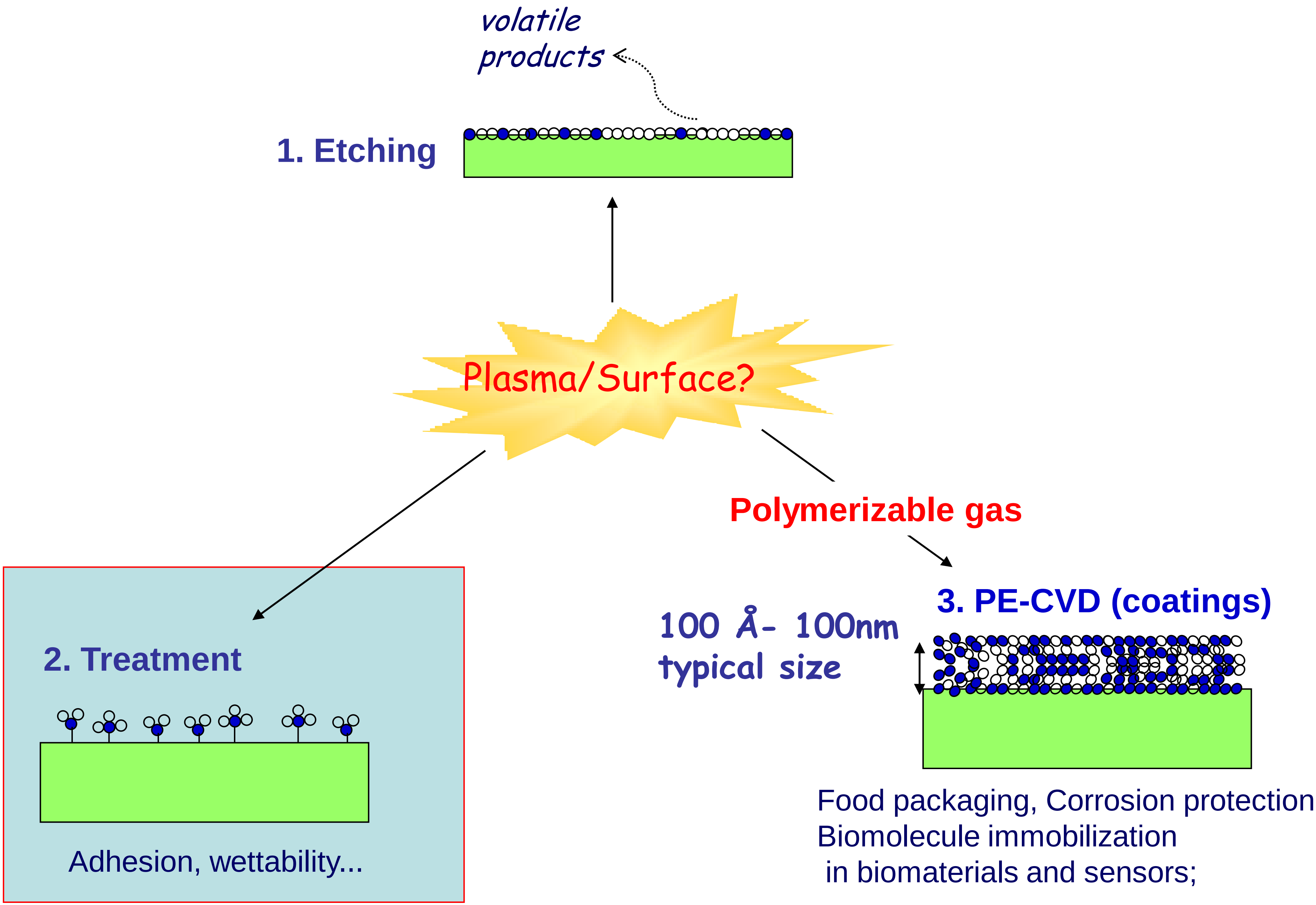
Plasma processing of materials?

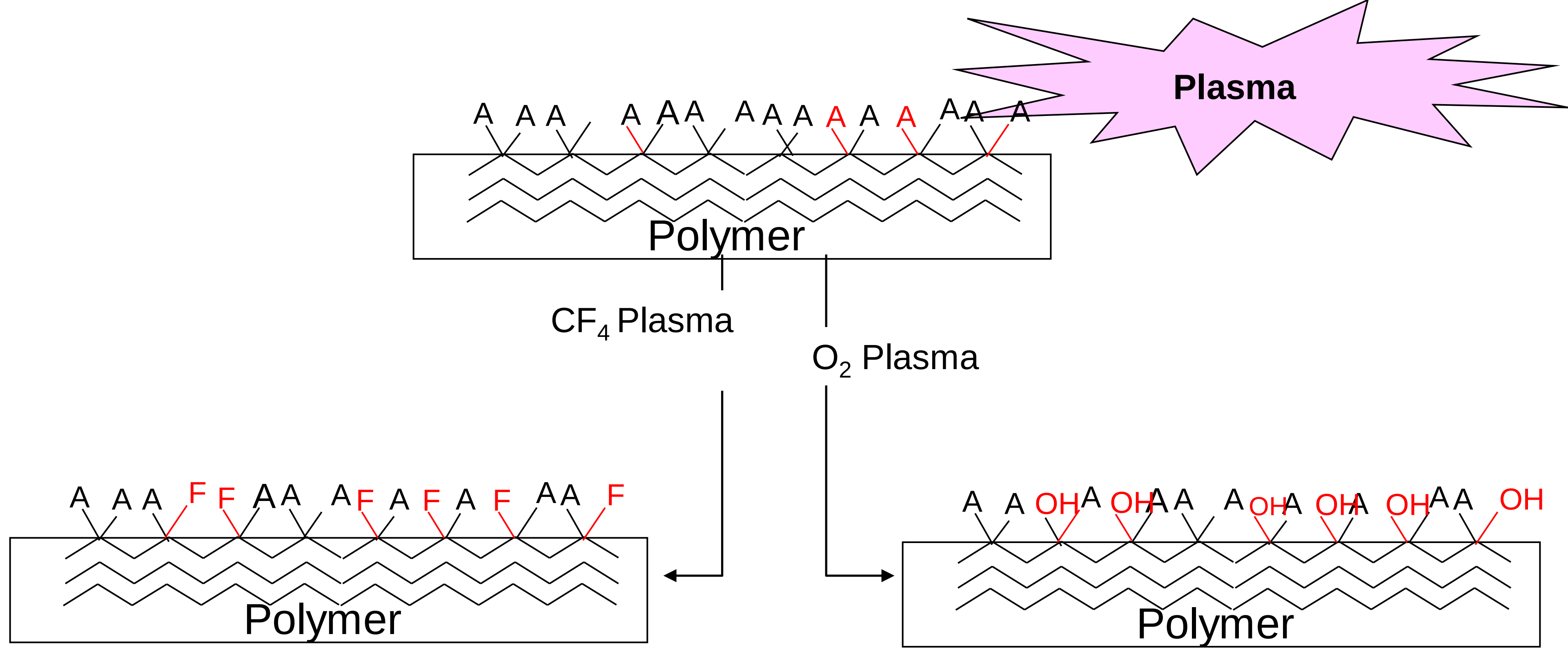
Positive and negative effects of plasma processing?

SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS

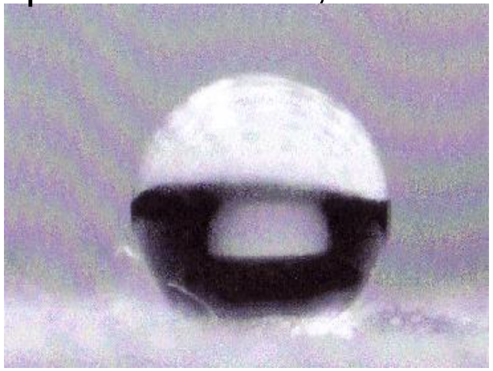


SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS



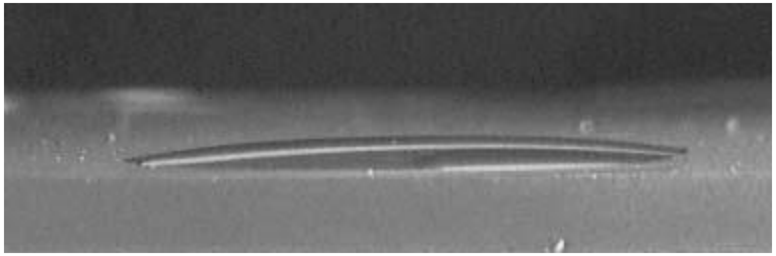


Non adhésion :
Hydrophobic material, non wettable



Applications :
Textile (stain resistant…)

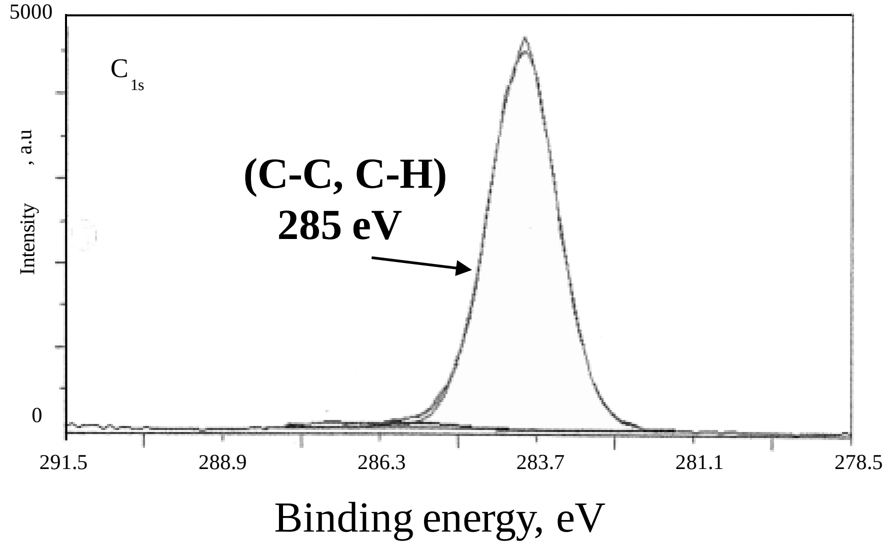
Adhésion :
Hydrophilic surfaces, wettable



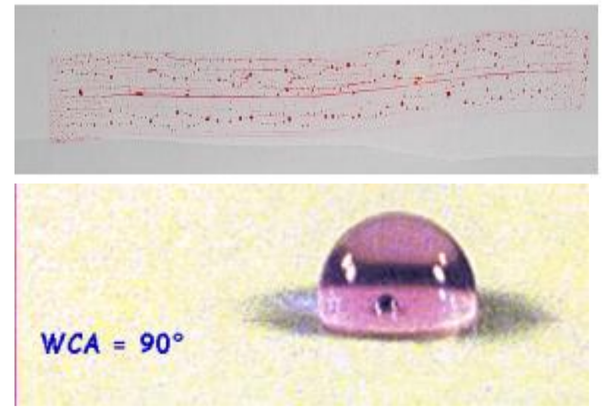
Applications :
metal/polymer adhesion , ink/polymer

Plasma surface modifications of PE with NH3 plasma

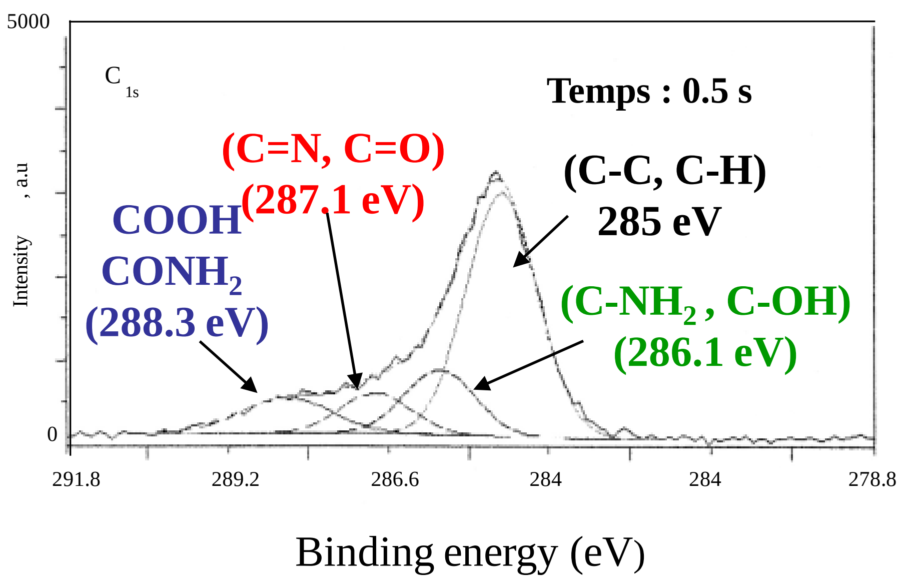
Untreated PE



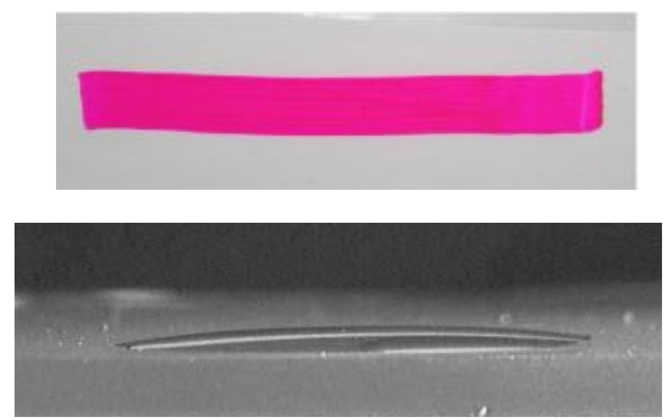
Untreated PE



NH3 Plasma treated PE

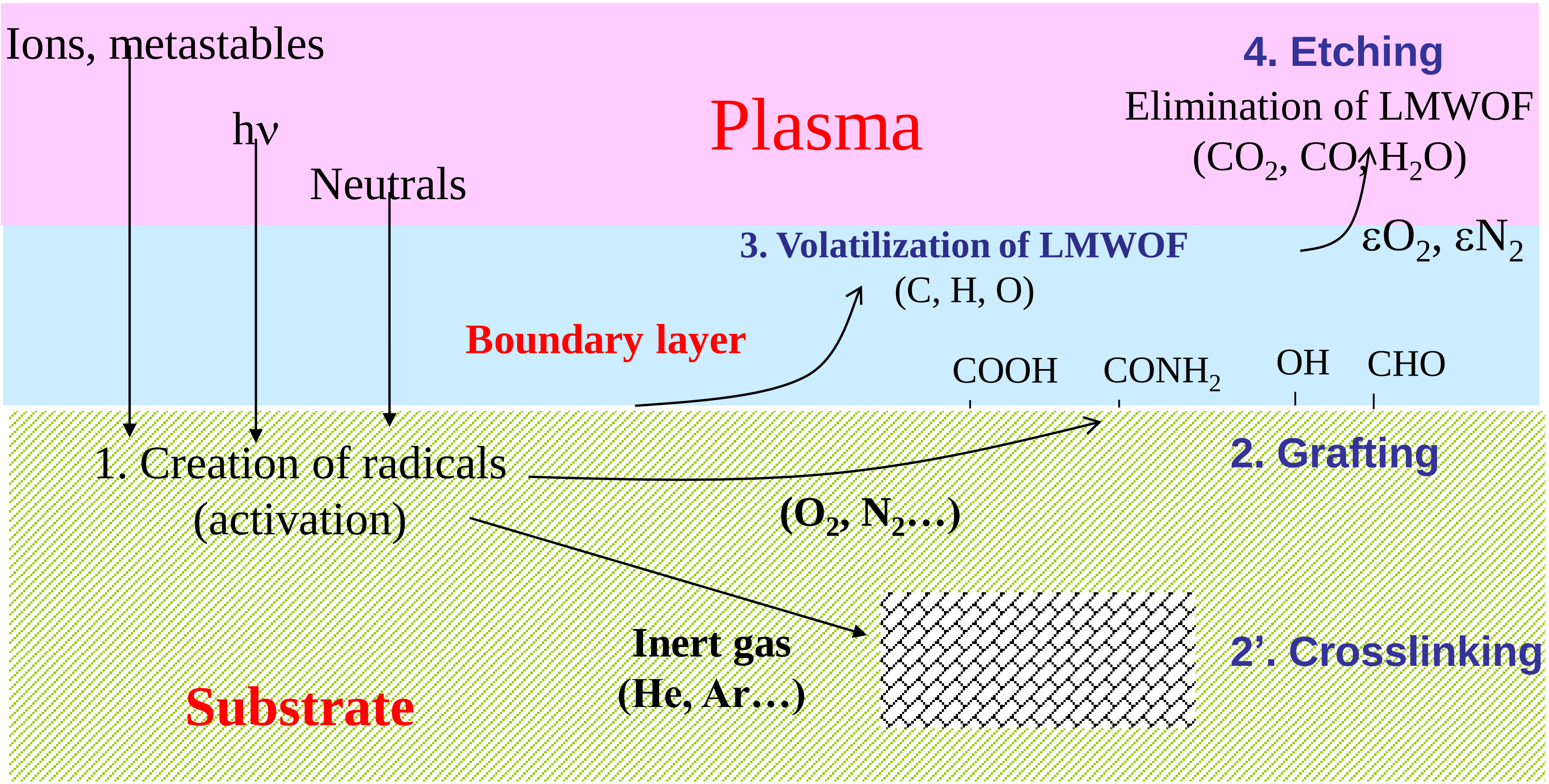


NH3 Plasma treated PE



Adhesion

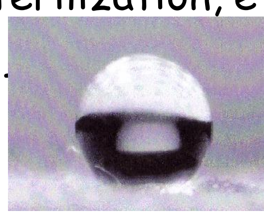
PLASMA TREATMENTS OF POLYMERS



Ar, He : Cross-linking by ion bombardment, VUV

O_2, air, CO_2 …: Increased surf. energy & wettability, sterilization, etching occurs.

CF_4, CF_4/O_2 … etching occurs,



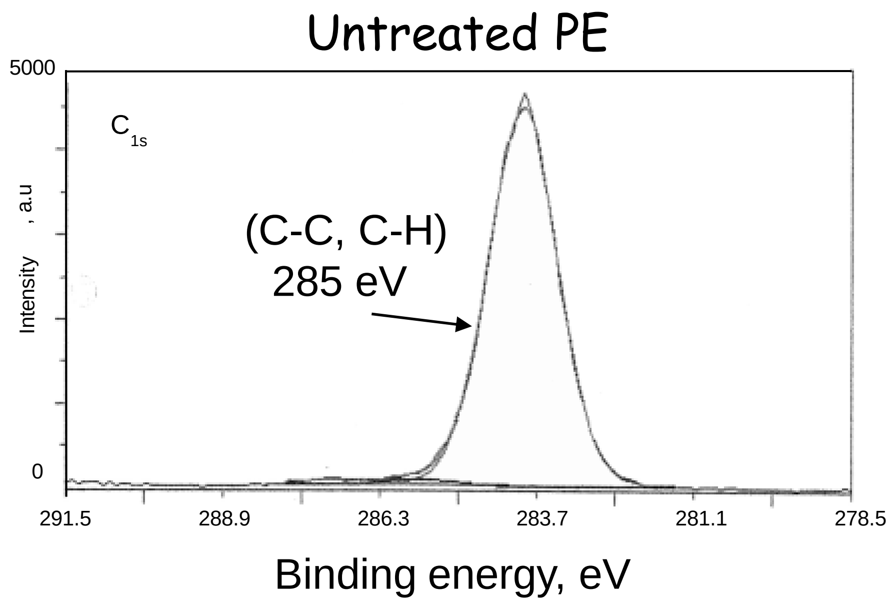
Textile (stain resistant…)

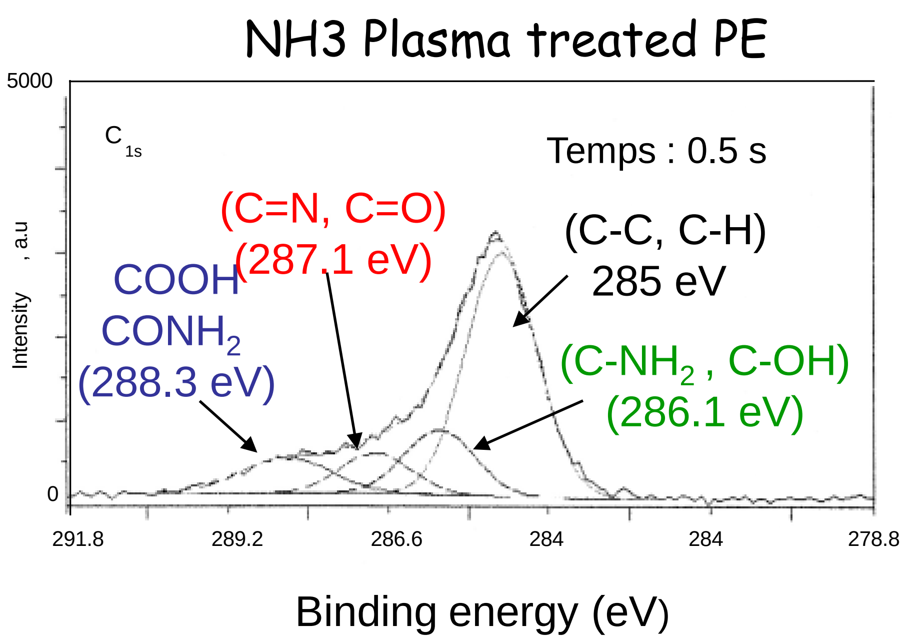
H_2 : For pre-treatments, F-abstraction, cleaning, surface reduction.
Limited polymer degradation, mild treatments.

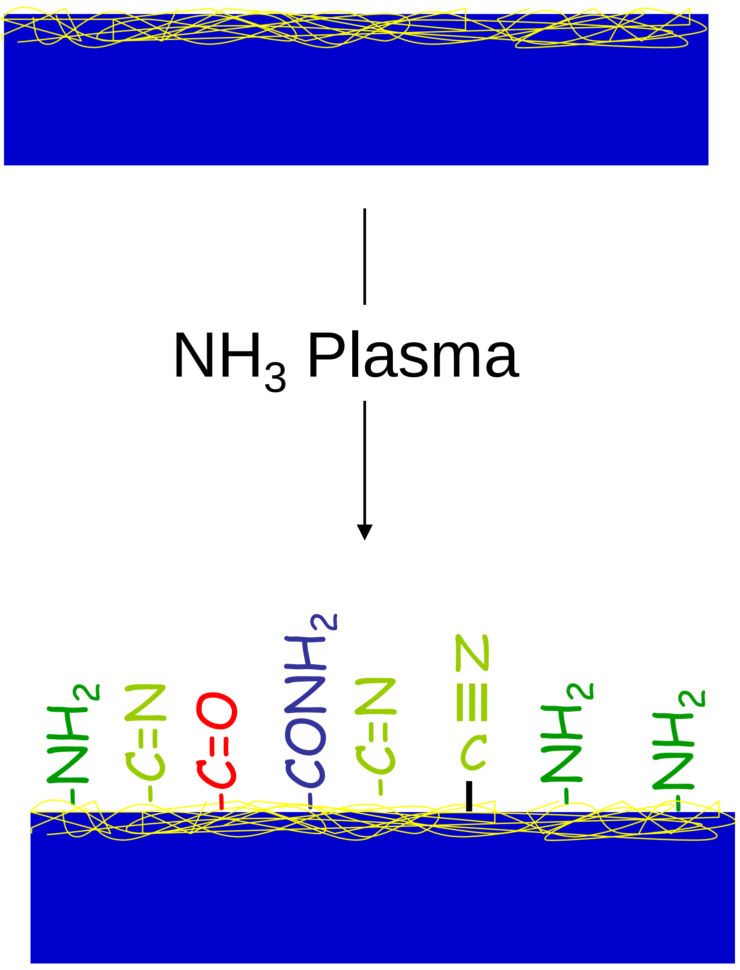
N_2, NH_3 …Grafting N-groups, increased surf. energy & wettability, limited etching, poor selectivity, sensitive to ageing

Drawback 1: Poor selectivity of the plasma treatment process

Drawback 1: Poor selectivity of the plasma treatment process



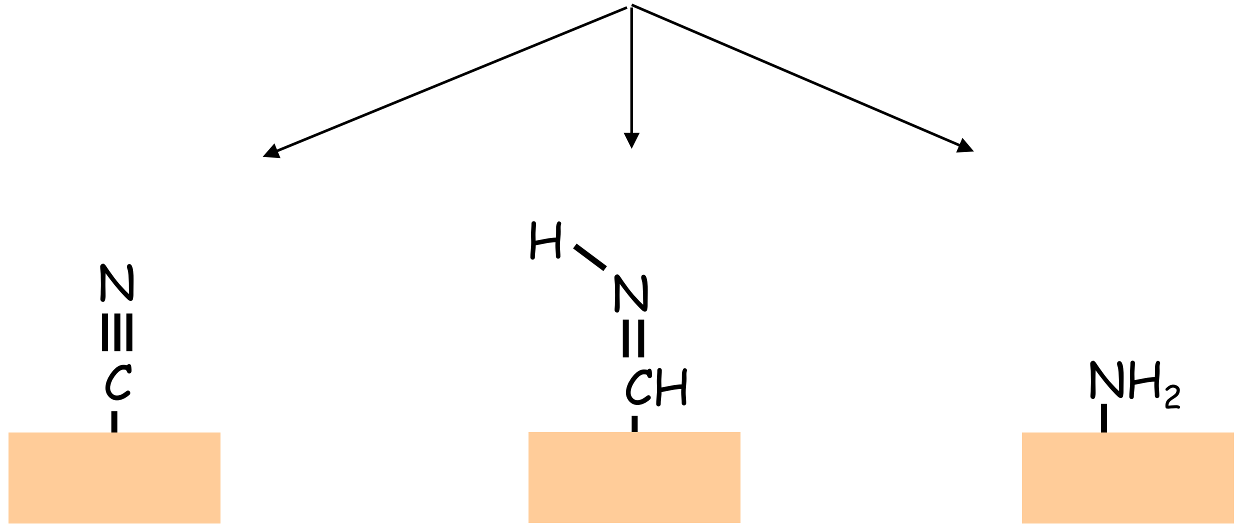




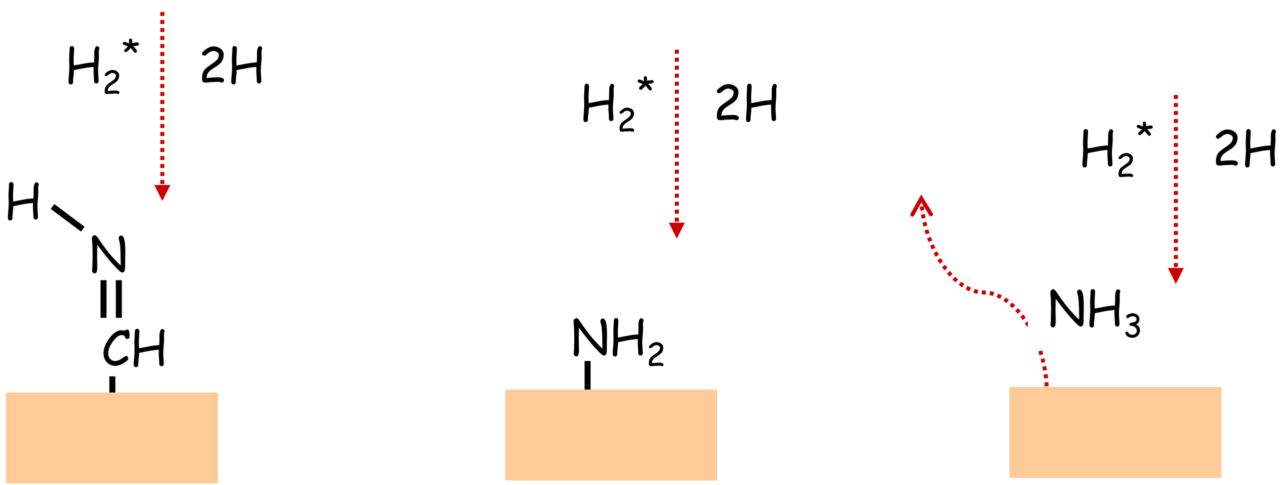
Poor selectivity of the process

SOLUTION???

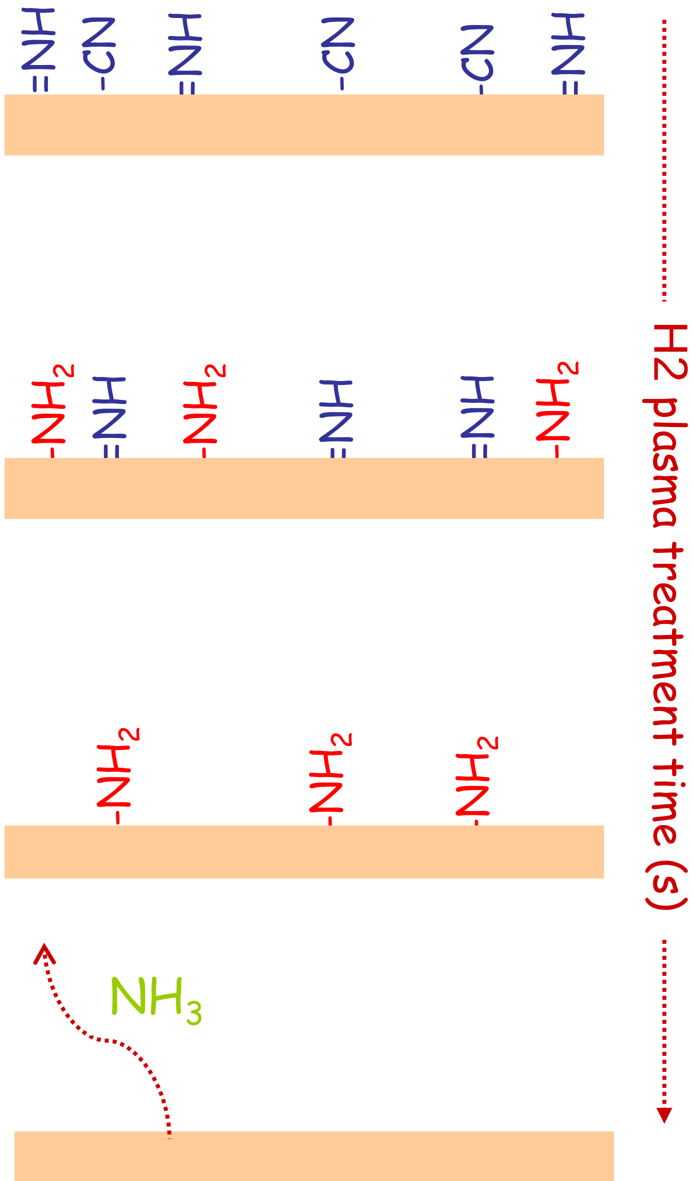
1. NH3 Plasma



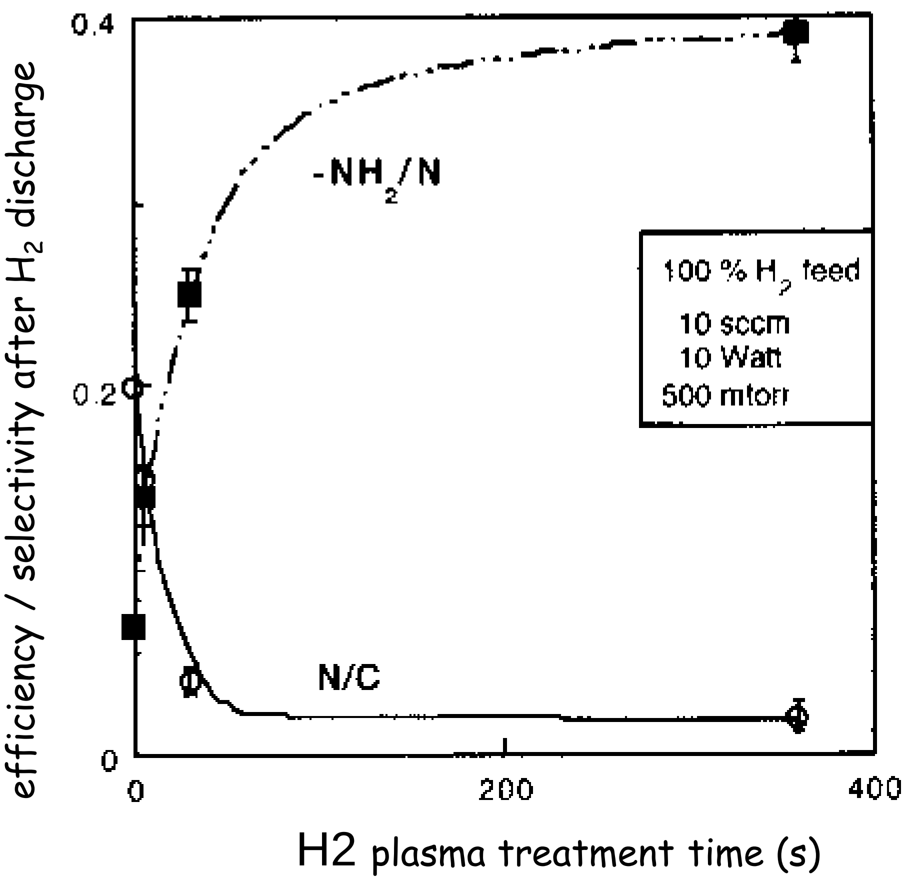
2. H2 Plasma



Selective grafting of $-NH_2$ groups on PE by means of plasma treatments in NH_3 and H2

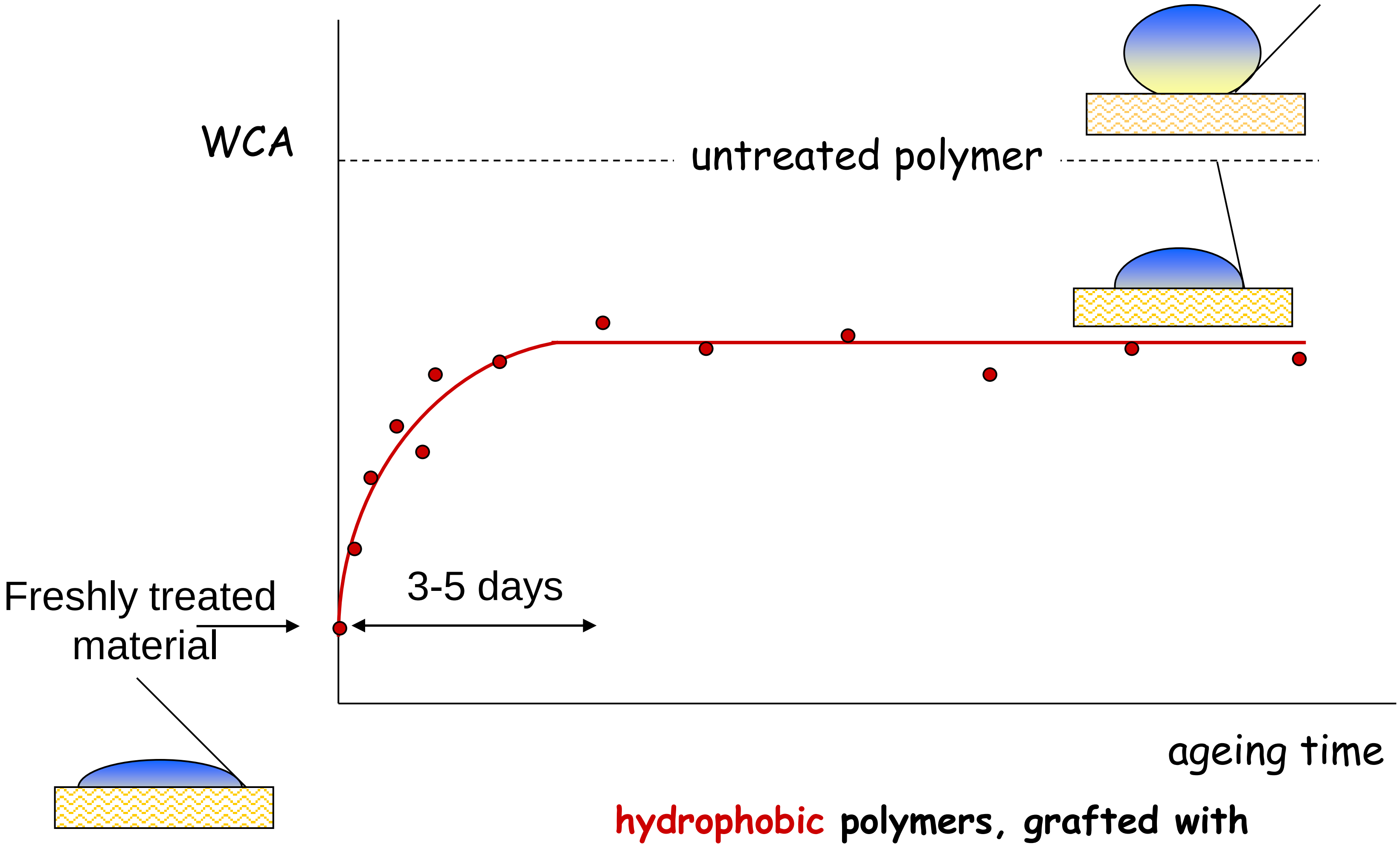


P. Favia et al, Plasmas & Polymers; 1, 91, 1996



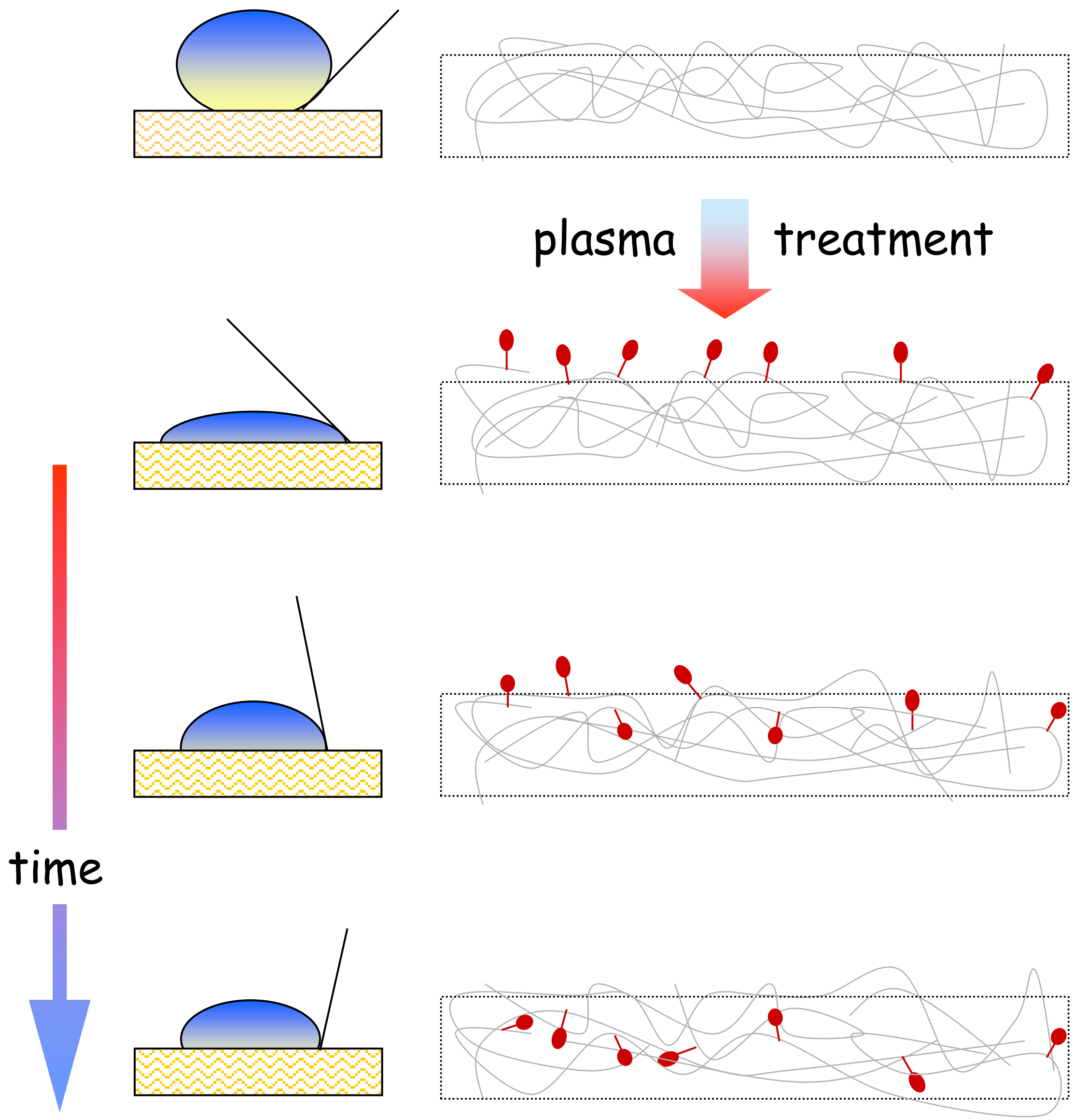
Drawback 2: Plasma treated polymeric materials aged quickly…

Ageing of plasma treated materials



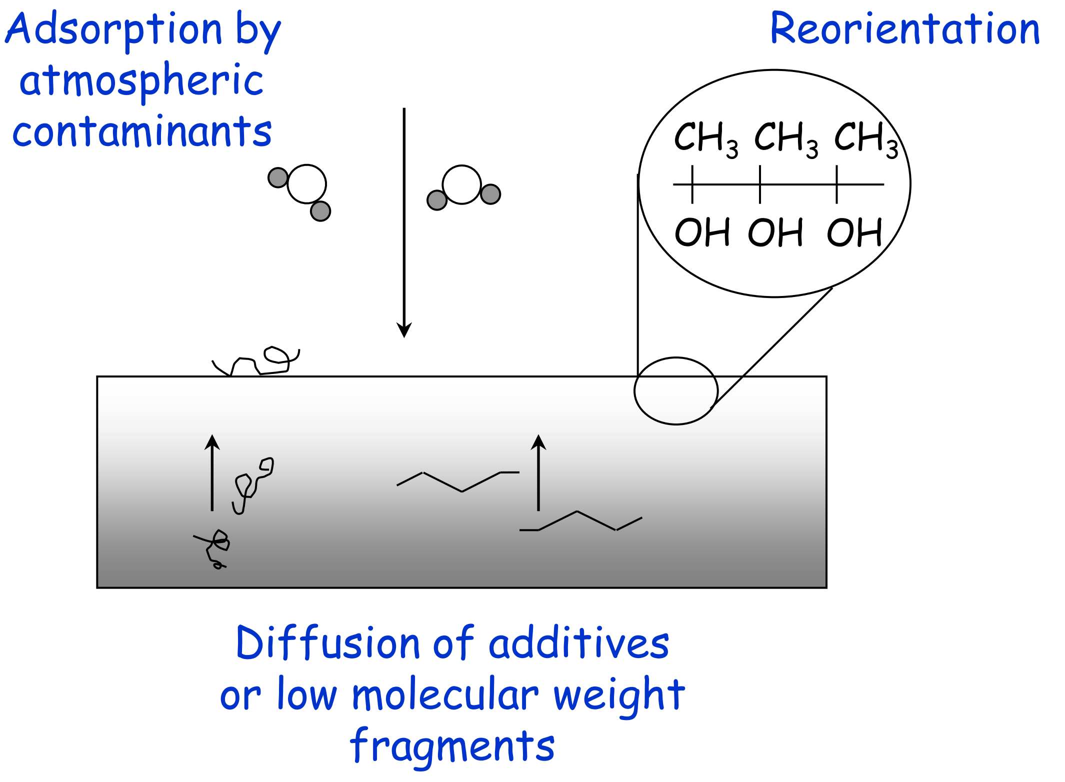
hydrophobic polymers, grafted with polar (hydrophilic) groups, loose properties with time in air (= hydrophobic recovery)

The physical problem = ageing



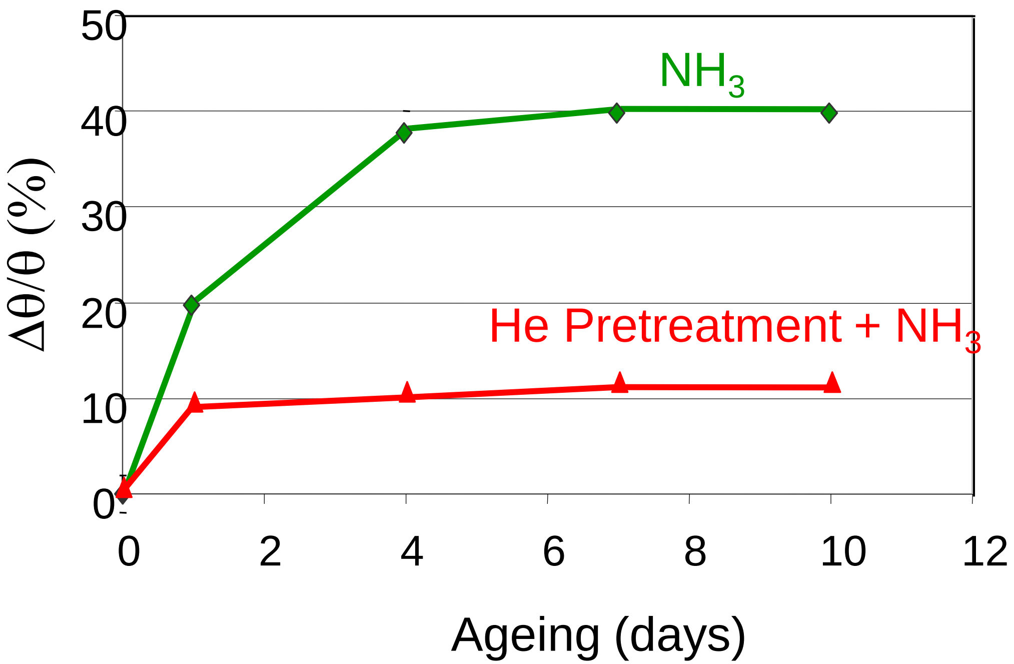
HYDROPHOBIC RECOVERY

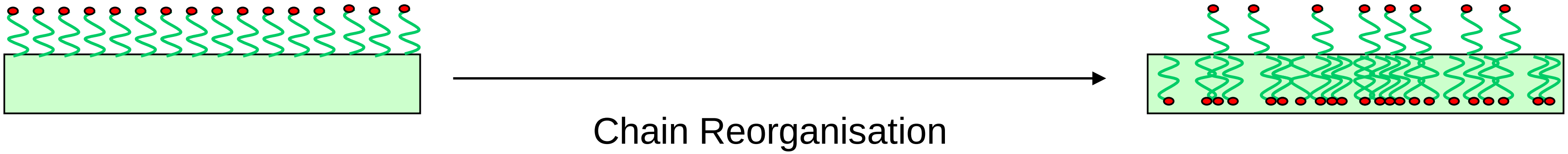
Mécanisms



To avoid superficial degradation of the topmost surface layer
To reinforce the cohesive strength of the tompost surface layer via CASING process

How to limit ageing?





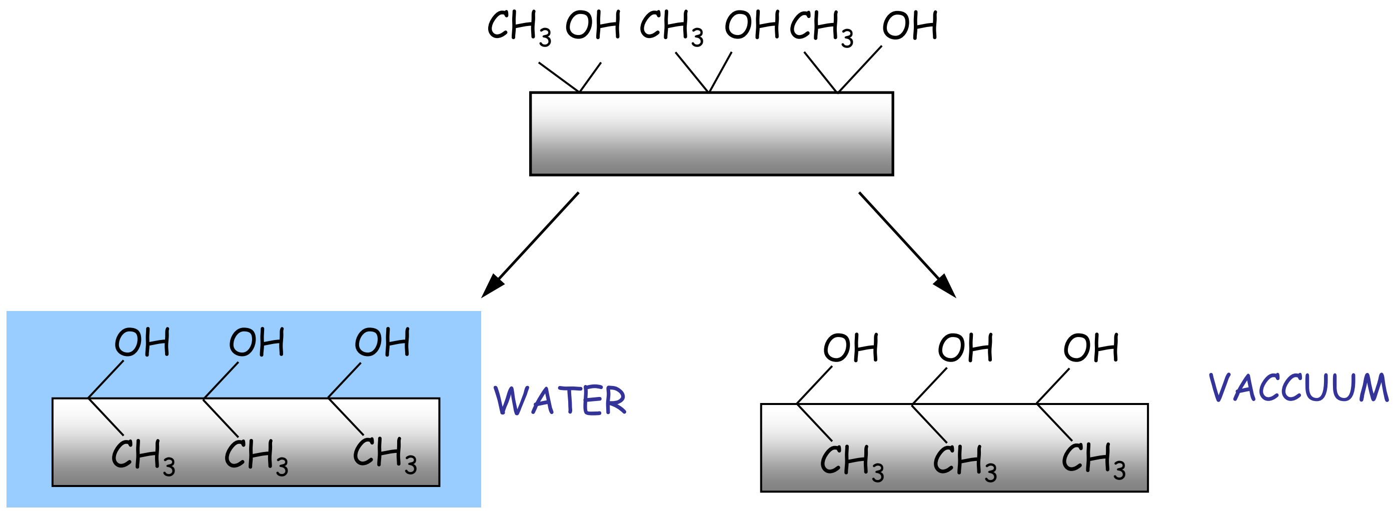
To limit the chain mobility by crosslinking reactions

Other solution??

How to decrease the ageing of PT polymers?

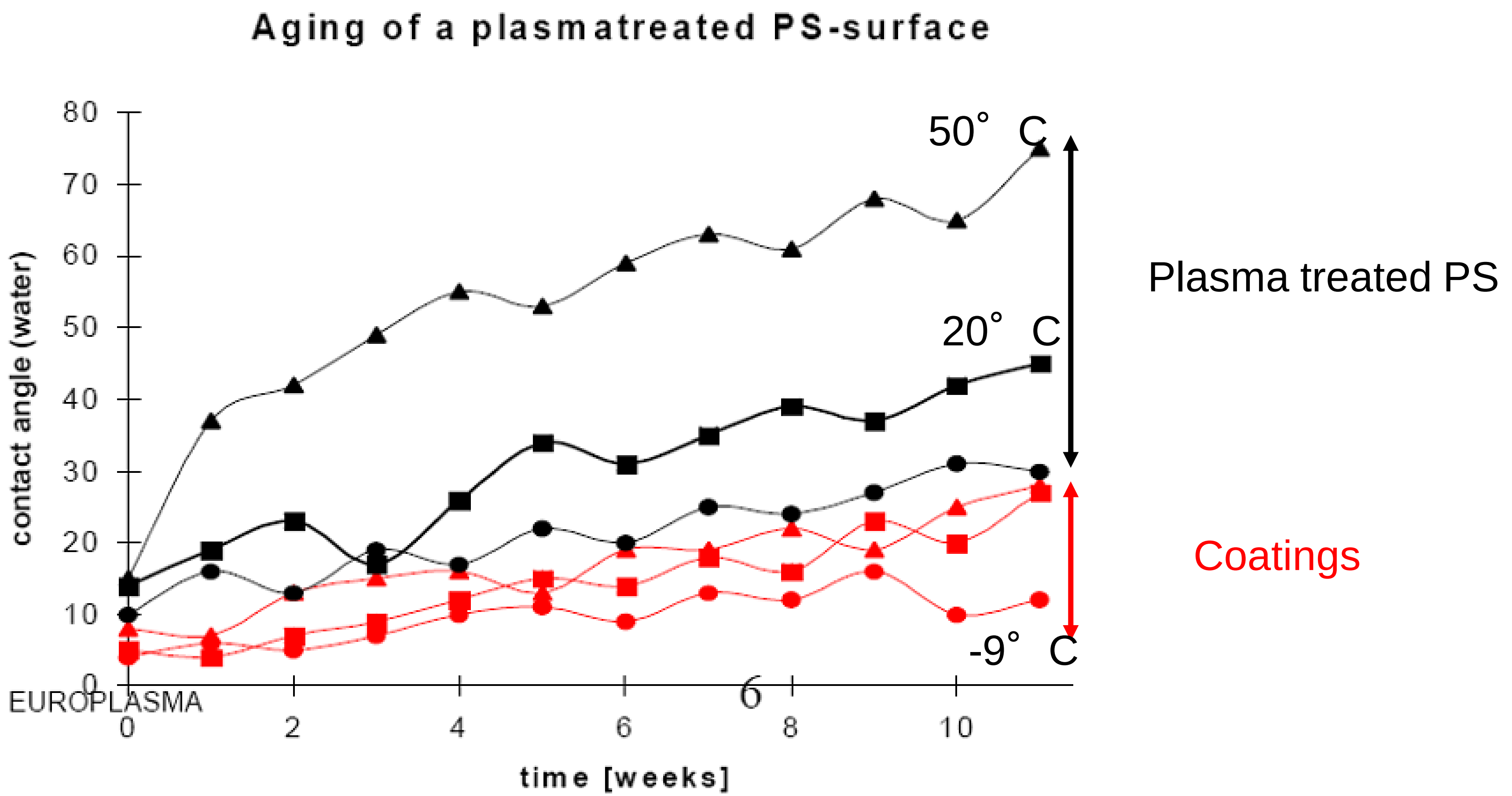
1. Immobilization of adherent immediately after the treatment

2. To avoid the rearangement of grafted polar groups



3. To crosslink the topmost surface layer by He pretreatment

Other solution→ Plasma deposition of a thin coating

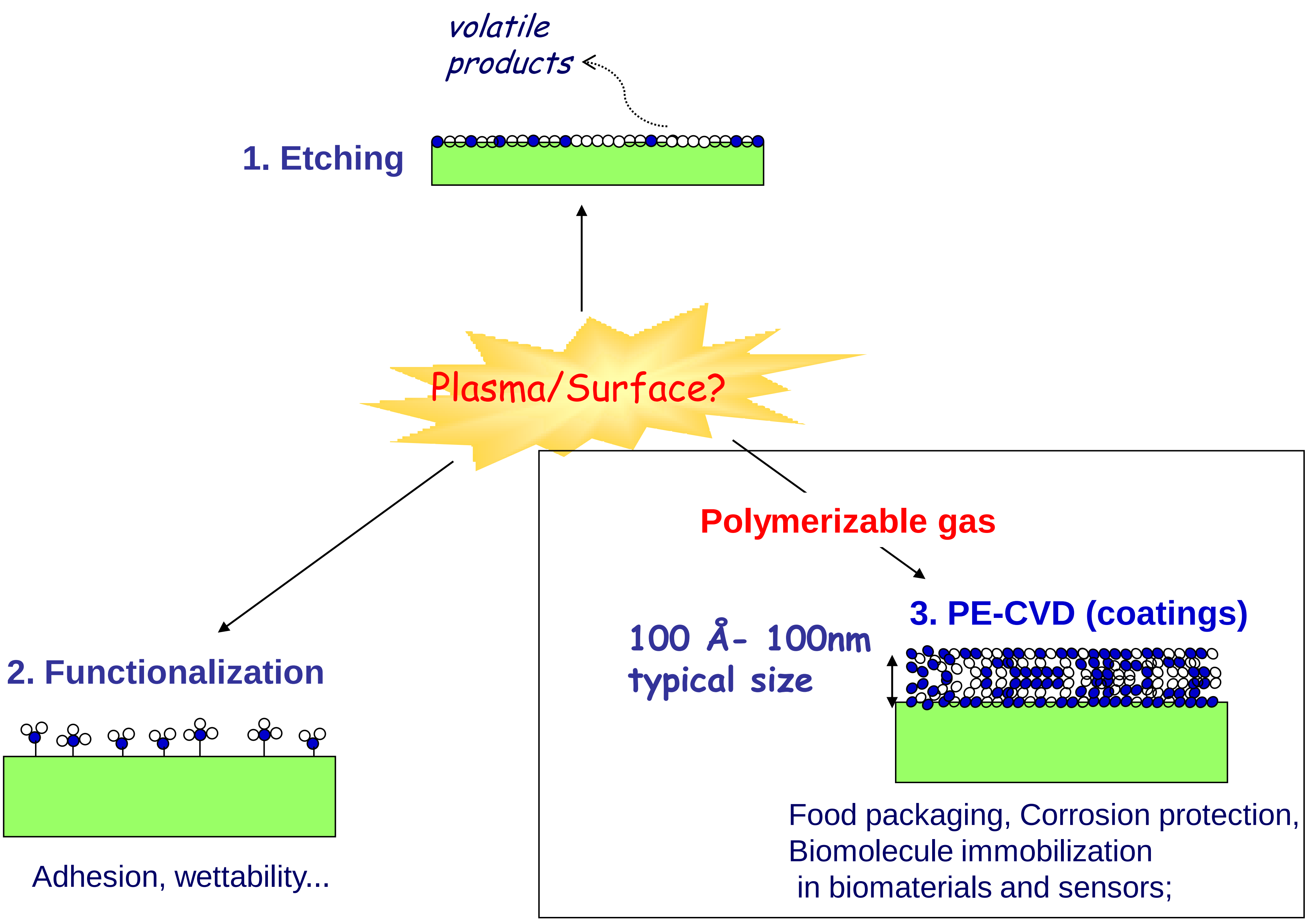


NV. EUROPLASMA

EUROPLASMA

YOUR PARTNER IN SURFACE TREATMENT

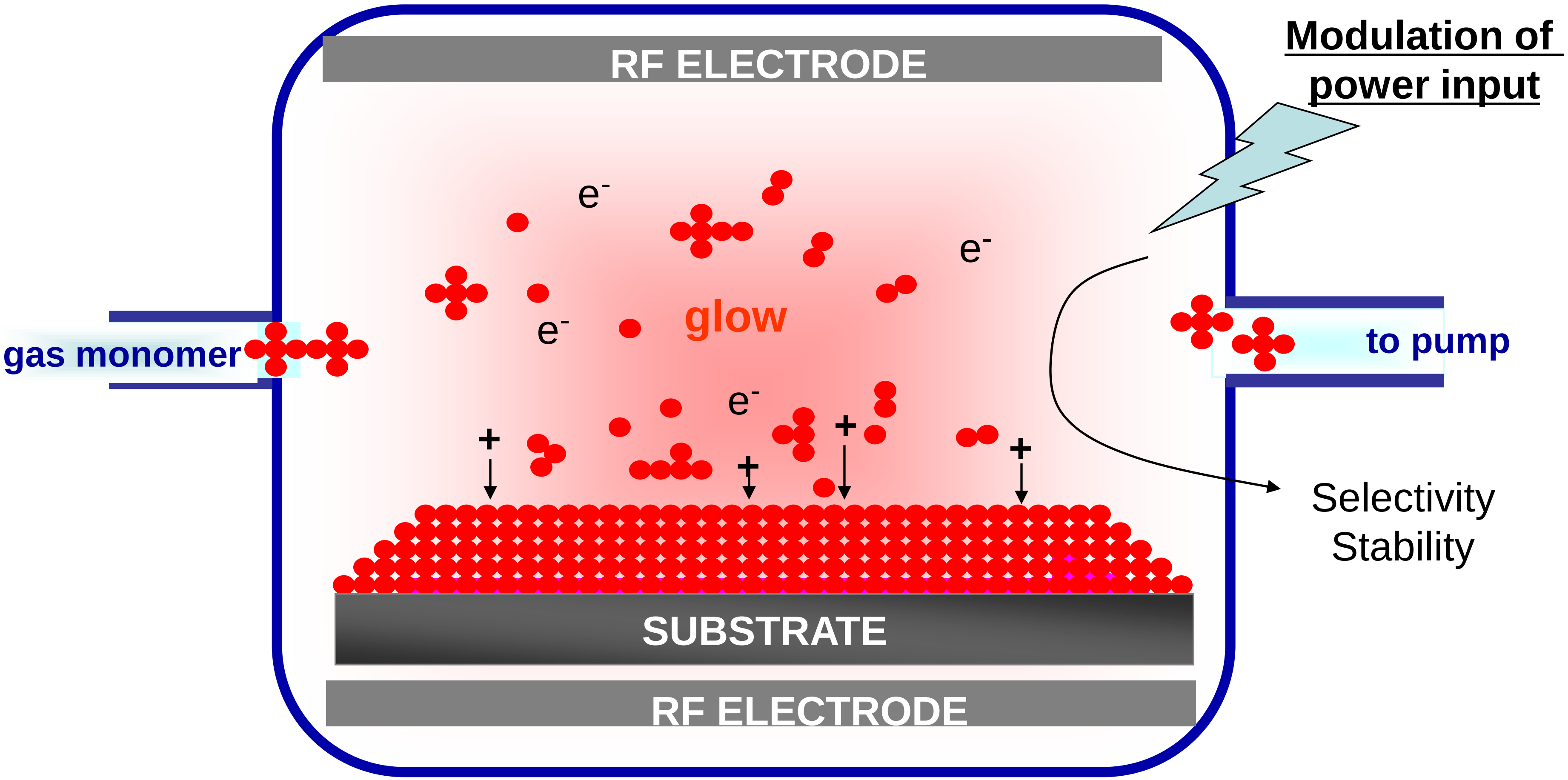
SURFACE MODIFICATION PROCESSES IN COLD, LOW PRESSURE PLASMAS



2. Polymerisable gas → PECVD

PE-CVD PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

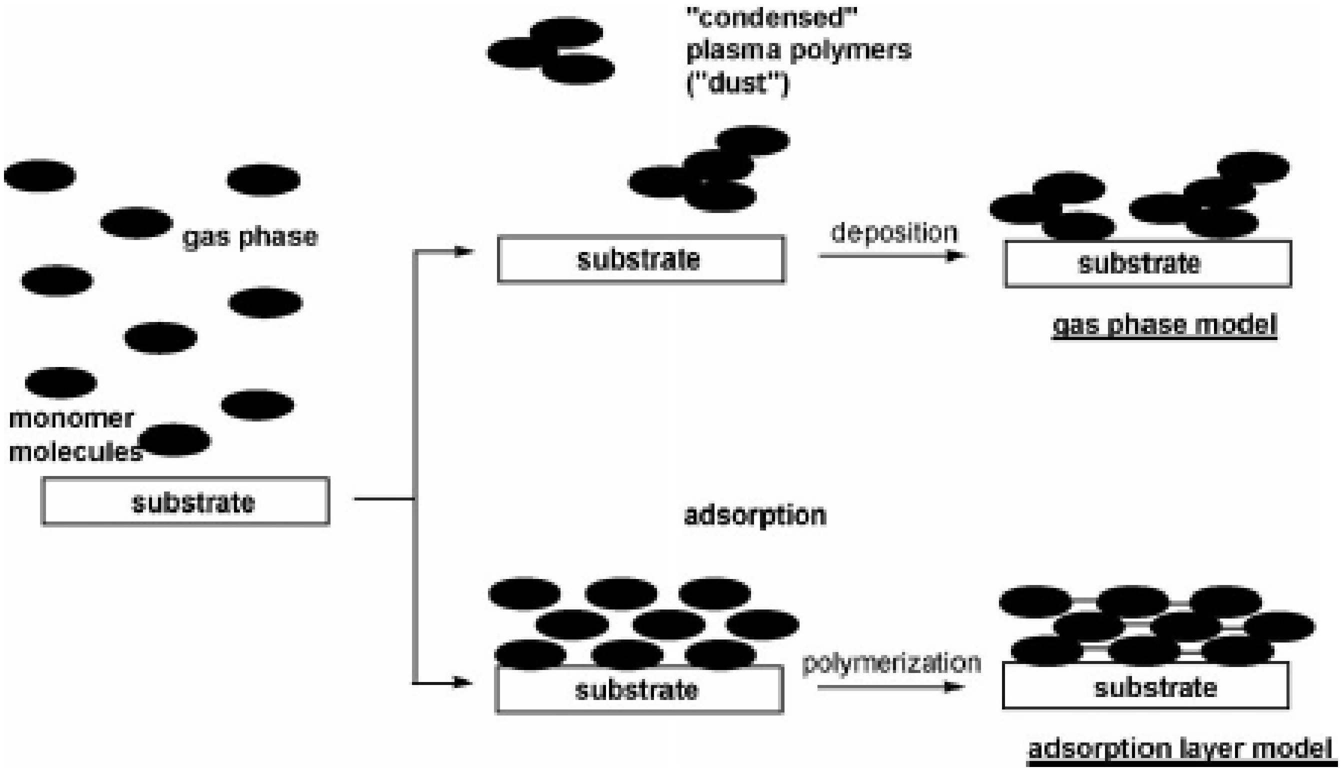
Inorganic (SiO_2, DLCs...) and organic (silicone-, PEO- teflon-like...) coatings can be deposited.
PLASMA POLYMERIZATION is jargon name for PE-CVD of organic coatings;



Mechanisms of Plasma Polymerization?

The preferred locus of plasma polymerization is a subject of controversy…

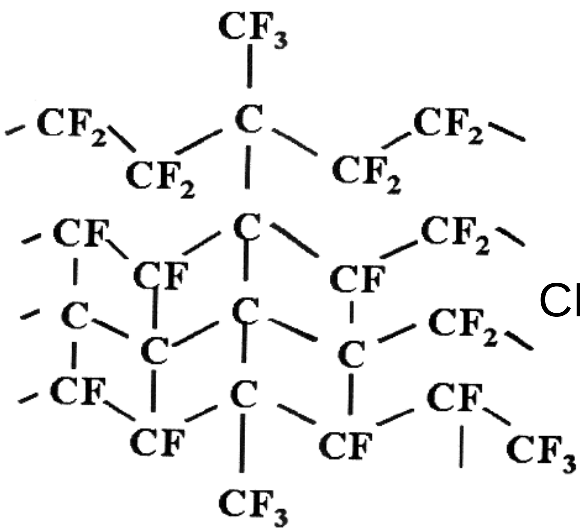
(i)In the gas phase
(ii)Or in the layer adsorbed on the substrate



Jörg Friedrich, Plasma Process. Polym, 2011, 8, 783-802

Plasma polymerisation process

C_2F_4, C_2F_6 —Plasma→



Presence of
different groupments
CF_2, CF_3, CF, C-CF, CHF, CHF_2

3D structure (depending on the degree of crosslinking)

Specificity of plasma polymerised coatings

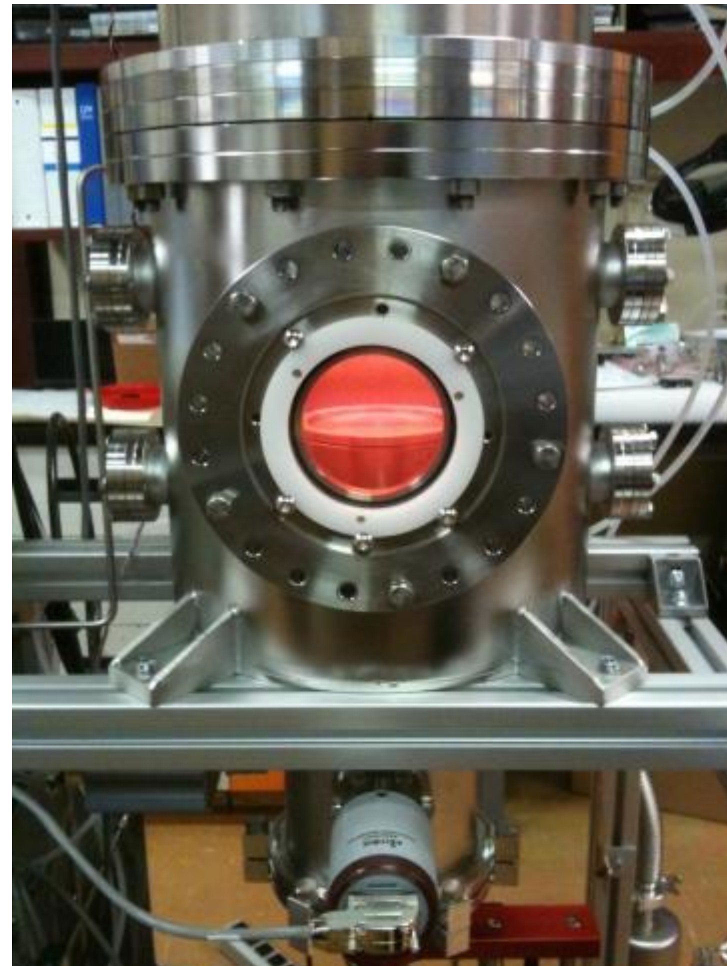
1. Ultra thin, pinhole-free layers of various compositions can be deposited as plasma polymers

2. Not a conventional polymerisation process: No repetition of the structure of the initial monomer

1. The physico-chemical properties of the coating are controlled by the plasma parameters (power, pressure) and not only by the starting monomer

Plasma-enhanced chemical Vapor deposition Reactor for Organic/inorganic coatings

Plasmionique



Today:
there is a strong need to retain the momomer structure during plasma polymerisation process

X X X

CH2=CH CH2=CH CH2=CH —Vinyl→ CH2=CH-CH2-CH-CH2-CH-

with X above each CH.

n monomer with functional groups X

Polymer with n-y functional groups X

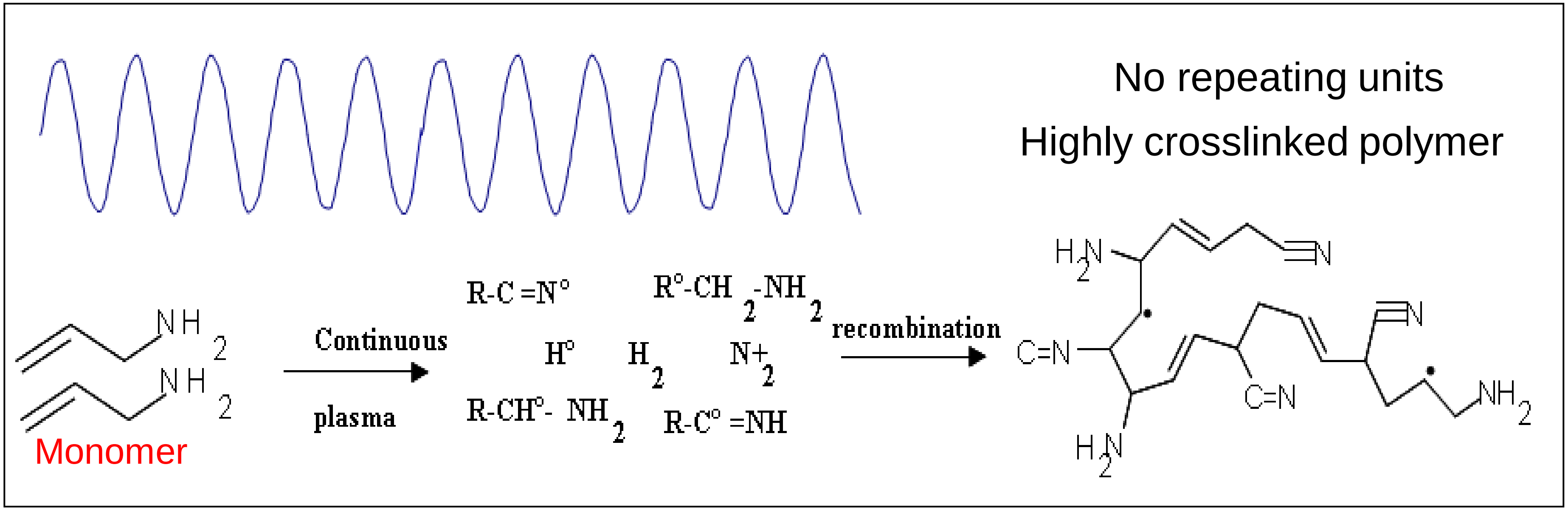
X : Functional group= NH_2, COOH, SH…

To control the reaction selectivity
To control the stability of the coating

Use of modulated discharges (Pulsed discharges)

How to control the selectivity of the process?

Polymerization under continuous wave plasma



H. Yasuda introduced an important factor (Yasuda factor)
YF = W/FM (wattage/Molar mass x monomer flow)

For the case of high values of W/FM, all monomer molecules are extensively fragmented into single atomsand the monomer composition and –structure is barely recognizable in the resulting plasma polymer structure and composition

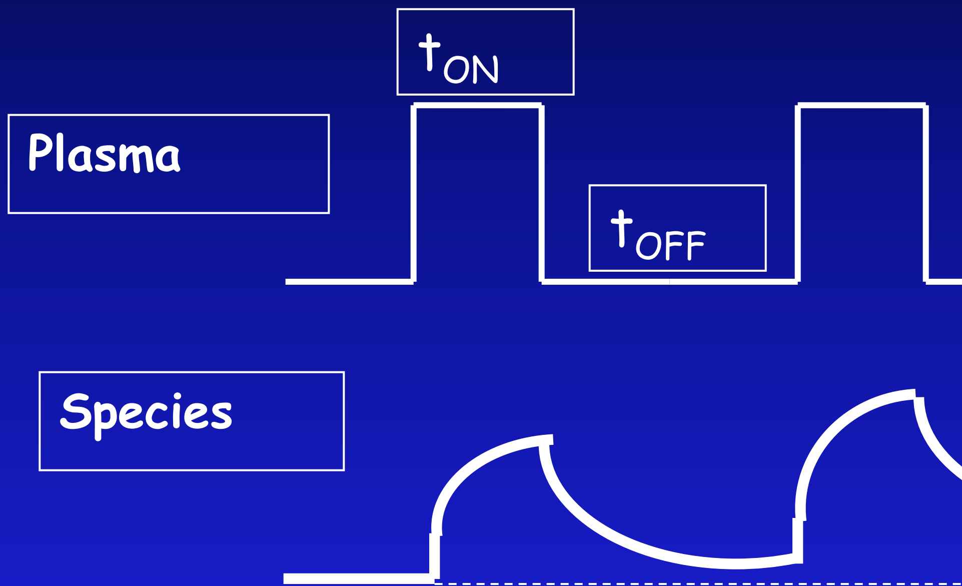
ABCDEF + plasma → A + B + CD + E + F → [FCABDE]n

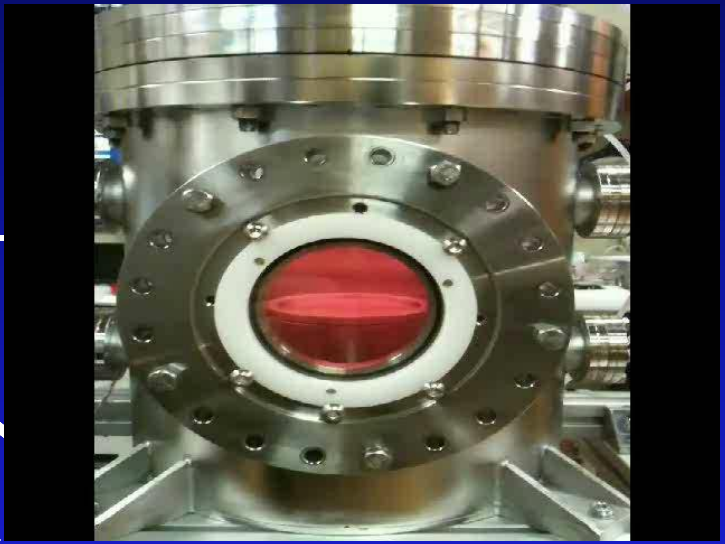
Yasuda proposed a new mechanistic concept in the 70’s which he called « Atomic polymerization »

How to use LOW values of W/FM ??

Introduction of the pulsed-plasma technique, which corresponds to the greatest Innovation in the field of plasma polymerization was …

POWER MODULATION





Modulation Parameters

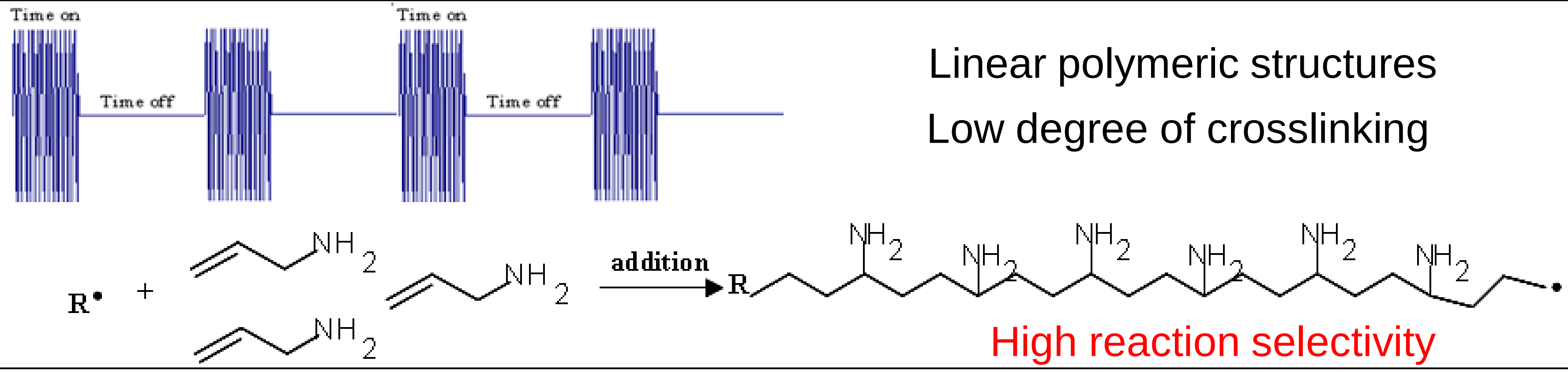
Period = $t_{ON} + t_{OFF}$

Duty Cycle = $(t_{ON}/\text{Period}) * 100$

Effective power

$W_{eff} = W_{tot} \times DC$

Polymerization under pulsed discharge



Linear polymeric structures

Low degree of crosslinking

High reaction selectivity

A clever choice of « monomer » must be done to produce specifc charcateristics corrosion resistant coatings

transparent barrier
Films for food packaging

(Silica coatings from Organosilanes...)

antifouling coatings
Ether rich coatings
From glycols precursors

anti-fog

poly(vinyl alcohol) (PVA) layers

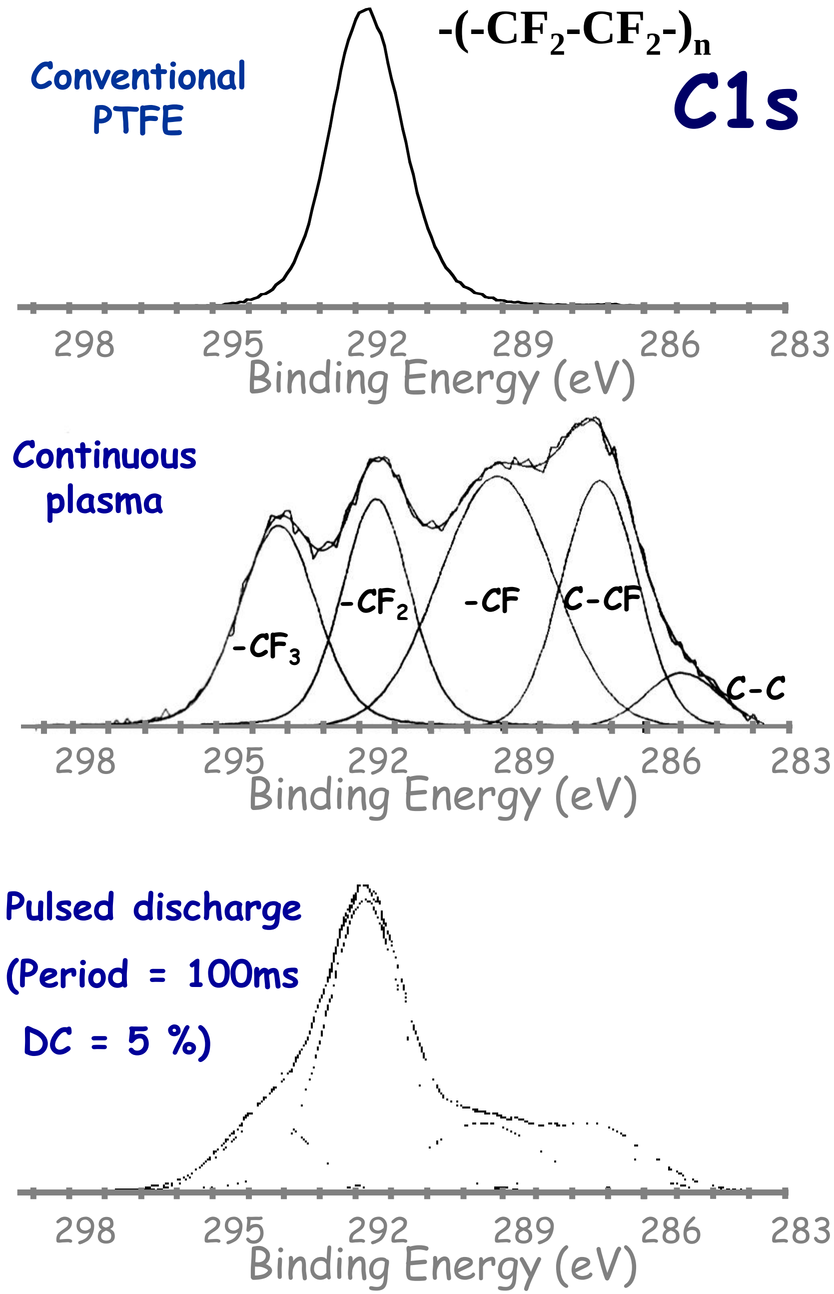
Scratch and abrasion-resistance (DLC coatings from CH4/Ar plasmas)

anti-ice on plane wings

Super hydrophobic coatings

anti-stain clothes

Teflon like coatings…
from fluorinated monomers



XPS

Decrease of the DC (low W_{eff})

↓

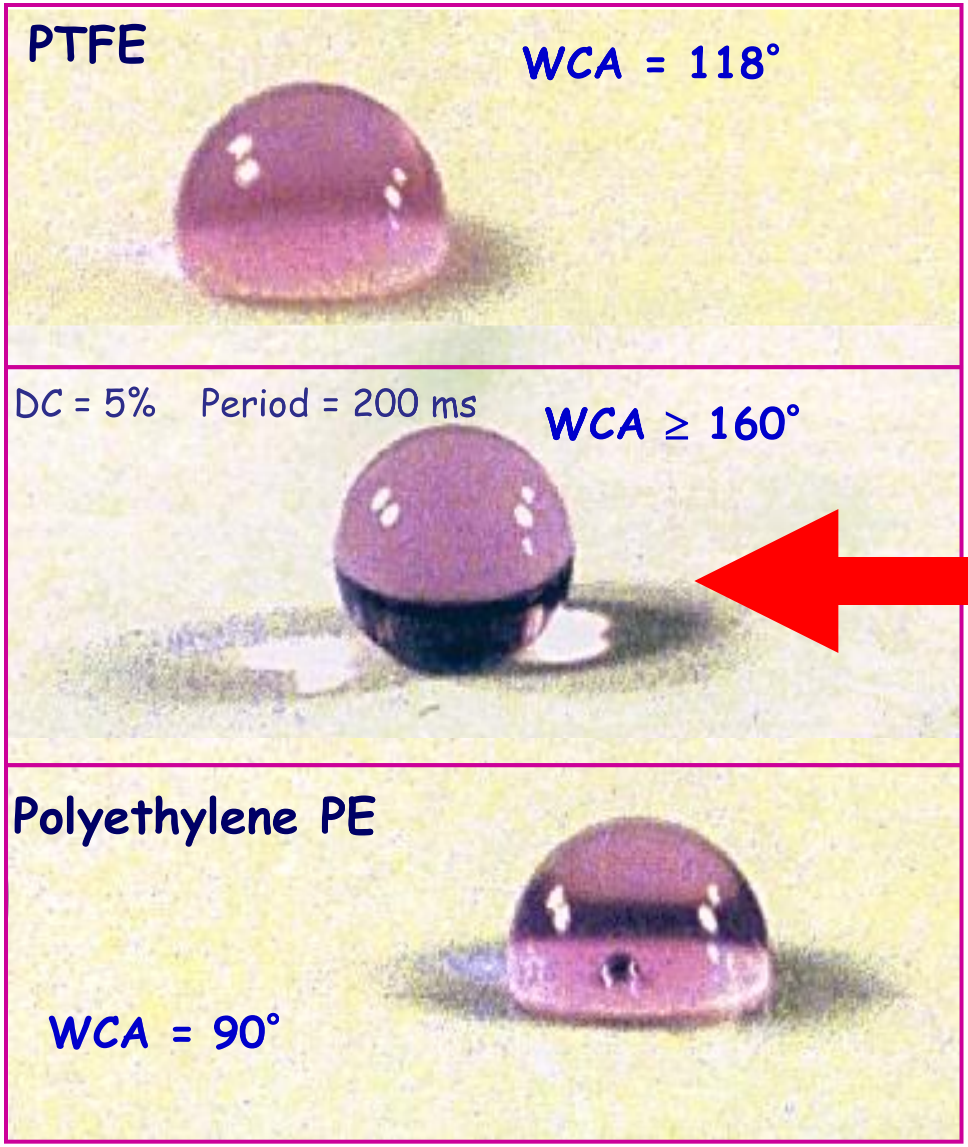
Increase of % CF_2

↓

"teflon-like" structure

R. d' Agostino (Bari, Italie)
Plasmas Processes and Polymers, 2004

"Super Hydrophobic" Plasma Deposited Coating



Nanosized ribbons of crystalline teflon produced with modulated Discharges (releasing coating)

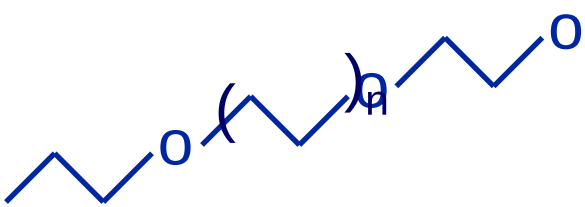
R. D'Agostino et al.

Plasma processes for cell adhesion

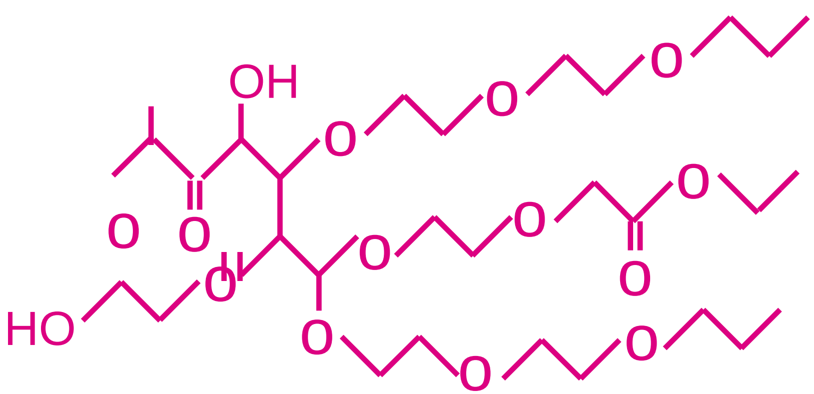
INHIBITION

PEO-like coatings

PEO $-(CH_2CH_2O)_n-$



PEO-like



PROMOTION

Grafted N-groups

-COOH functional coatings

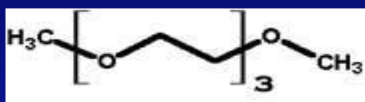
Key Parameter
retention of the PEO
structure in the coating

Feed :glycols

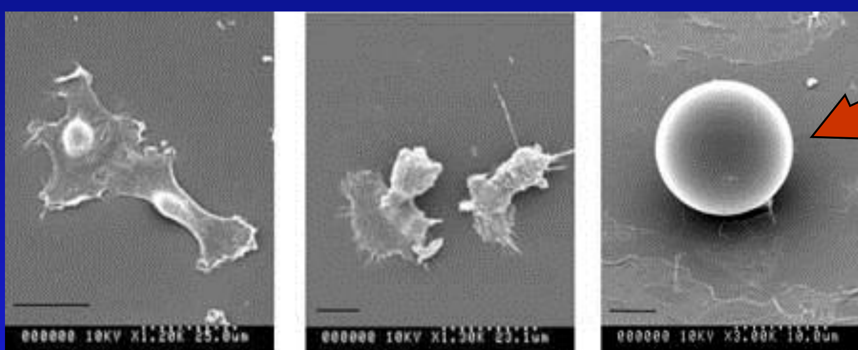
H-tert BJ1 fibroblasts on PEO-like 5W, a cell-repulsive surface

1. Oligoglymes ($(CH_3\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}CH_3$, n=1-4)

R. D'Agostino et al. Plasma processes and Polymers, Vol 1:57-62 (2004)



Diglyme (n=2) Di(ethylene glycol) dimethyl ether ou 2-Methoxyethyl ether ($C_6H_{14}O_3$)



PEO15W PEO -10W PEO - 5W

<u>DIGLYME 5W :</u>

- antifouling +++ sur fibroblastes
- Surface de contact cellule/support minimale

R. Gristina et al.

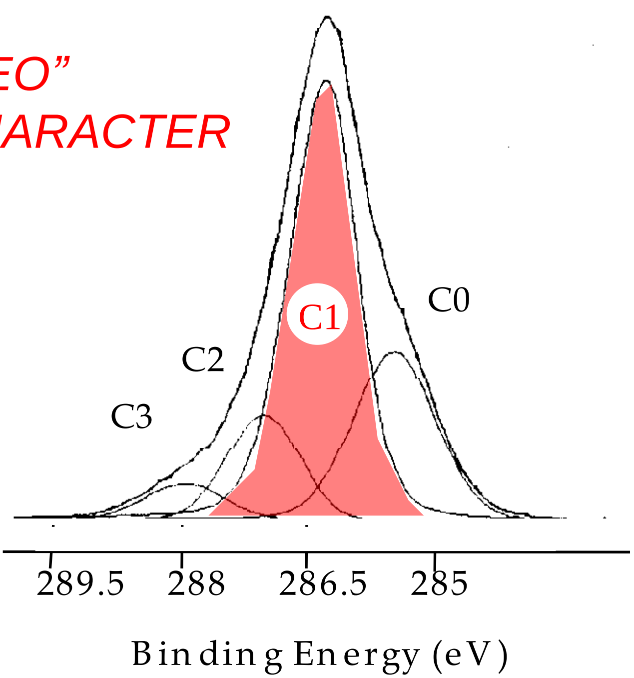
PE-CVD PEO-like COATINGS

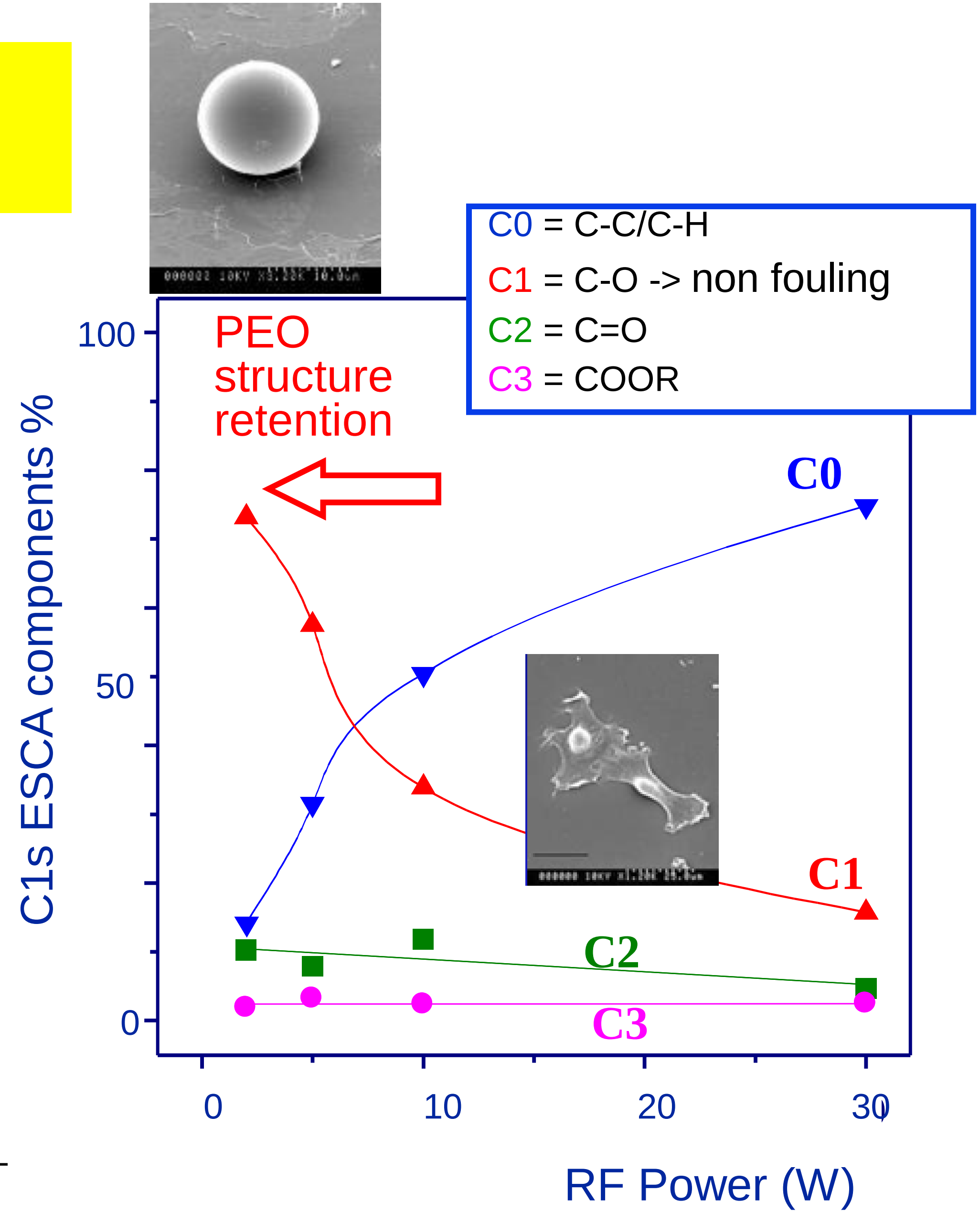
XPS MEASUREMENTS

CH_3O-$(CH_2CH_2O)_3$-CH_3

TEGDME monomer

"PEO" CHARACTER





R. d' Agostino et al.

TRANSPARENT BARRIER FILMS SiOx

featuring
- LOW GAS TRANSMISSION RATE (food, pharmaceutical packaging)
- MW compatibility
- HARDNESS
- TRANSPARENCY
- INERTNESS
- CORROSION RESISTANCE
- DIELECTRIC PROPERTIES

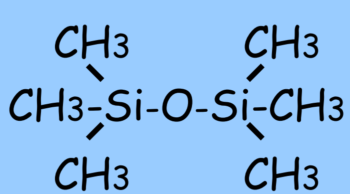
- in optimum conditions, O_2 GTR in industrial scale ranging between 3 and 10 $cm^3\ m^{-2}$ day

Key Parameters

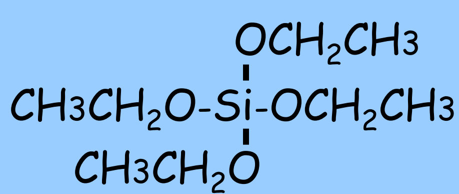
monomer/O_2 ratio

input power (fragmentation)

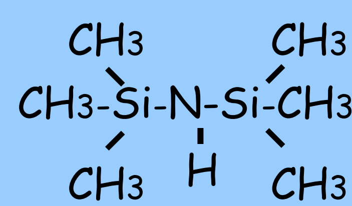
MONOMERES



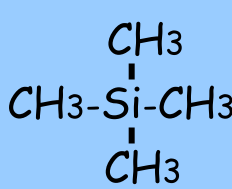
HMDSO



TEOS



HMDSN

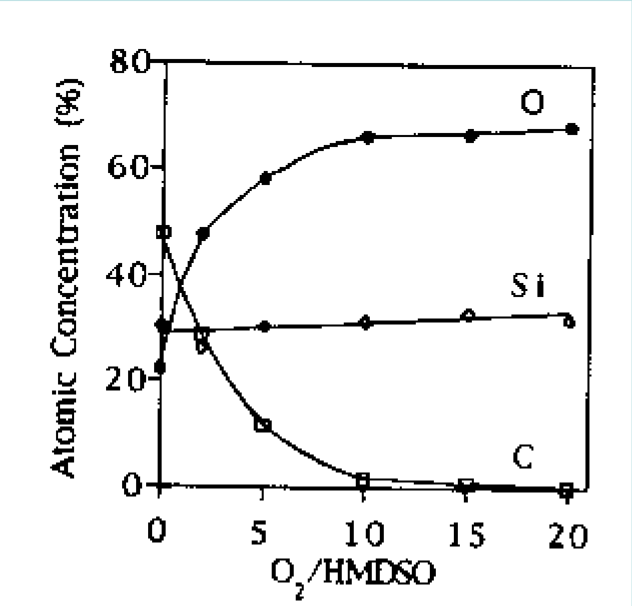


TMS

HMDSO/O2

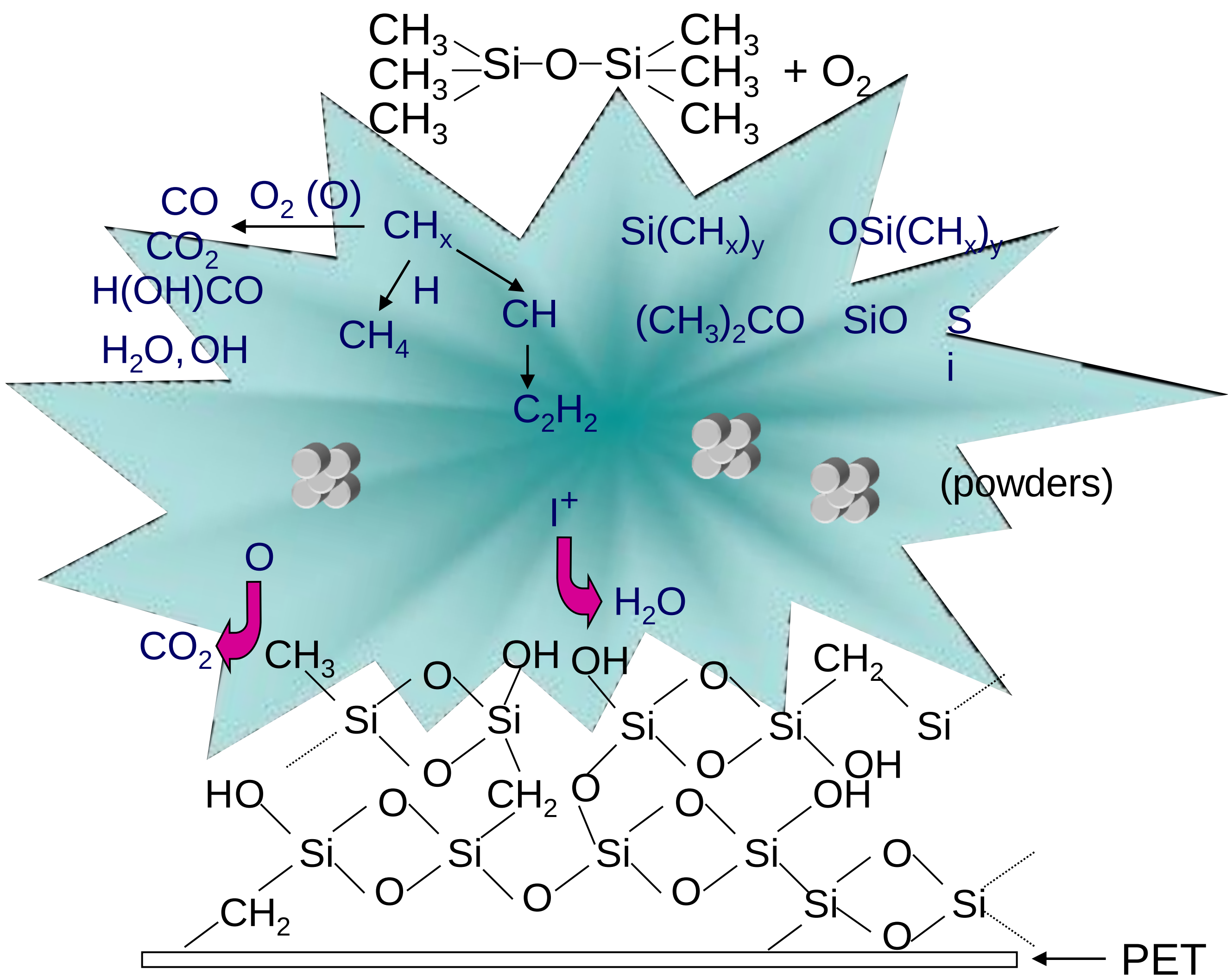
RF GLOW DISCHARGES

SiOx film composition at different feed ratios

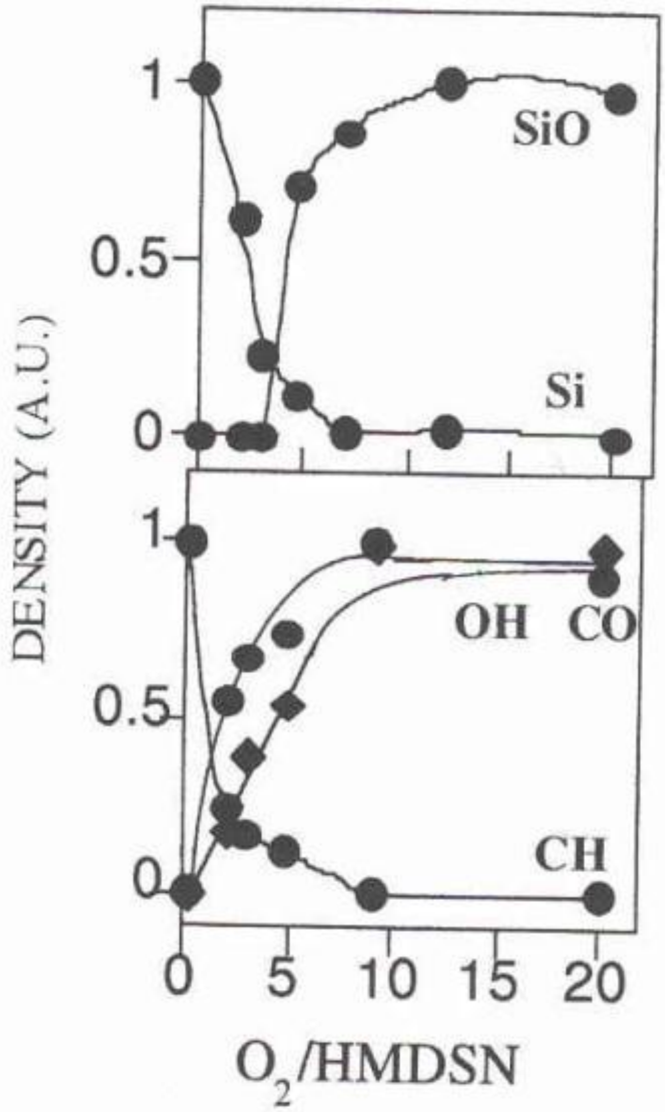


R. D'agostino et al.

PECVD of SiO_2-like films



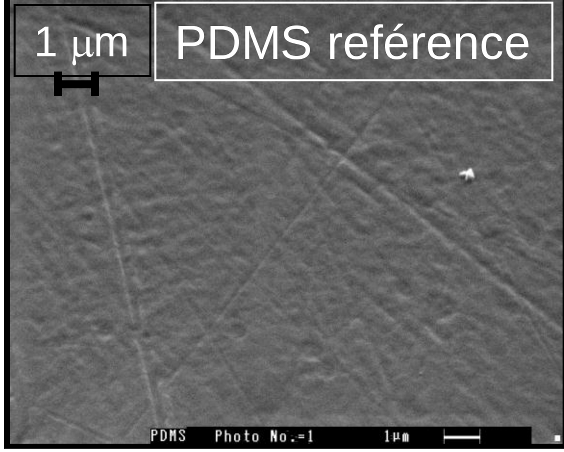
Silanols drill holes in high density SiOx

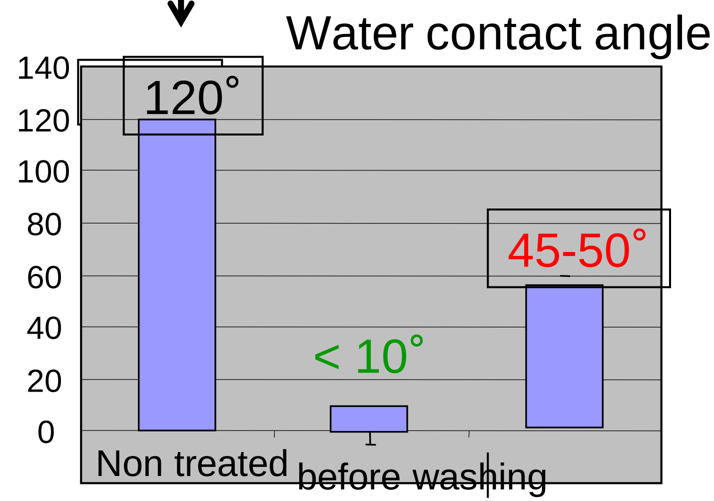


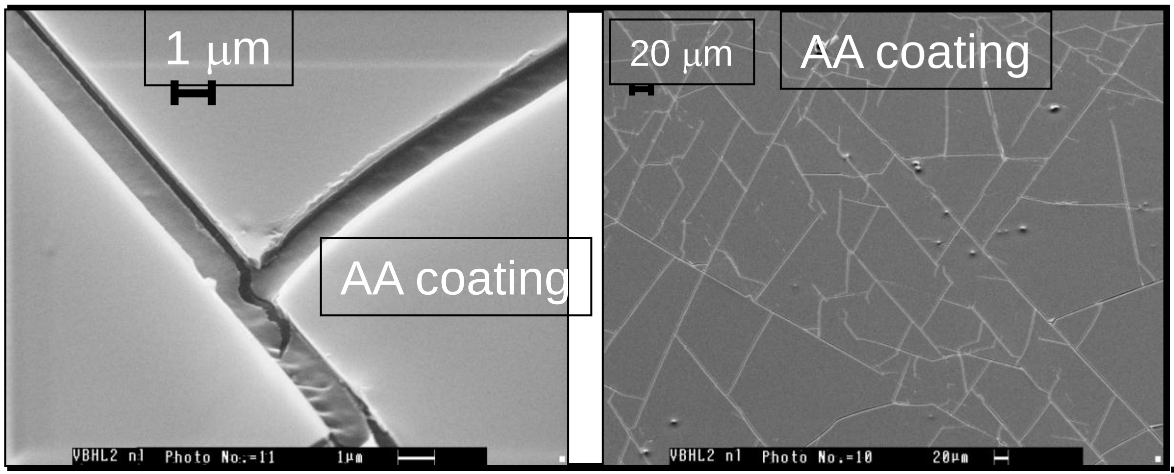
1
0.5
0
SiO
Si
DENSITY (A.U.)
1
0.5
0
OH
CO
CH
0
5
10
15
20
O_2/HMDSN

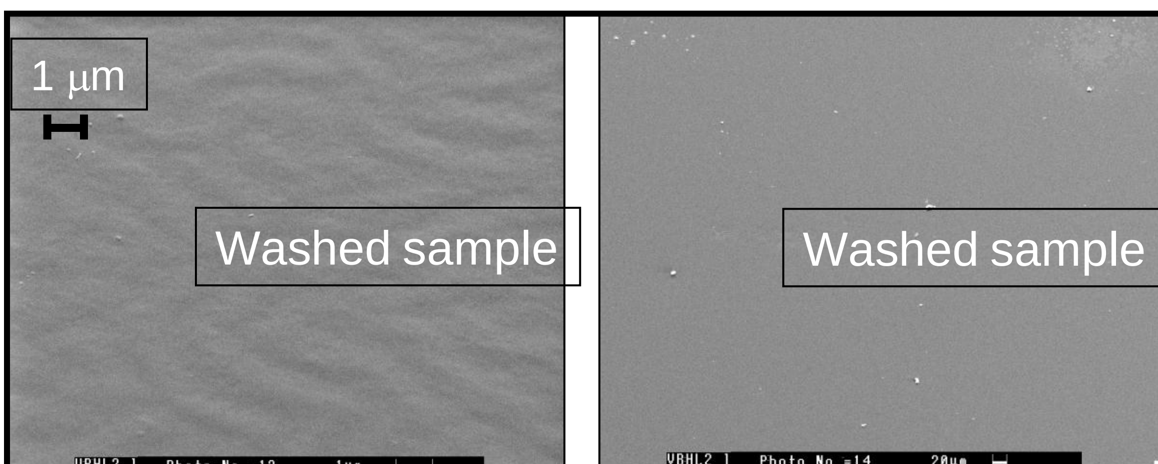
Stability??

ORIGIN OF AGEING

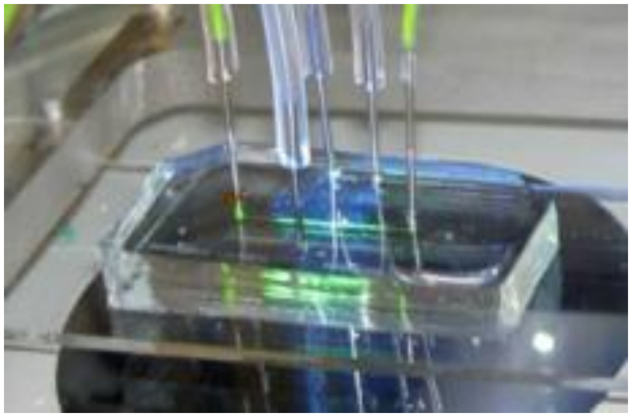


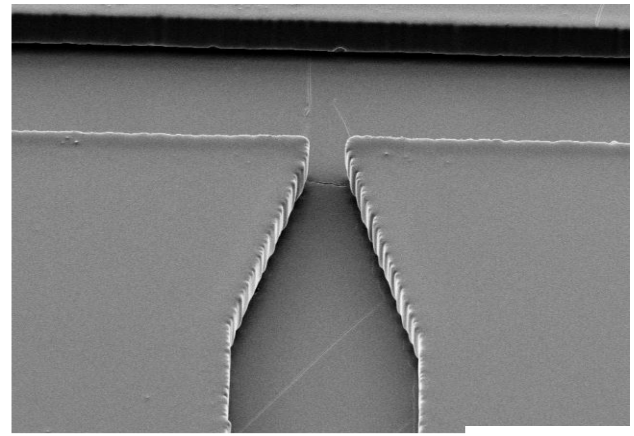






Use of microfluidic devices to understand the properties of plasma deposited materials

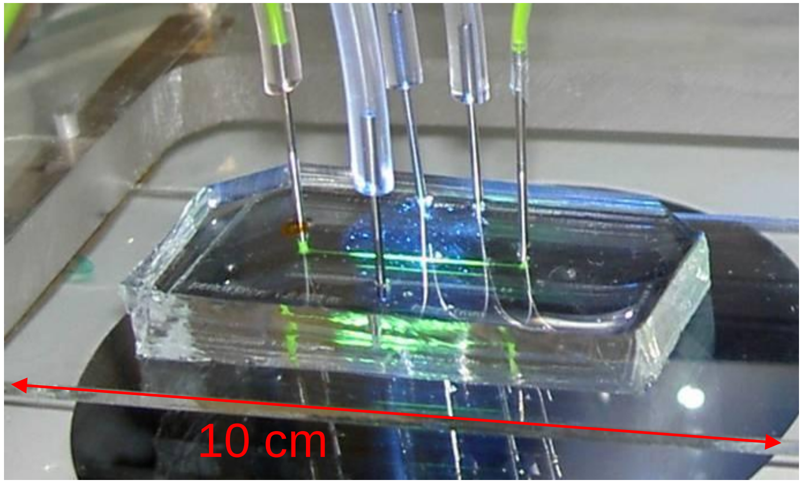




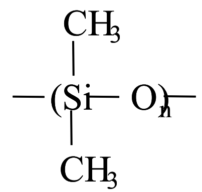
IPGGM: Pierre Gilles de Gennes Institute for microfluidic

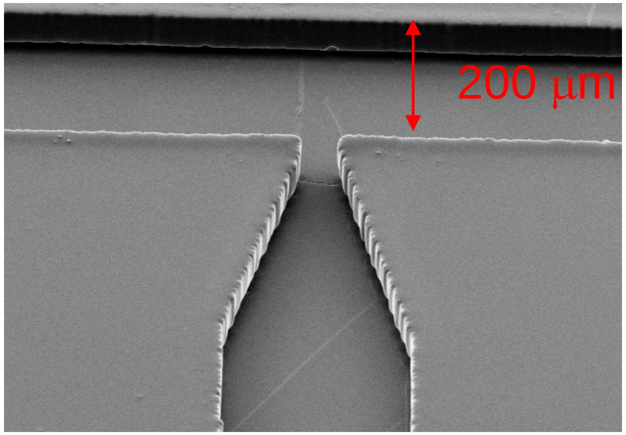
INSTITUT PIERRE-GILLES DE GENNES
Pour la microfluidique

Microfluidic device : A tool to evaluate the stabilty of Plasma polymerized coatings

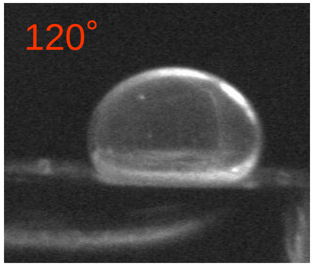


PDMS





- Elastomer, rather inert, hydrophobic
- Dedicated material for micro-fabrication

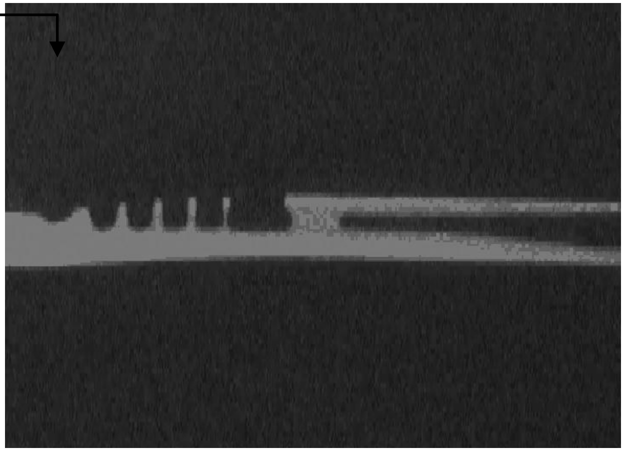


Uncoated PDMS

Emulsions: oil in water (O/W)

Oil

Continous phase (Water)

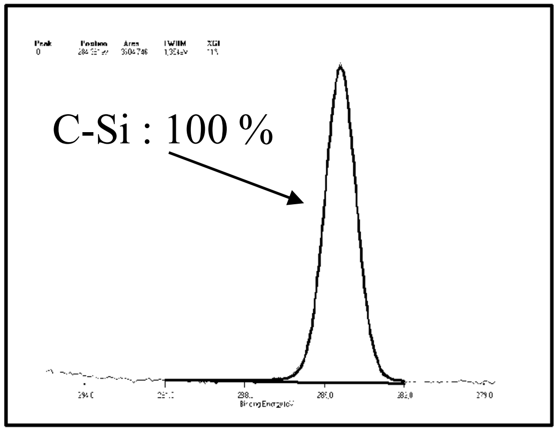


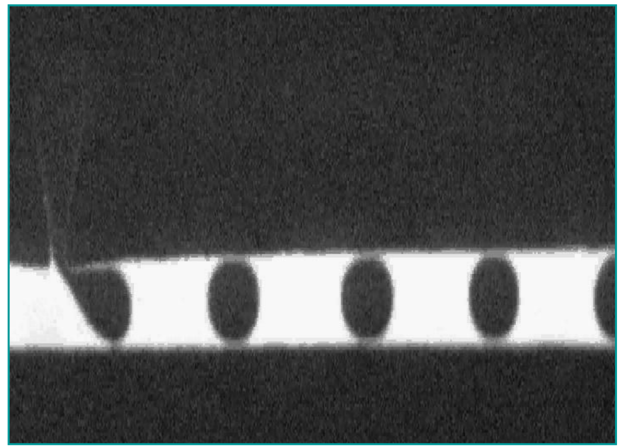
→ Modification of PDMS surface is necessary

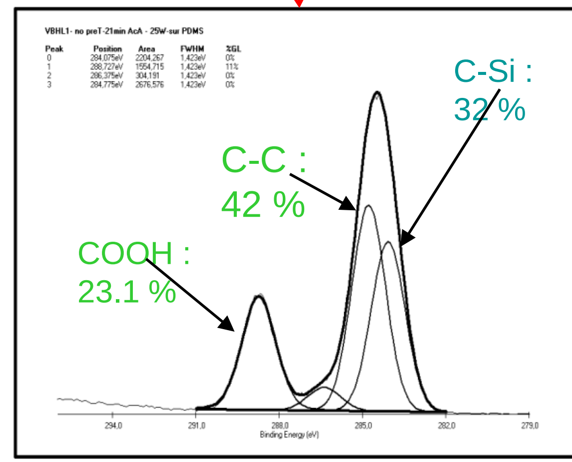
After optimization of the plasma process parameters…

+ dépôt AA

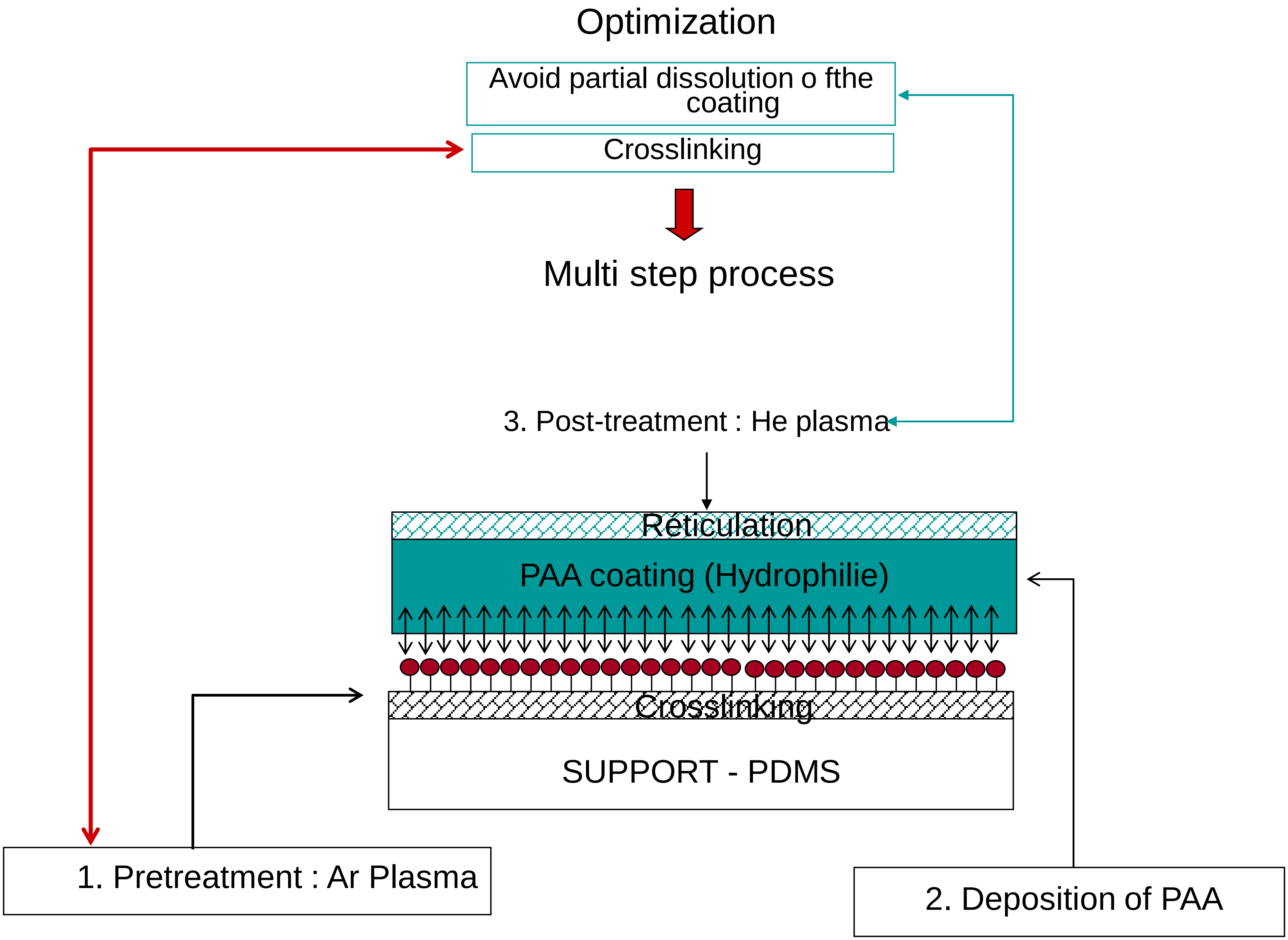
PDMS



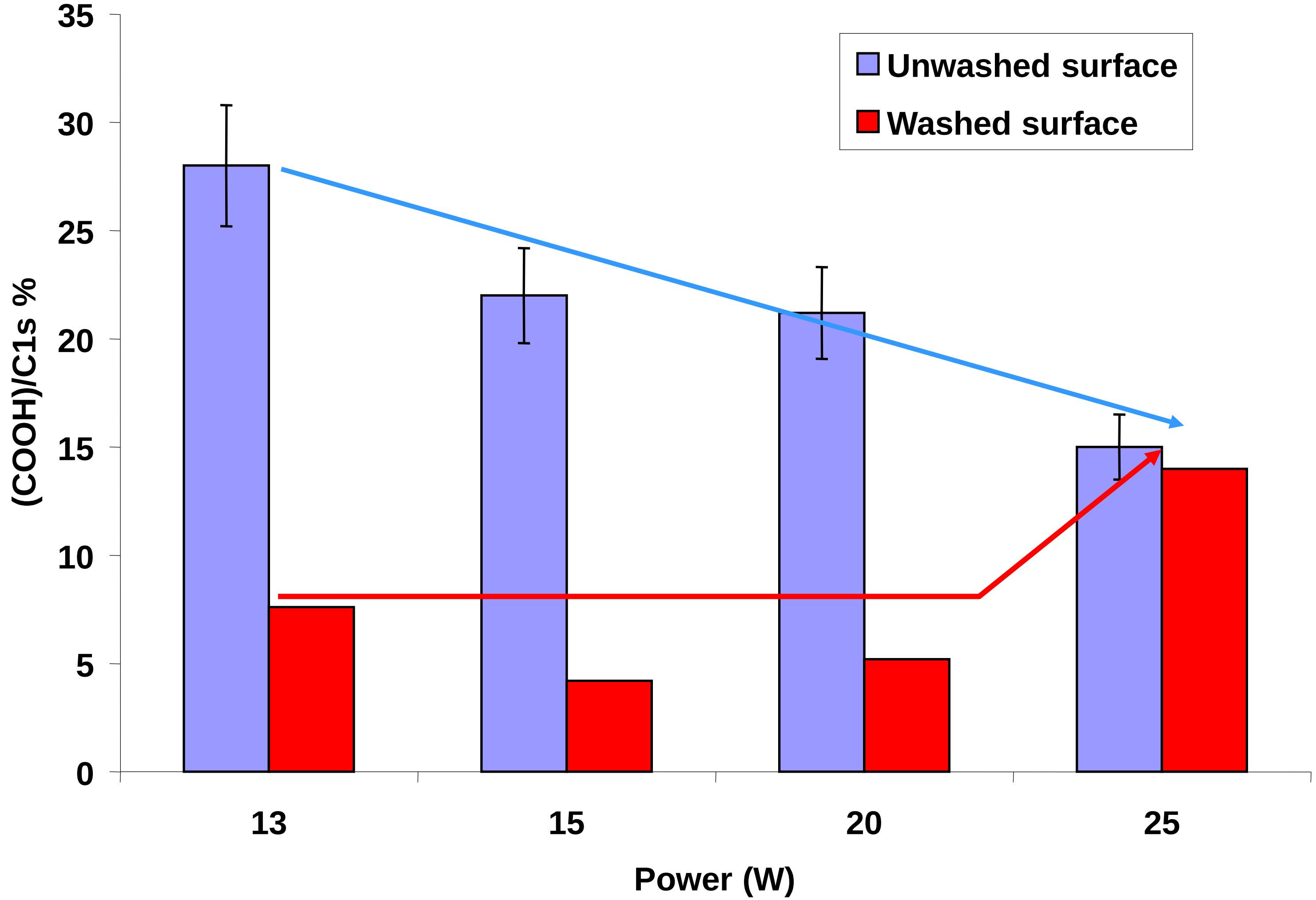




wettable



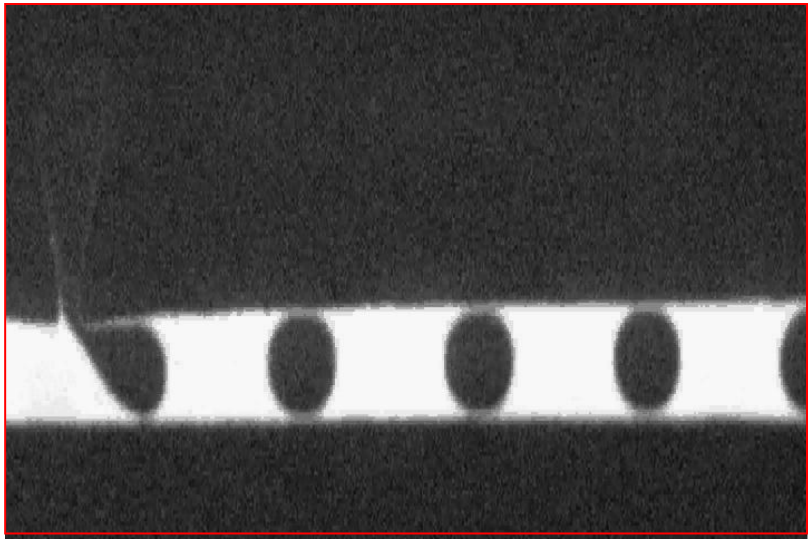
Optimization
Avoid partial dissolution o fthe coating
Crosslinking
Multi step process
3. Post-treatment : He plasma
Réticulation
PAA coating (Hydrophilie)
Crosslinking
SUPPORT - PDMS
1. Pretreatment : Ar Plasma
2. Deposition of PAA



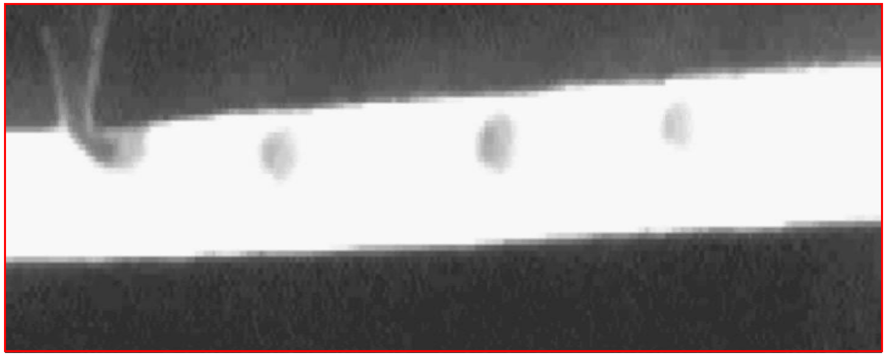
R. Jafari, et al., Thin Solid Films (2009), doi:10.1016/j.tsf.2009.03.217

Use of an O2 plasma treatment

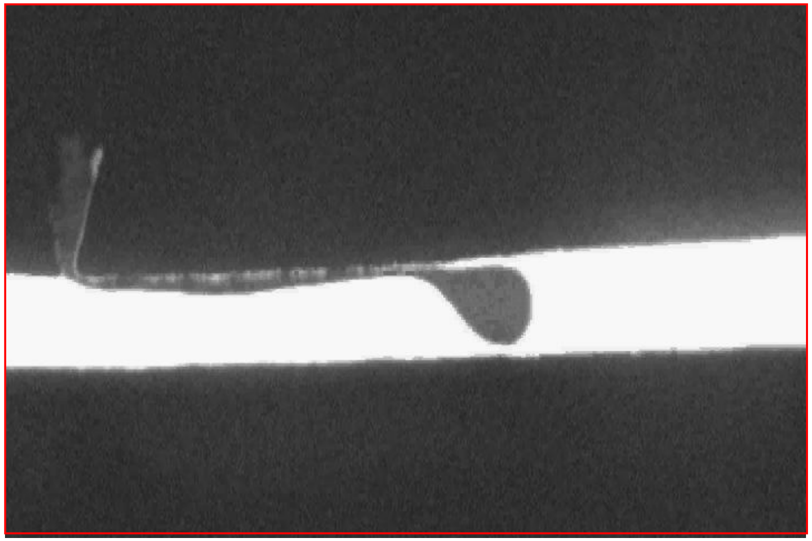
0h



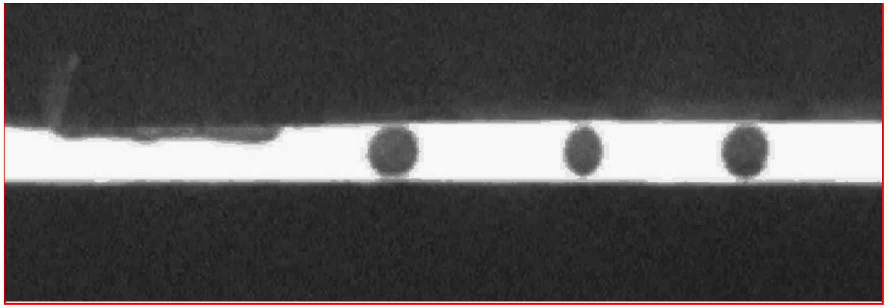
24h



36h



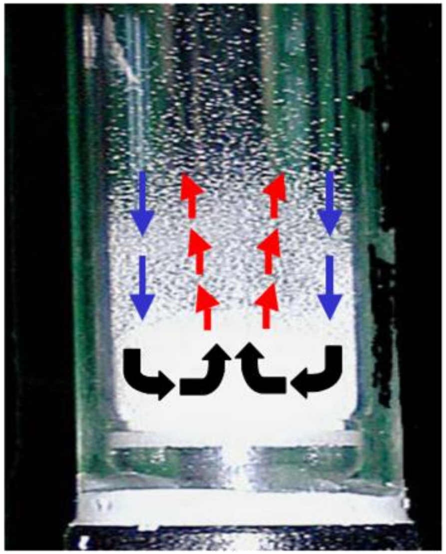
48h



Ageing

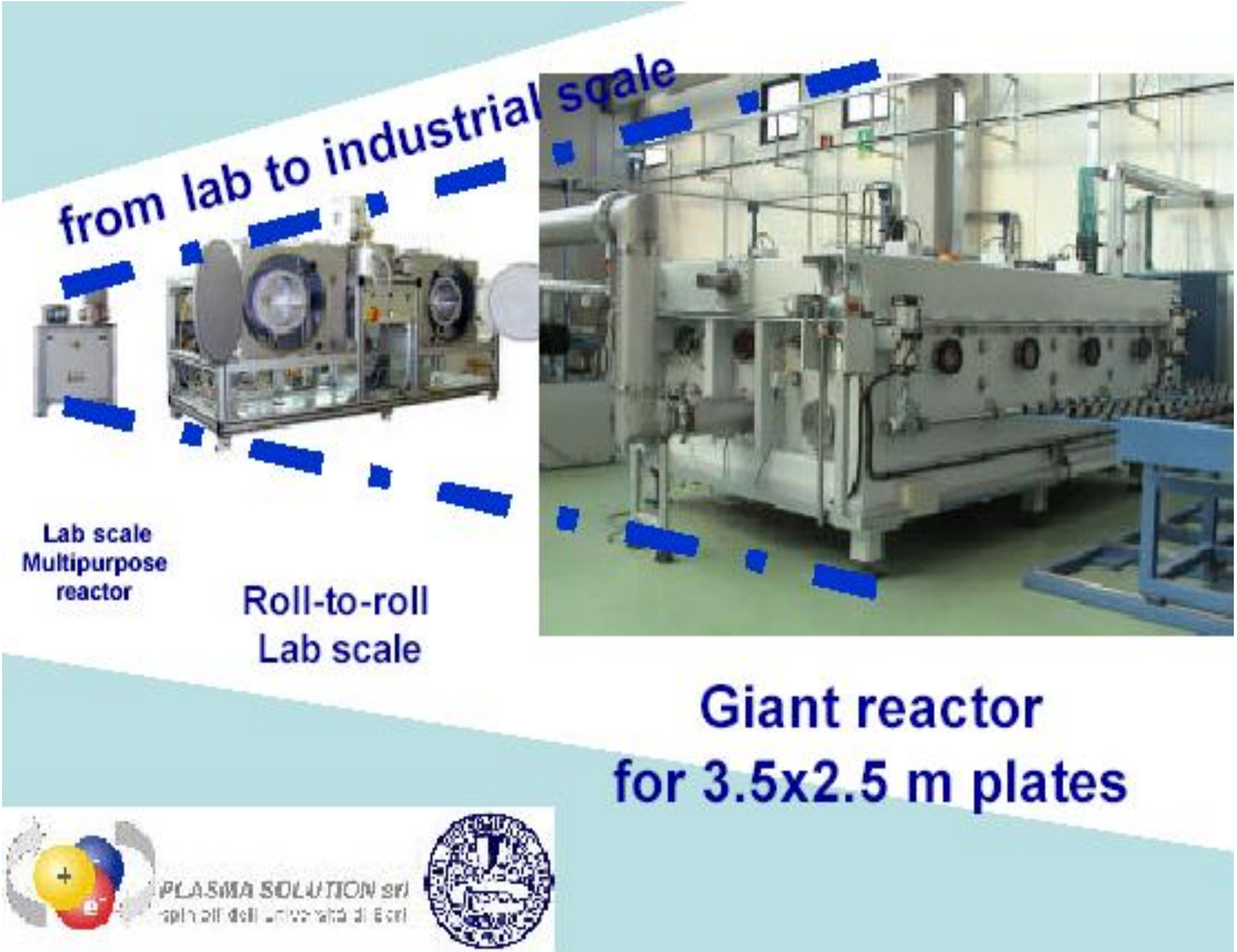
Treatment of flat substrates is easy…
3D objects?

Plasma treatment of powders in a Fluidized Bed Plasma Reactor
Diameter: few microns to hundred of microns…



- ✓ Continuous agitation of the particles: homogeneity in the treatment of powders
- ✓ Decrease of the particle agglomeration
- ✓ Large exchange surface between the particles and the gas phase (plasma)
- ✓ Excellent heat transfer: reducing the risk of thermal degradation

Industrial plasma reactors…

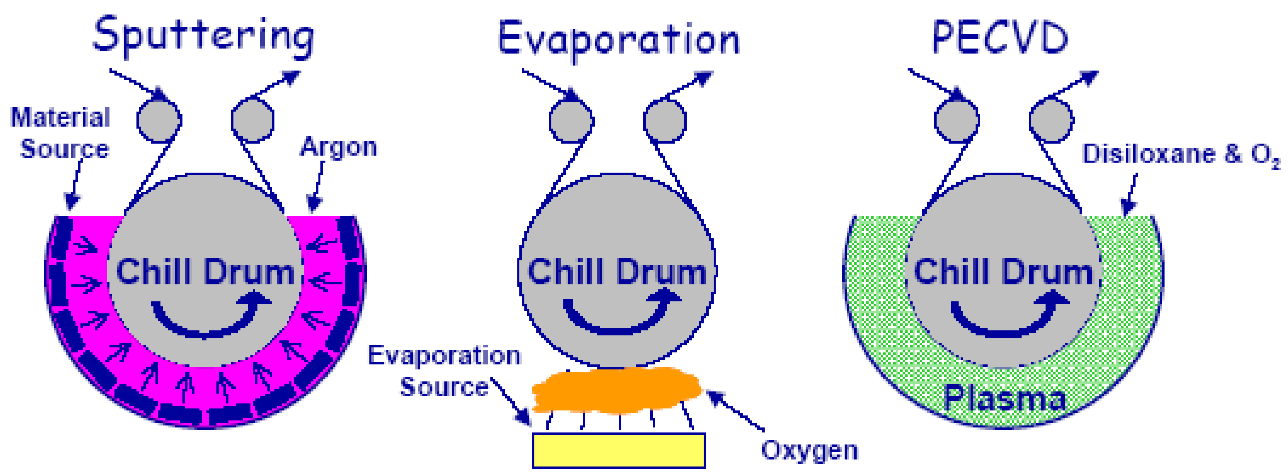


With the courtesy of Prof. D'Agostino

Dépôts de couches SiO_x (couches barrière) sur films de PET pour les applications alimentaire

Research & Development One World One Team One Vision

Industrial Coating Technologies for SiOx Barrier Material



200 m/min	300 m/min	200 m/min
40 – 50 nm	100 – 500 nm	15 – 20 nm
3 $cm^3/(m^2$ day atm)	3 $cm^3/(m^2$ day atm)	3 $cm^3/(m^2$ day atm)
Low mechnical resist	Low mechnical resist.	High mechnical resist.
High heat input	High heat input	Low heat input

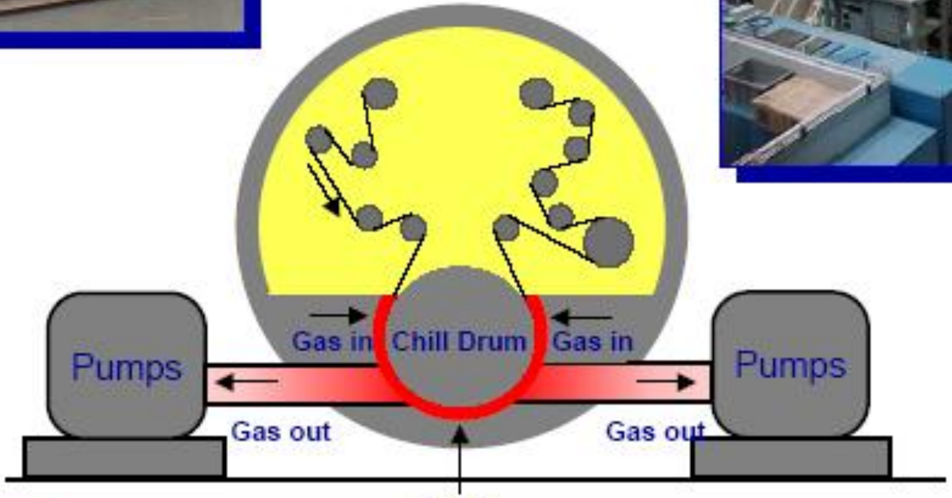
Tetra Pak protects what's good™ Tetra Pak R&D Proprietary Document

Tetra Pak R&D, PF/030318

Industrial PECVD Equipment at Tetra Pak

Plain PET 12 µm
120 $cm^3/m^2/day/atm$

PET/SiOx (15 nm)
< 3 $cm^3/m^2/day/atm$



Plasma = Electrical Power + Gas mixture (Disiloxane, Oxygen)

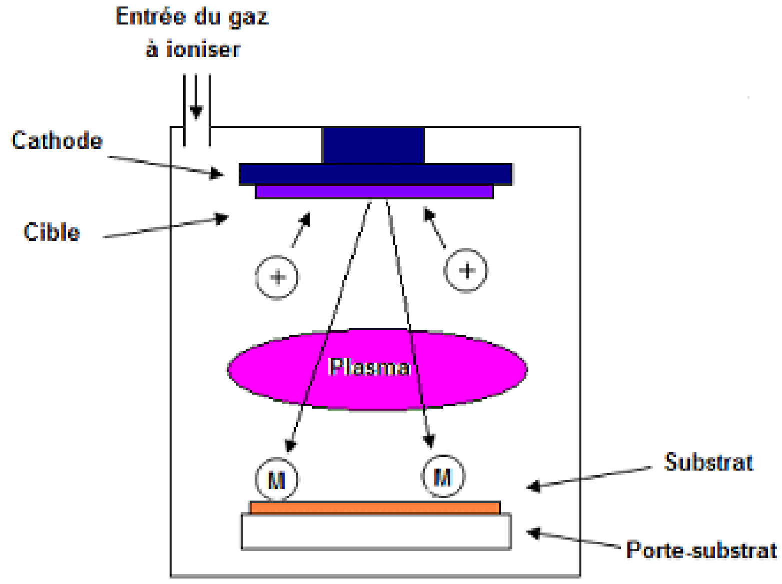
Our plasma reactors…

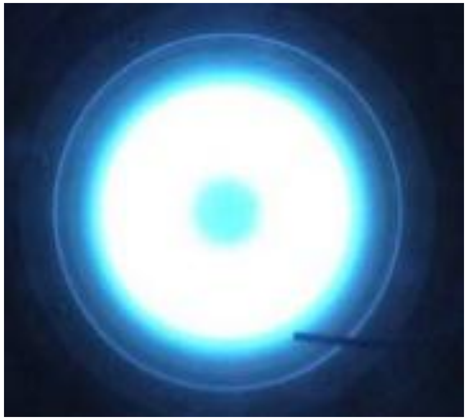
Advancing Plasma-Based Technologies
PLASMIONIQUE
À l'Avant-Garde des Technologies Plasmas

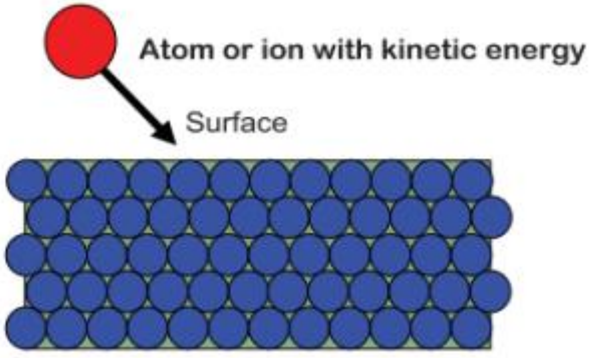
PECVD

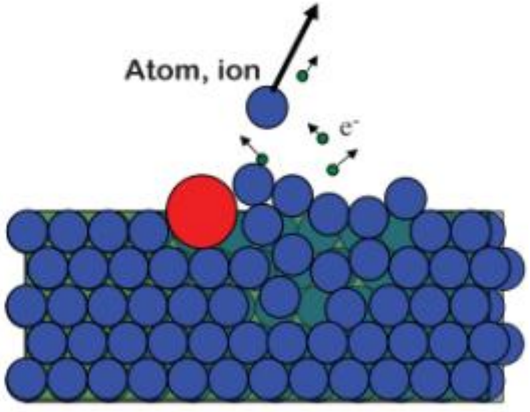
PECVD/Sputtering/Evaporation

Other technique :
RF SPUTTERING TECHNIQUE

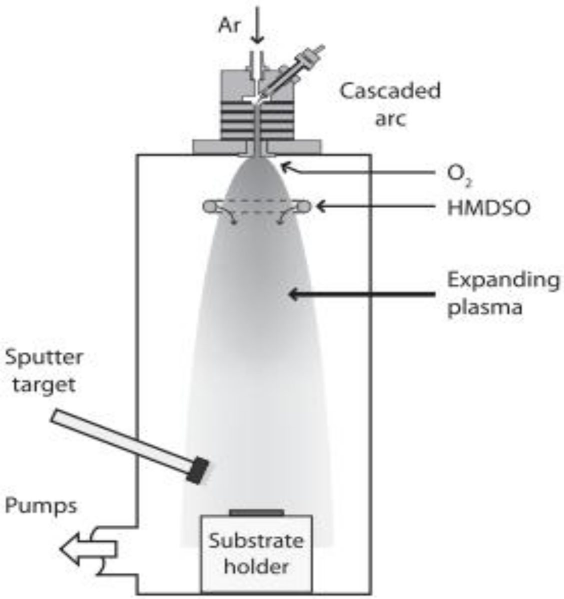




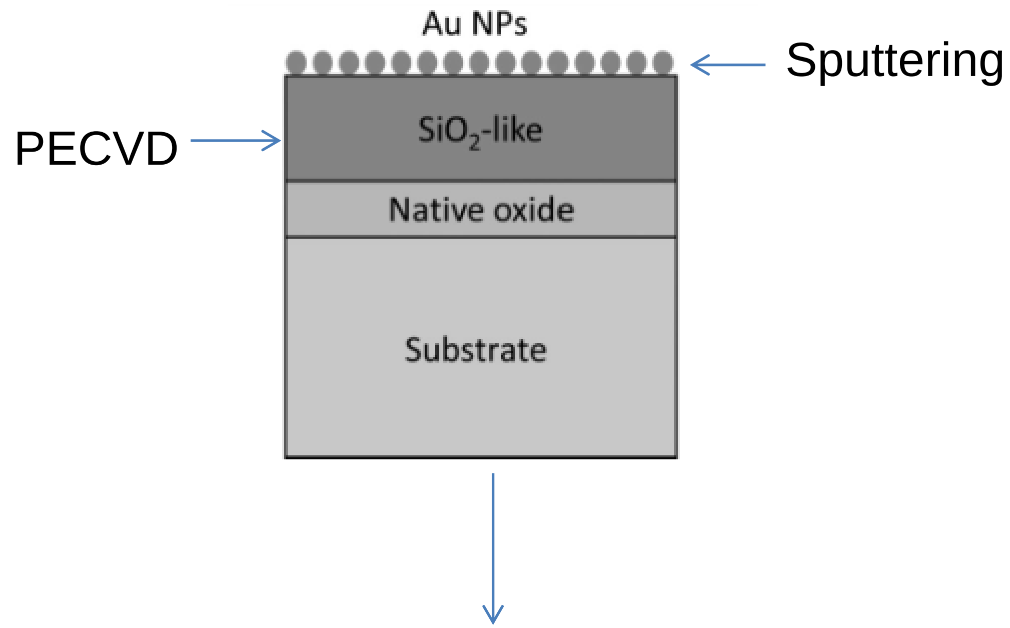




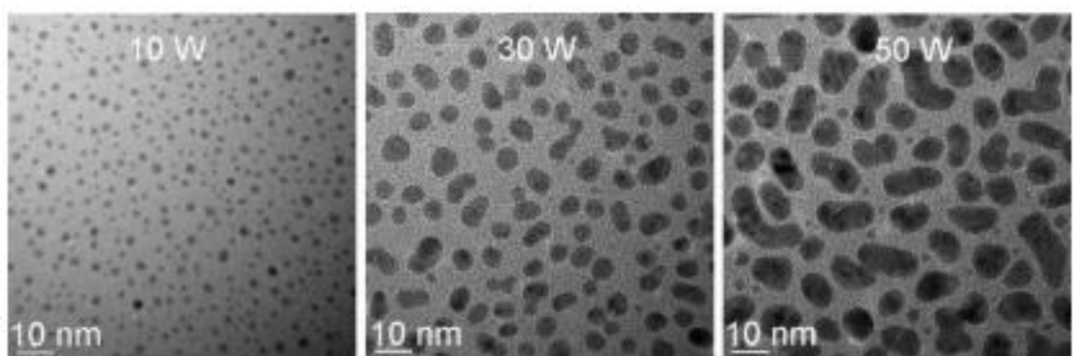
HYBRID SPUTTERING-REMOTE PECVD: Deposition of Au Nanoparticles on SiO_2 Layers



The hybrid RF magnetron sputtering and expanding thermal plasma CVD setup



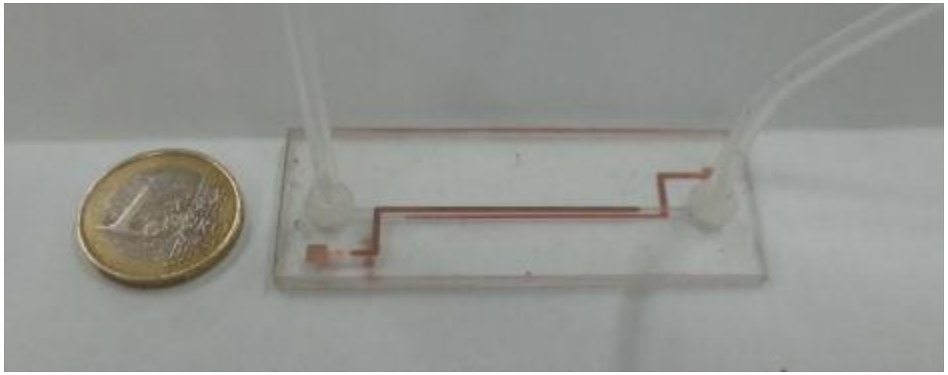
TEM images of Au nanoparticles prepared on carbon-coated copper grids at various RF-power settings



Nanoparticules size 1,6 nm 4,7 nm 7 nm

Haile Takele Beyene, Frans D. Tichelaar, Paul Peeters, Ivan Kolev, Mauritius C. M. van de Sanden, Mariadriana Creatore. Plasma Process. Polym. 2010, 7, 657–664

Microreactors!!!

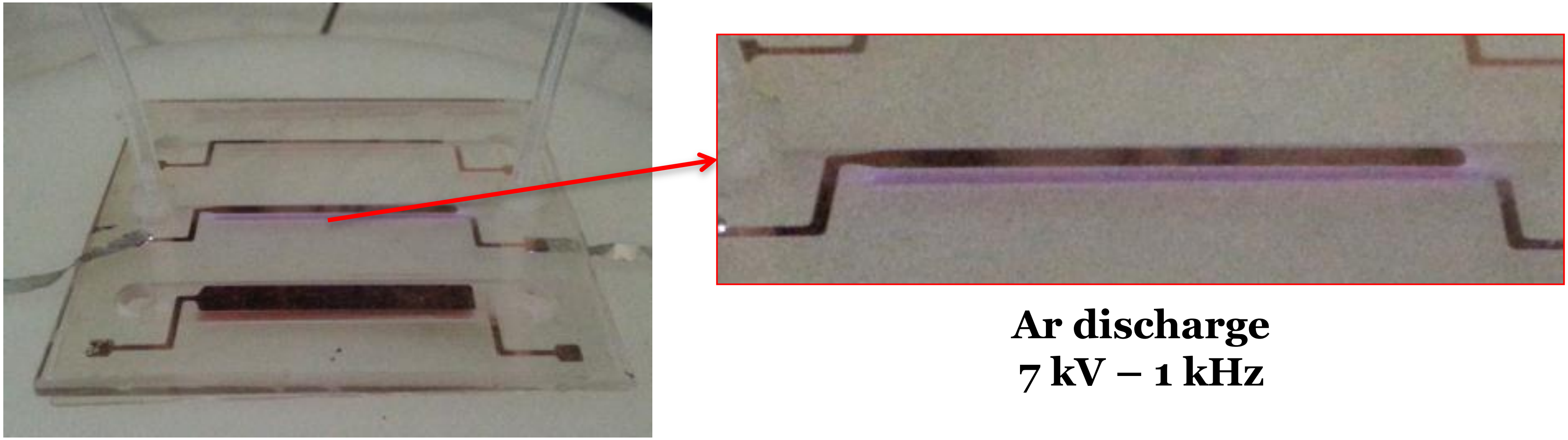


µChannel :

Width = 4 mm

Length = 50 mm

Depth = 500 µm



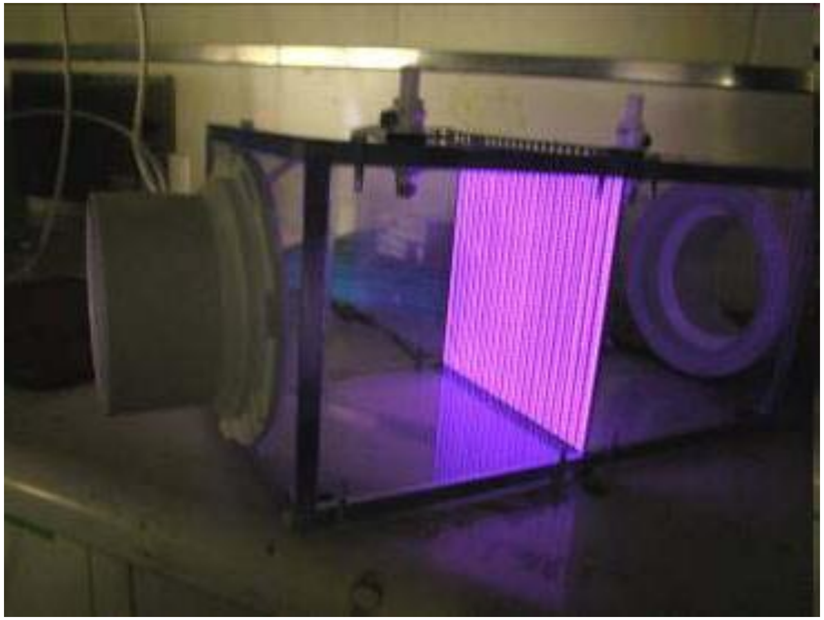
Ar discharge
7 kV – 1 kHz

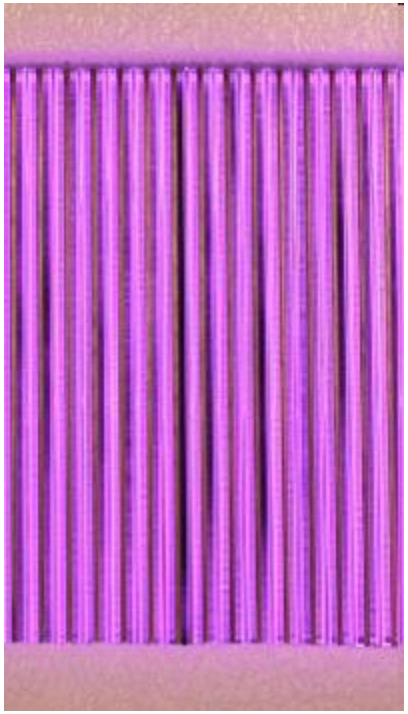
Other applications…

Non-thermal plasma in air at atmospheric pressure

Typical applications:
- Ozone production
- Treatment of polluted gaseous effluents

DBD device for air treatment



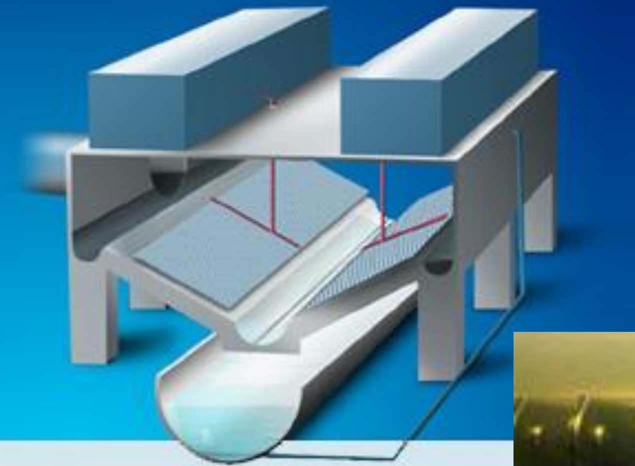


AquaPure Technologies Ltd.

our technology

The expanding pollution of drinking water sources and increasingly stringent regulations promote the development of new, innovative treatment technologies.

Conventional water treatment methods are often not effective in the removal of micro-pollutants such as Volatile Organic compounds (VOC's) because of their physical and chemical characteristics.

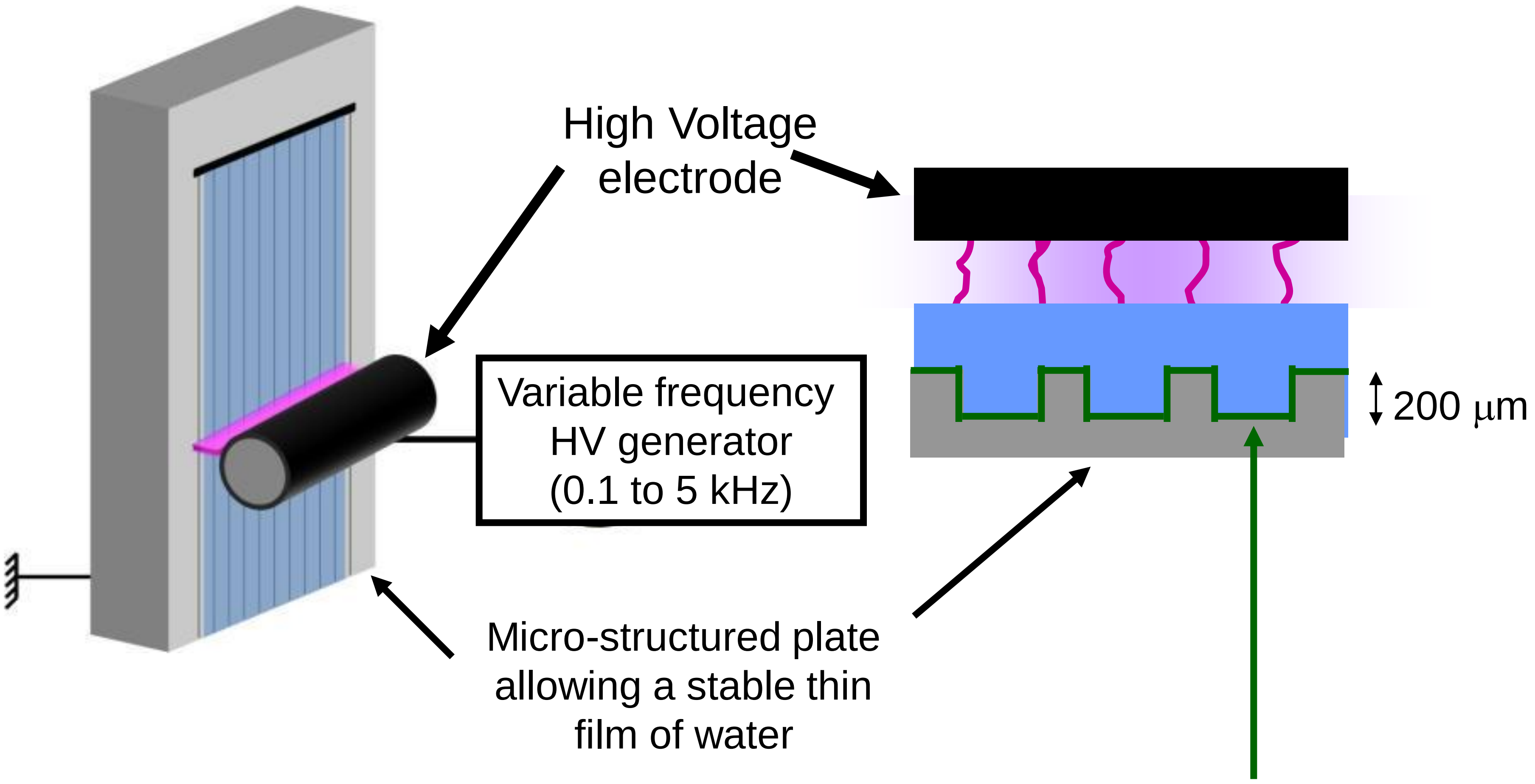


	kW/hr/m3 kW/hr/1000gal
TCE	1.21
MIB	1.67
NDMA	0.63
1,4 dioxane	1.24
MTBE	3.8

Henry's law constants at 25° C (atm.m^3.mol-1)

heptanol	2×10^{-5}
TCE	1×10^{-4}
MIB	6.5×10^{-5}
NDMA	3.34×10^{-5}
1,4 dioxane	5×10^{-5}
MTBE	6×10^{-4}

New non-thermal plasma reactor

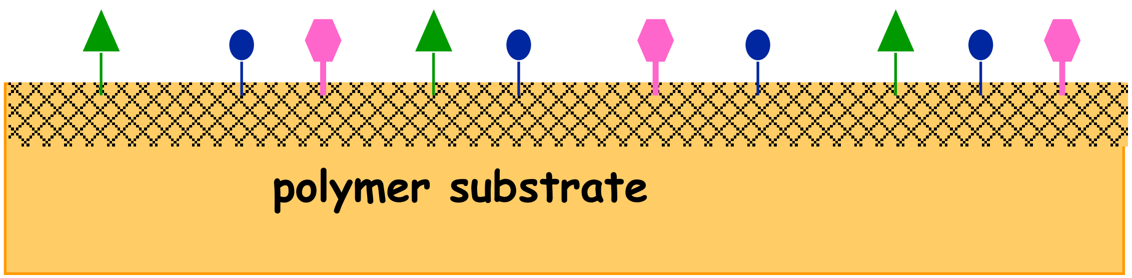


The micro-structured electrode is covered by a coating exhibiting catalytic and hydrophilic properties

CONCLUSION :
SURFACE MODIFICATION OF MATERIALS WITH LP PLASMA TECHNIQUES

PLASMA TREATMENTS : Modification of the topmost layers of materials (polymers) by grafting chemical groups

Selectivity : (-) → Controlled by gas feed
Stability : Problem of ageing → Additional pretreatment in inert gas (He, Ar…)



PE-CVD PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

High reaction selectivity : (+) → Controlled by the modulation of power input
Stability : Problem of dissolution → Control of the degree of crosslinking

CONCLUSION :
Consider PLASMA a tool for new applications

- Polymer activation for enhancing metal adhesion
- Polimer activation for enhancing color adhesion (e.g. car bumpers, plastic bags, textiles, …)
- Stain-resistant clothings and garments
- Super-hydrophobic coatings

- Corrosion resistant coatings for alloies
- Tissue engineering and microstructuring of polymers for contact guidance of cells
- Anti-trombotic coatings for prostheses
- Bacterial resistant materials for food packaging and prostheses
- Non fouling coatings

Acknowledgements

Partnership &Collaborators

Chimie Paris ParisTech

ESPCI ParisTech

INSTITUT PIERRE-GILLES DE GENNES
Pour la microfluidique

AMOLF FOM

Fundings

AGENCE NATIONALE DE LA RECHERCHE ANR

Liberté • Égalité • Fraternité
RÉPUBLIQUE FRANÇAISE
MINISTÈRE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE


Cédric Guyon


Stephanie Ognier


Fréderic Rousseau


Isabelle Mabille


Michaël Tatoulian


Daniel Morvan


Siméon Cavadias


Jacques Amouroux


Daniel Bonn


Willy Morscheidt


Dalila Chili


Daniela D'Elia

Thank you for your attention


Christos Anggelopoulos


Guillaume Schelcher


Bradley DaSilva


Alexandre MA


Olivier Lesage


Rao Xi


Rafik Benrabbah


Maxime Cloutier


Diane Gumuchian

IRCP Institut de Recherche de Chimie Paris


Bruno Pelat


Fatiha Laurence