Cold Plasma Technology: Applications in Food Industry

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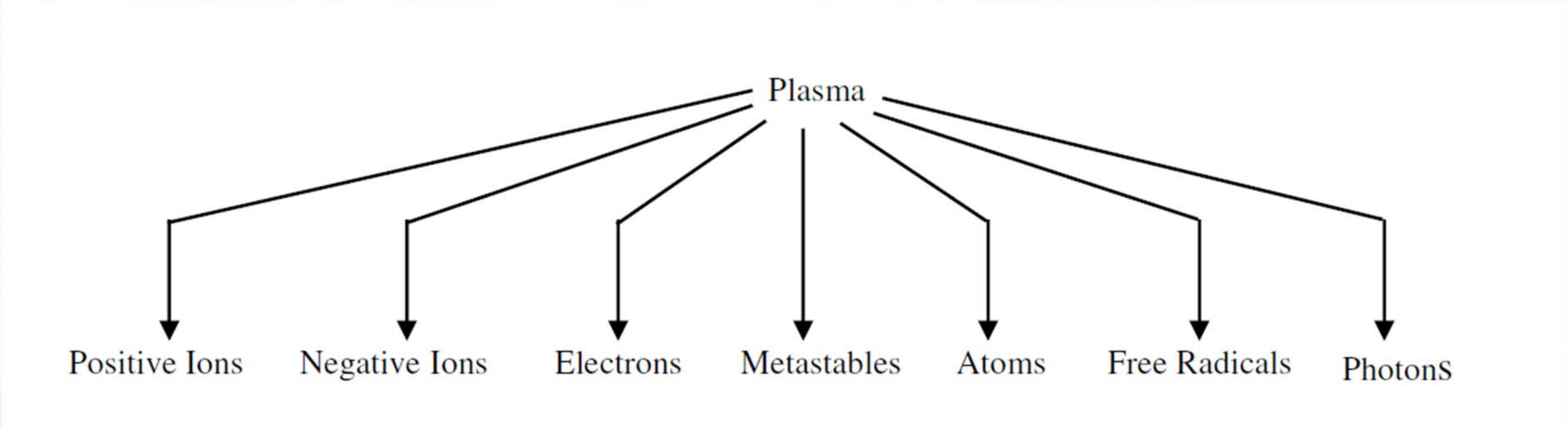
Outline

- ✓ **Plasma physics**
- ✓ **Plasma sources**
- ✓ **Plasma application in Food Processing**

Plasma physics

- Plasma, a quasi-neutral gas, is considered to be the fourth state of matter, following the more familiar states of solid, liquid & gas and constitutes more than 99% matter of the universe.

- It is more or less an electrified gas with a chemically reactive media that consists of a large number of different species such as electrons, positive and negative ions, free radicals, gas atoms and molecules in the ground or any higher state of any form of excited species

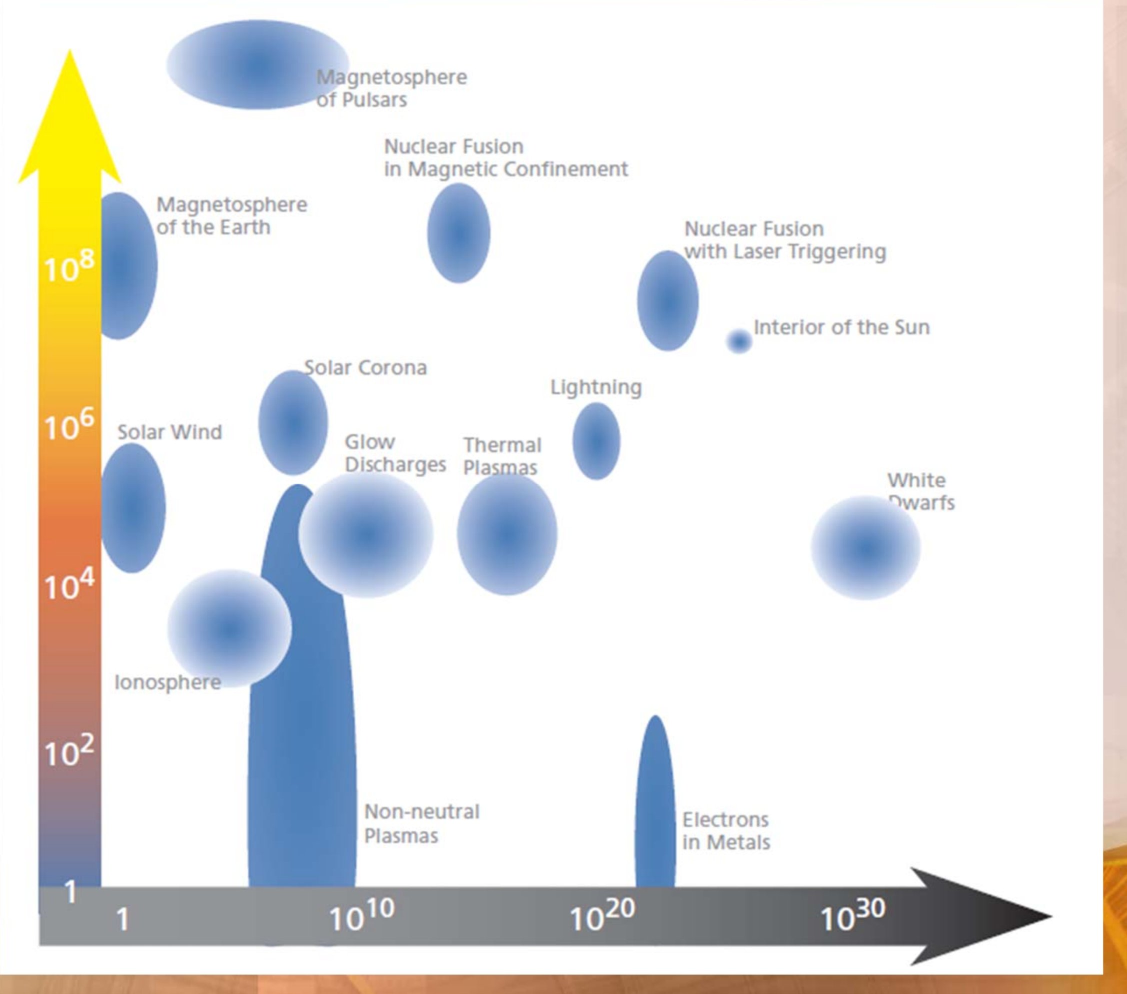


Plasma physics

- It can exist over an extremely wide range of temperature and pressure.
- It can be produced at low-pressure or atmospheric pressure by coupling energy to a gaseous medium by several means such as mechanical, thermal, chemical, radiant, nuclear, or by applying a voltage, or by injecting electromagnetic waves and also by a combination of these to dissociate the gaseous component molecules into a collection of ions, electrons, charge-neutral gas molecules, and other species.
- The name was provided by the New York chemist Irving Langmuir (1881–1957).
- In 1923 Langmuir observed, in an ionized gas, characteristic oscillations that depended on the electron density and mass. These collective oscillations in a system of many charged particles he called ‘plasma oscillations.‘

Plasma physics

✓ **It can exist over an extremely wide range of temperature and pressure.**



Plasma physics

- ✓ Broadly speaking, plasmas can be distinguished into two main groups i.e., the high temperature or fusion plasmas and the so called low temperatures or gas discharges(LTE).
- ✓ A typical classification and parameters of different kinds of plasmas is given in the following table.

Plasma	State	Example
High temperature plasma (Equilibrium plasma)	$T_e \approx T_i \approx T_g, T_p = 10^6 - 10^8 K$ $n_e \geq 10^{20} m^{-3}$	Laser fusion plasma
Low temperature plasma		
Thermal plasma (Quasi-equilibrium plasma)	$T_e \approx T_i \approx T_g \leq 2\times10^4 K$ $n_e \geq 10^{20} m^{-3}$	Arc plasma, plasma torches, RF inductively coupled discharges
Non thermal plasma (Non-equilibrium plasma)	$T_e >> T_i \approx T_g = 300.........10^3 K$ $n_e \approx 10^{10} m^{-3}$	Glow, corona, APPJ, DBD, MHCD, OAUGDP, plasma needle etc

Plasma physics

- ✓ **High temperature plasma implies that all species (electrons, ions and neutral species) are in a thermal equilibrium state.**

- ✓ **Low temperature plasma is further subdivided into thermal plasma, also called quasi-equilibrium plasma, which is in a local thermal equilibrium (LTE) state, and non thermal plasma (NTP), also called non-equilibrium plasma or cold plasma.**

Plasma physics

- ✓ High temperature of TPs can process even the most recalcitrant wastes including municipal solids, toxic, medical, biohazard, industrial and nuclear waste into elemental form, ultimately reducing environmental pollution caused due to them.

- ✓ But for several technological applications, the high temperature characteristic of TPs is neither required nor desired, and in some cases it even becomes prohibitive. In such application areas, cold plasmas become more suited.

Plasma physics

- ✓ **Cold plasmas refer to the plasmas where most of the coupled electrical energy is primarily channeled to the electron component of the plasma, thereby producing energetic electrons instead of heating the entire gas stream; while the plasma ions and neutral components remain at or near room temperature.**

- ✓ **Because the ions and the neutrals remain relatively cold, this characteristic provides the possibility of using cold plasmas for low temperature plasma chemistry and for the treatment of heat sensitive materials including polymers and biological tissues.**

- ✓ **The remarkable characteristic features of cold plasma that include a strong thermodynamic non- equilibrium nature, low gas temperature, presence of reactive chemical species and high selectivity offer a tremendous potential to utilize these cold plasma sources in a wide range of applications.**

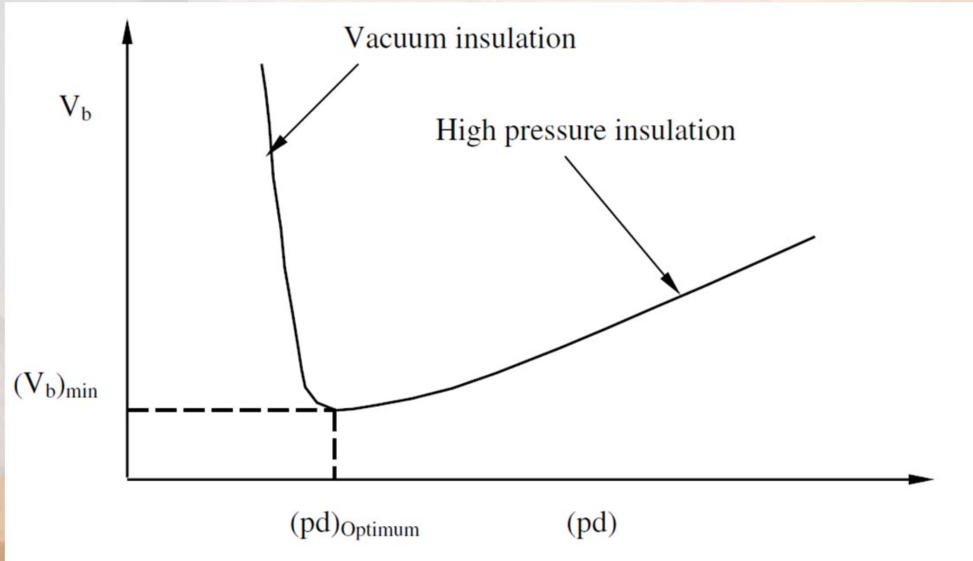
Plasma physics

- ✓ Gas phase reactions involving electrons and heavy species

Name	Reactions	Description
Etching	$AB + C_{solid} \rightarrow A + BC_{vapour}$	Material erosion.
Adsorption	$M_g + S \rightarrow M_s$ $R_g + S \rightarrow R_s$	Molecules or radicals from a plasma come in contact with a surface exposed to the plasma and are adsorbed on surfaces.
Deposition	$AB \rightarrow A + B_{solid}$	Thin film formation.
Recombination	$S - A + A \rightarrow S + A_2$ $S - R + R_1 \rightarrow S + M$	Atoms or radicals from the plasma can react with the species already adsorbed on the surface to combine and form a compound.
Metastable de-excitation	$S + A^* \rightarrow A$	Excited species on collision with a solid surface return to the ground state.
Sputtering	$S - B + A^+ \rightarrow S^+ + B + A$	Positive ions accelerated from the plasma towards the surface with sufficient energy can remove an atom from the surface.
Polymerization	$R_g + R_s \rightarrow P_s$ $M_g + R_s \rightarrow P_s'$	Radicals in the plasma can react with radicals adsorbed on the surface and form polymers.

Plasma physics

- To sustain plasma, the applied voltage must exceed the breakdown voltage for the gases. When this voltage is reached, the gases lose their dielectric properties and turn into a conductor.
- Paschen's Law, named after Friedrich Paschen, was first stated in 1889.
- He studied the breakdown voltage of gas between parallel plates as a function of pressure and gap distance. The voltage necessary to arc across the gap decreased up to a point as the pressure was reduced. It then increased, gradually exceeding its original value



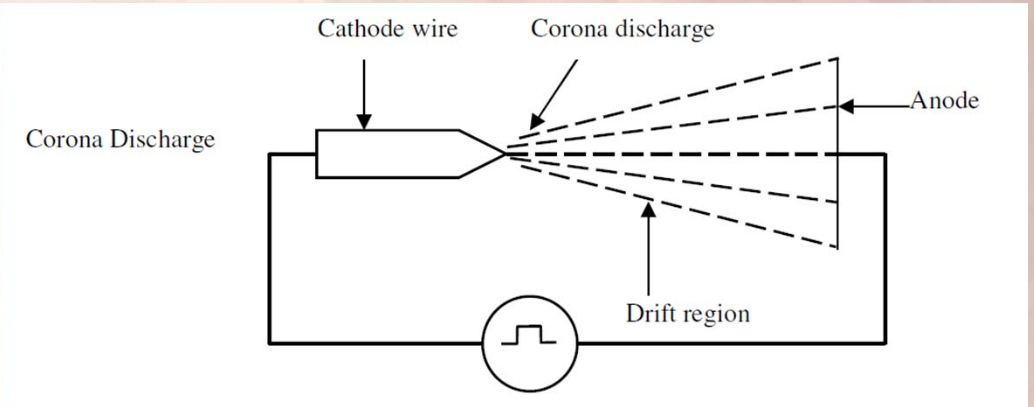
Plasma physics

✓ **Technologies to produce Atmospheric Non Thermal Plasmas (ANTP)**

Parameters	Corona Discharge	DBD	APPJ	Atmospheric glow MHCD
Method and Type	Sharply pointed electrode	Dielectric barrier cover on electrodes	RF capacitvely coupled	DC glow with micro hollow cathode electrode
Excitation	Pulsed DC	AC or RF	RF 13.5 MHz	DC
Pressure (bar)	1bar	1bar	760 torr	1bar
Electron energies (eV)	5 variable	1-10	1-2	....
Electron Density, cm^{-3}	10^{9}-10^{13} variable	$\approx 10^{12}$ -10^{15}	10^{11}-10^{12}	
Breakdown Voltage (kV)	10-50	5-25	0.05-0.2	....
Scalability & Flexibility	No	Yes	Yes	Yes
T_{max} Temp T (K)	Room	Average gas Temp (300)	400	2000
Gas	....	N_2+ O_2+ NO+ Rare gas/Rare gas halides	Helium, Argon	Rare gas Rare gas/Rare gas halides

Plasma physics

✓ **Corona Discharge**



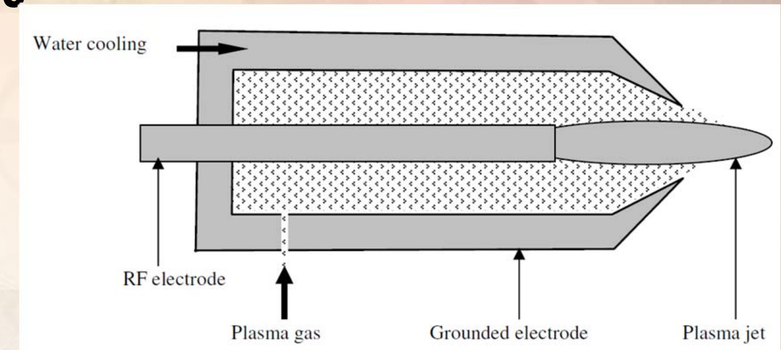
✓ **This type of discharge is the characteristic of an asymmetric electrode pair and results from the electric field that surrounds inhomogeneous electrode arrangements powered with a continuous or pulsed dc voltage.**

✓ **In a highly non-uniform electric field, as for example, point plane gap or wire cylindrical gap, the high electric field near the point electrode or wire electrode far exceeds the breakdown strength of the gas and a weakly ionized plasma is created.**

✓ **Coronas are thus inherently non-uniform discharges that develop in the high field region near the sharp electrode spreading out towards the planar electrode.**

Plasma physics

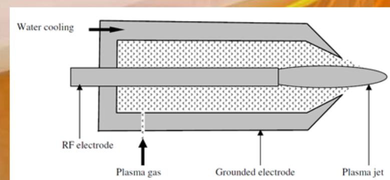
- Atmospheric-pressure plasma jet APPJ



- The APPJ consists of two concentric electrodes through which a mixture of helium, oxygen or other gases flows.
- In this arrangement, the inner electrode is coupled to 13.56 MHz radio frequency power at a voltage between 100-250 V and the outer electrode is grounded. By applying RF power, the discharge is ignited and operates on a feed stock gas, which flows between an outer grounded, cylindrical electrode and a central electrode and produces a high velocity effluent stream of highly reactive chemical species. Central electrodes driven by radio frequency power accelerate free electrons.
- These energetic electrons undergo inelastic collisions with the feed gas, producing excited state molecules, atoms, free radicals and additional ion-electron pairs.

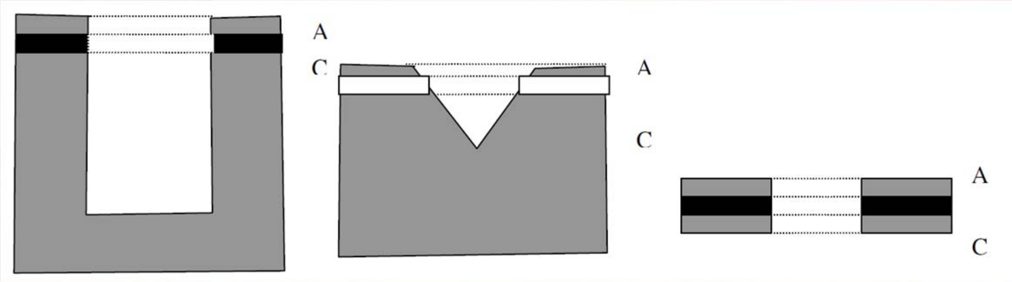
Plasma physics

- ✓ **Atmospheric-pressure plasma jet APPJ produces a stable, homogenous and uniform discharge at atmospheric pressure.**
- ✓ **Operates at radio frequency (RF) power of 250 W and frequency of 13.56 MHz.**
- ✓ **The ionized gas from the plasma jet exits through the nozzle where it is directed onto the substrate and hence utilized in downstream processing.**
- ✓ **It operates without a dielectric cover over the electrode, yet is free from filaments, streamers and arcing;**
- ✓ **The gas temperature of the discharge is as low as 50°C, allowing it to treat delicate surfaces without damage, or as high as 300°C, allowing it to treat robust surfaces much more aggressively.**



Plasma physics

- ✓ Microhollow cathode discharge.
- ✓ The general idea is that the modification of cathode shapes in linear discharge lead to an increase in the current density by several orders of magnitude as compared to linear discharge.
- ✓ It consists of a cathode, which contains some kind of a hole or a cavity or it may be a hollow cylinder, spherical segment or simply a pair of plane parallel plates, and an arbitrary shaped anode.



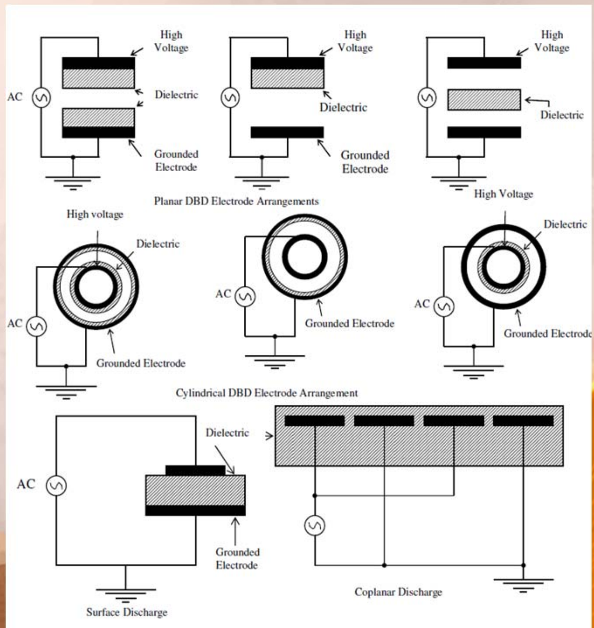
Plasma physics

✓ Dielectric barrier discharge.

✓ Dielectric barrier discharge, also referred to as barrier discharge or silent discharge is a specific type of AC discharge, which provides a strong thermodynamic, non-equilibrium plasma at atmospheric pressure, and at moderate gas temperature.

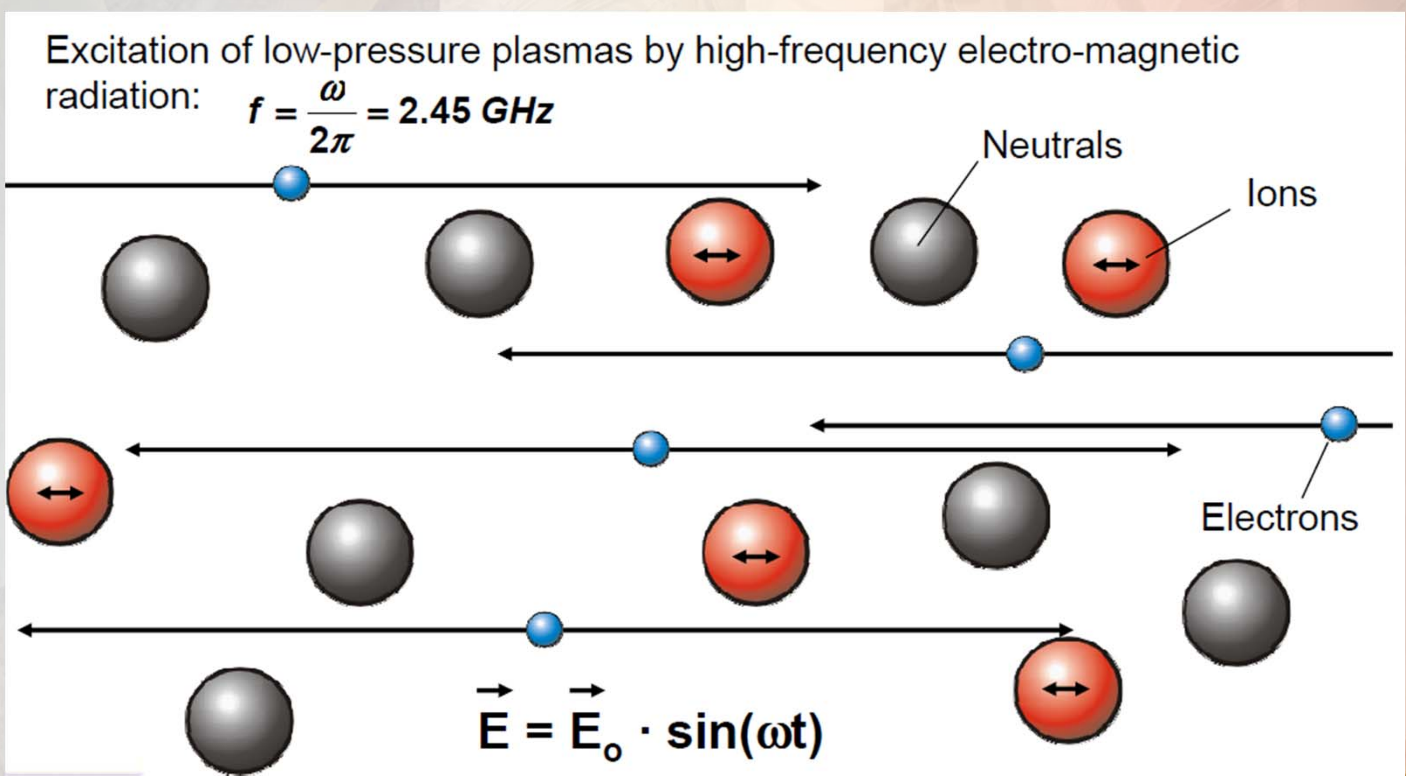
✓ It is produced in an arrangement consisting of two electrodes, at least one of which is covered with a dielectric layer placed in their current path between the metal electrodes.

✓ The presence of one or more insulating layer on/or between the two powered electrodes is one of the easiest ways to form non-equilibrium atmospheric pressure discharge.



Plasma physics

✓ **Microwave Plasma: Excitation by high-frequency electro-magnetic fields and low pressure conditions**



Plasma physics

✓ **Microwave Plasma: Excitation by high-frequency electro-magnetic fields and low pressure conditions**

The high-frequency electro-magnetic field ($f = \frac{\omega}{2\pi} = 2.45\ GHz$)

does not affect neutral atoms and molecules.

is not noticed by the heavy-weight ions due to their inertia.

} immovable background

accelerates the lightweight and easy-to-move free electrons.

Energy is transferred by impact of the accelerated free electrons on the electron sheath of the gas atoms and molecules:

excitation energy < dissociation energy < ionisation energy

Plasma physics

✓ **Microwave Plasma: characteristics**

- low ion energy

  ⇒ low damage and low thermal impact to the surface of the substrate

- high plasma density

  $\left(n_{e,critical} = 7.45 \cdot 10^{10} \frac{1}{cm^3}\right.$ @ 2.45 GHz)

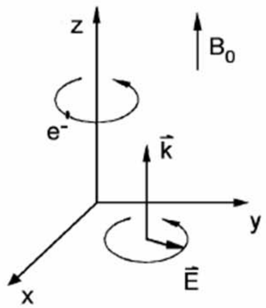
  ⇒ high plasma deposition rates

- scale-up?

  ⇒ easy scale-up feasible!

Plasma physics

✓ **Microwave Electron Cyclotron Resonance (ECR) Plasma: characteristics**

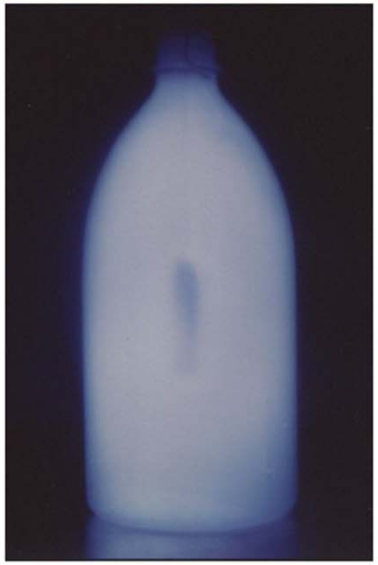


circular movement of free electrons

in the presence of a static and uniform magnetic field

due to Lorentz force

⇒ generation of a local intense, but non-thermal plasma



ECR condition: $\omega_{ce} = \frac{e \cdot B}{m_e}$

ω_{ce}: electron cyclotron frequency
e: elementary charge
B: magnetic field strength
m_e: mass of an electron

resonant magnetic field strength for $\omega/(2\cdot\pi)$ **= 2.45 GHz** is B **= 0.0875 T**

Applications to Food Processing

Common properties required for (polymer) food packaging

- **easy printability**
- **anti-mist properties**

→ surface activation and functionalization by plasma

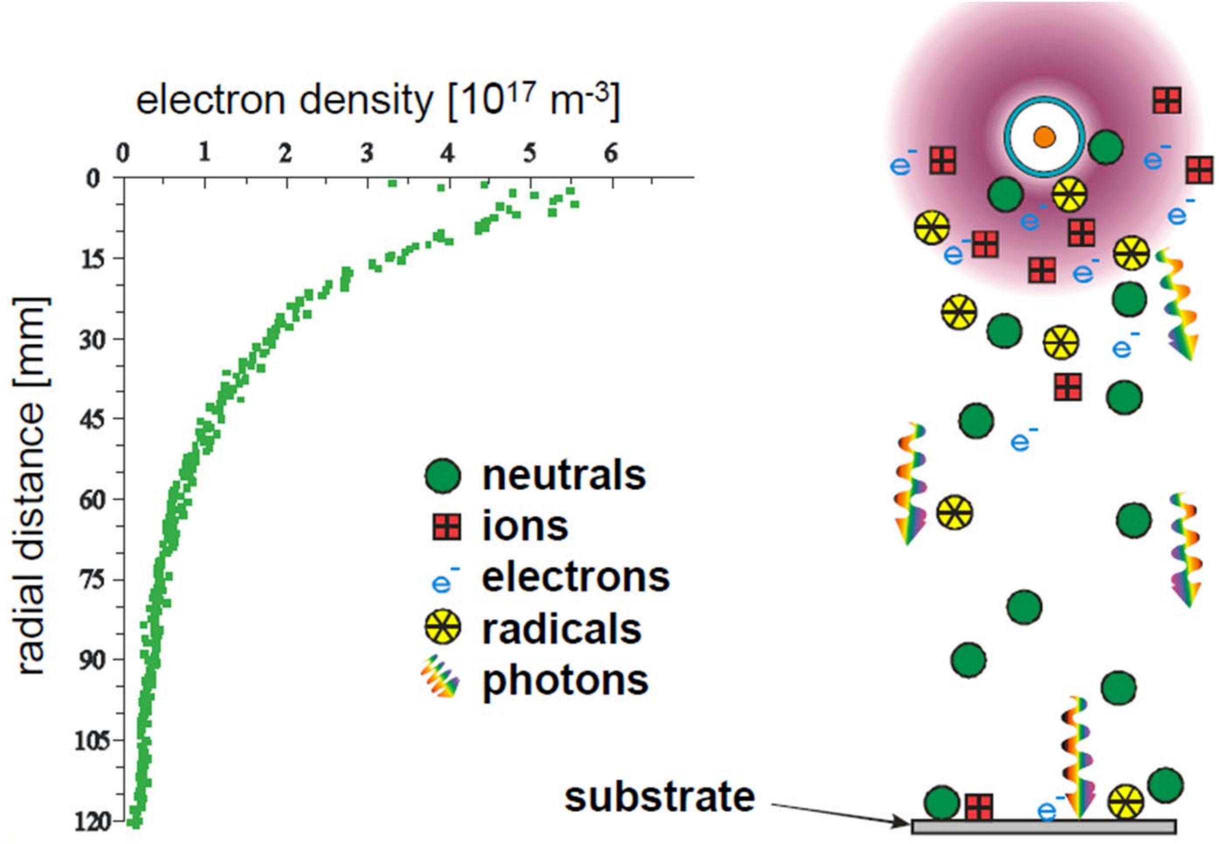
- **(gas) permeation barrier**
- **chemical safety**

→ plasma deposition of barrier coatings

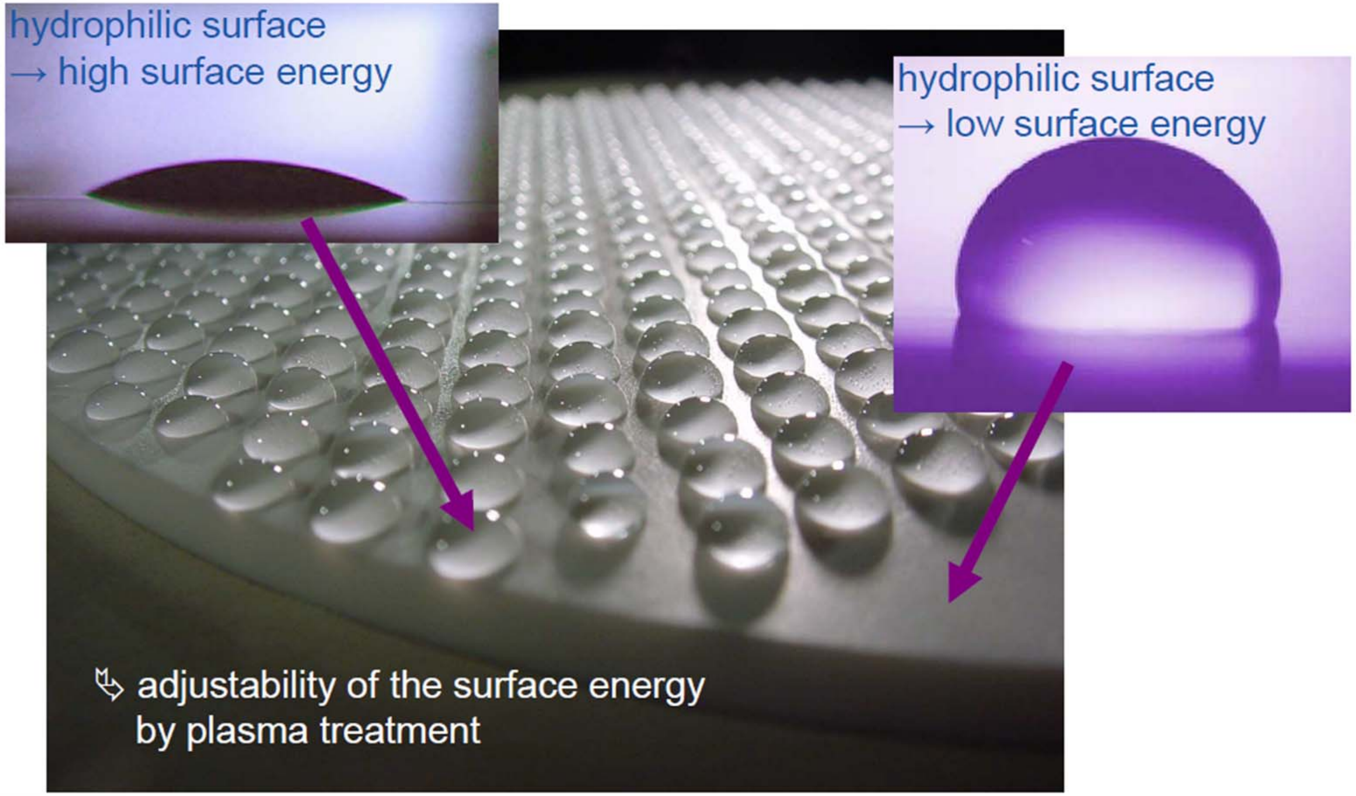
- **microbiological safety**

→ plasma sterilization

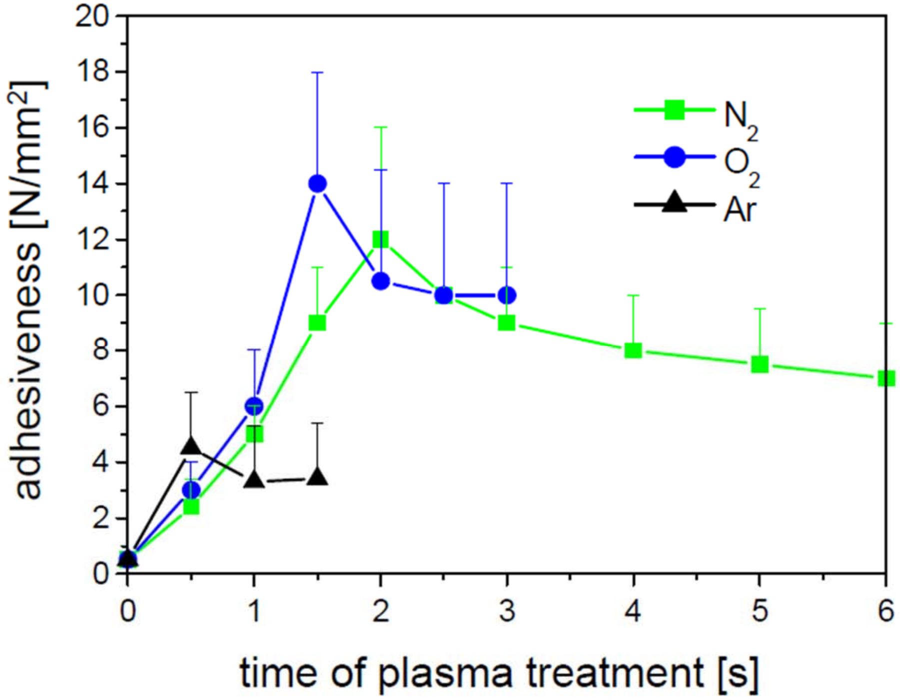
Plasma substrate interaction



Surface activation and functionalisation:surface activation of Teflon



Surface activation and functionalisation: surface activation of Teflon by different working gases



plasma treatment solely on surfaces where adhesion improvement is required, properties of untreated surfaces remain unchanged

Surface activation and functionalisation: surface activation of Teflon by different working gases

hydrophobic surface — plasma treatment of the surface

→ surface energy increased

from 35 mN/m — to 65-70 mN/m

⟹ significantly improved wettability of the surface

Improved surface wettability is necessary for the use of ecologically beneficial water based paints

Plasma Treatment

↓

adjustable surface energy

→ tunable adhesiveness
→ tunable hydrophobicity/hydrophilicity

⇒ creation of anti-mist surfaces
⇒ use of water-based paint and ink possible
⇒ positive environmental impact

Surface coating

Plasma Treatment

required properties

- ✓ (gas) permeation barrier
- ✓ chemical safety

Surface coating

Advantages of homopolymeric single layer materials compared to multi-layer polymer packaging materials:

- less material required → less weight
- lower-cost
- improved recyclability

Disadvantage of homopolymeric layer materials materials compared to multi-layer polymer packaging materials:
minor barrier properties

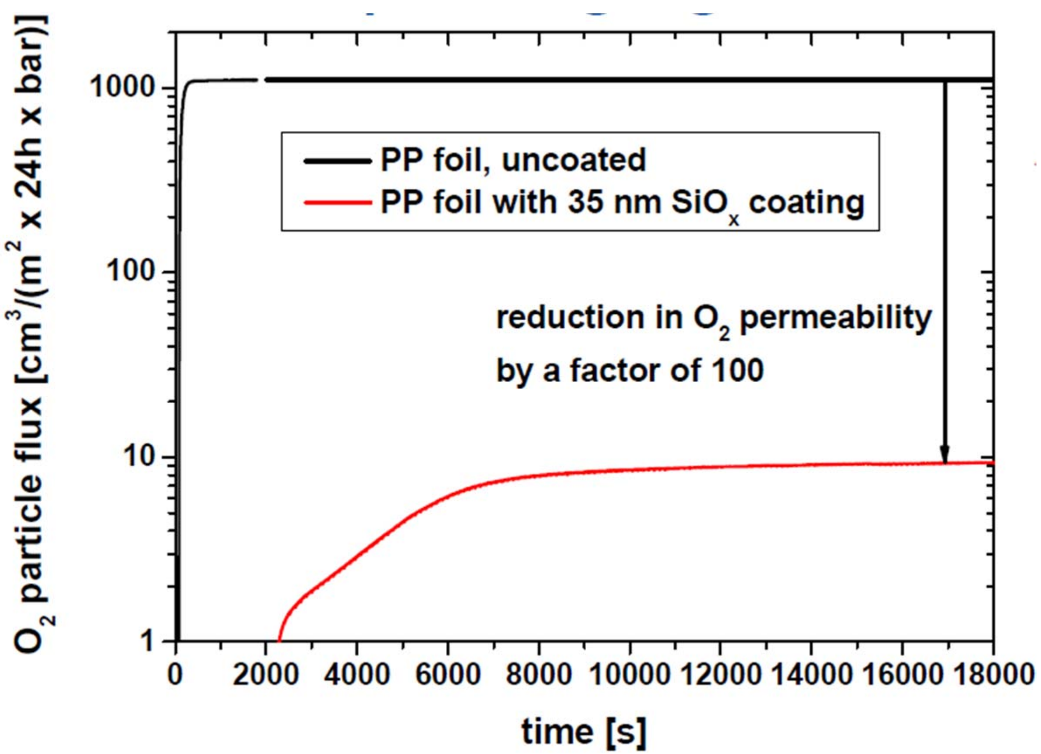
↓

compensation of this drawback by plasma surface coating

Surface coating

Additional requirements met by the SiOx barrier coating:

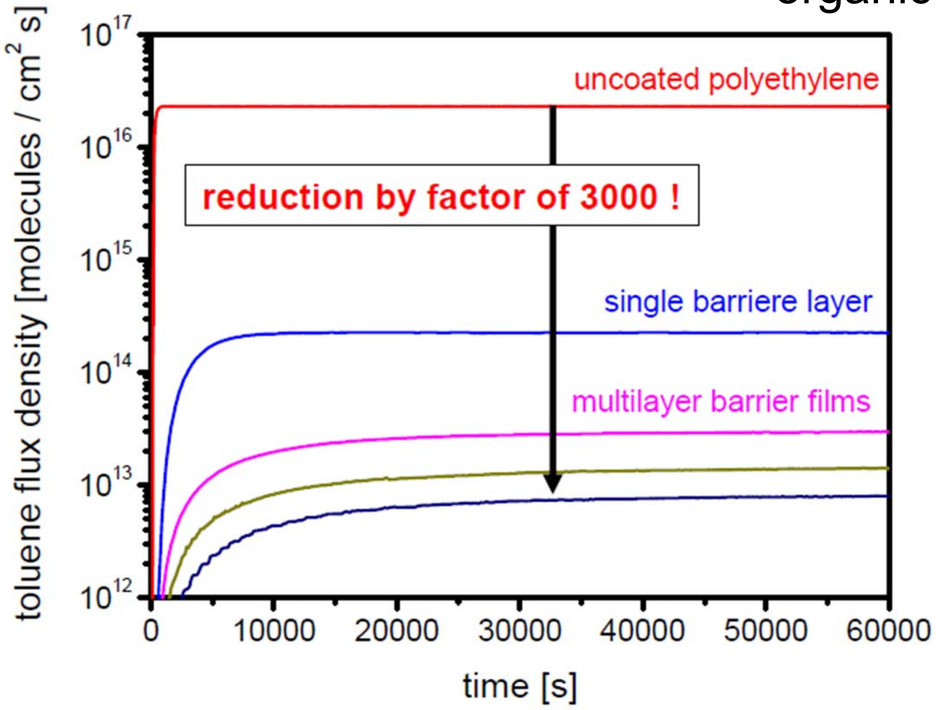
- ✓ flexibility
- ✓ transparency
- ✓ good adhesion to the surface of the polymer



Best performing SiOx barrier layers obtained for O2:HMDSO (**Hexamethyldisiloxane)** mixture ratios between 20:1 and 25:1 by use of the plasma source

Barrier films on polyethylene (PE)

CH/CF (carbon fluoride free radicals , CF_4) -layers deposited on PE as barrier against organic solvents



to prevent:

• rediffusion of (organic) solvents (e.g. residues of cleaning agents)

• diffusion of plasticisers from the polymer packaging into the beverage or foodstuff (particularly important for recycled polymer material)

Surface coating

↓

Plasma deposition of barrier coatings provides:

- **significant reduction of gas (oxygen, carbon dioxide, water vapour, …) permeability**

- **good adhesion of those barrier coatings to the surface of the polymer packaging material**

- **transparency**

- **flexibility**

Advantages of homopolymeric single layer materials:

- **less material required → less weight**
- **lower-cost and**
- **improved recyclability, can be maintained**

Sterilisation

required property:

- **MICROBIOLOGICAL SAFETY**

Sterilisation

Experimental test :4 different test spores were used:

1. **Aspergillus niger**
2. **Bacillus subtilis**
3. **Bacillus stearothermophilus**
4. **Saccharomyces cerevisiae**

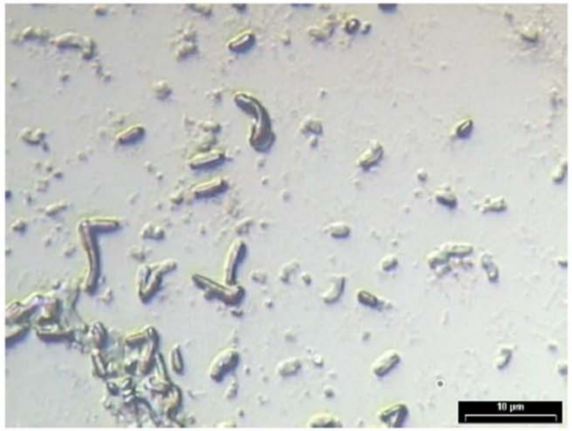
• typical substrate size and material:
10 x 10 cm² PET-foil 190µm

5 x 5 cm² PET-foil 190µm

• homogeneous contamination of the test samples:
homogeneous distribution of 10^6 spores by use of a spraying technique

• counting of the colony forming units CFU after the plasma treatment

Sterilisation: Homogeneous spray contamination



Bacillus Subtilis

Aspergillus Niger

spores are homogeneously sprayed

onto an area of 7x7 cm^2 ↳ **spore density: $2.0 \cdot 10^4/cm^2$**

and an area of 4x4 cm^2 ↳ **spore density: $6.4 \cdot 10^4/cm^2$**

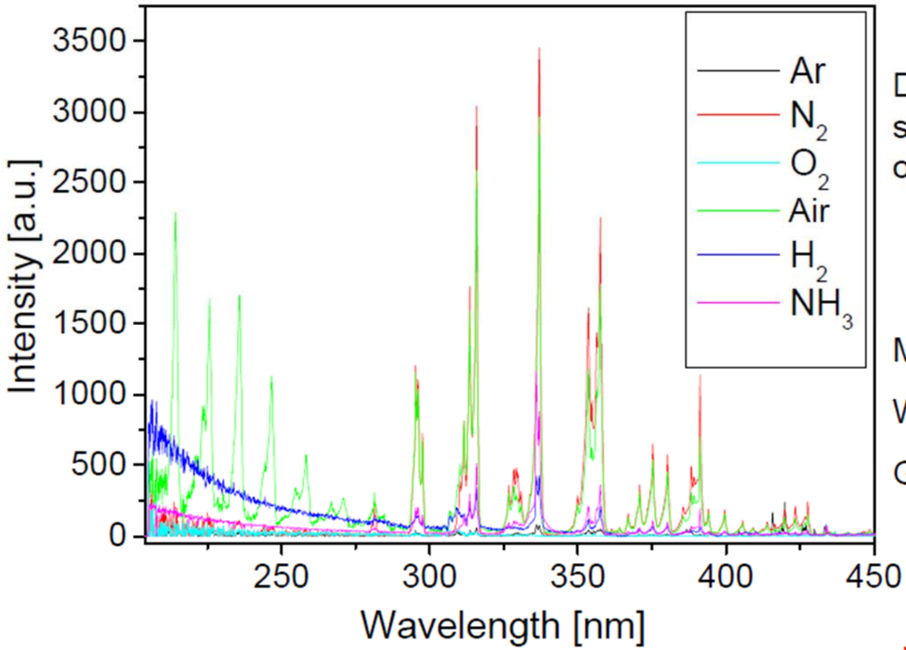
Reduction mechanisms of microwave plasmas

↓

A low-pressure microwave plasma provides several possible mechanisms for the inactivation of spores:

1. Plasma-particles: neutrals, radicals, ions, electrons, ...
2. Electromagnetic radiation from VUV to IR
3. Microwave
4. Vacuum
5. Heat

Plasma light emission spectra



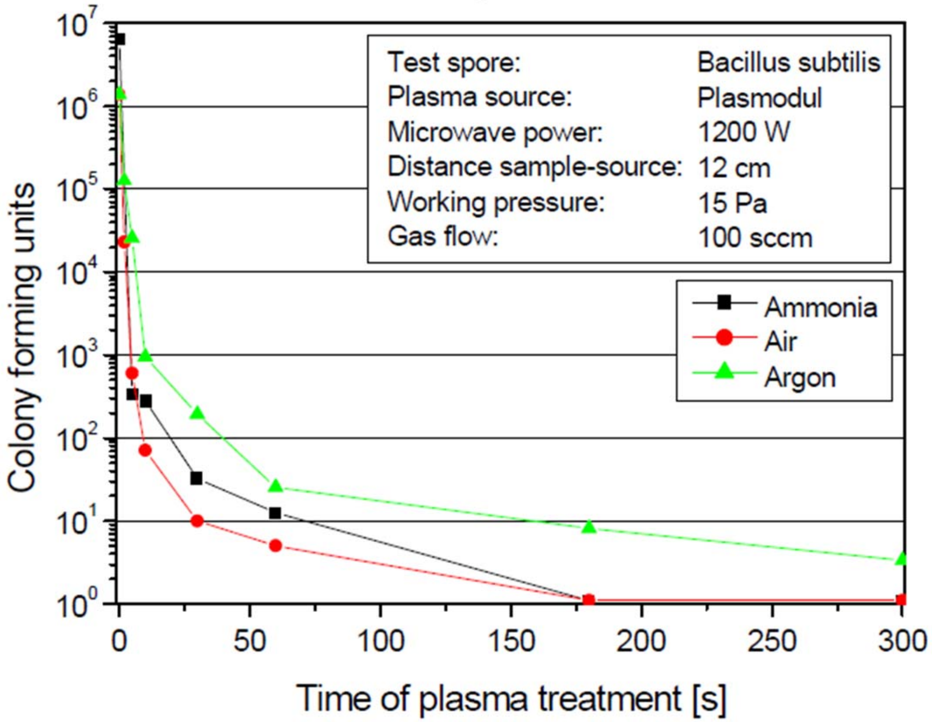
Distance between plasma source (Plasmodul®) and optical fibre:

- 30 cm for NH_3
- 10 cm for all other working gases

Microwave power:	1200 W
Working pressure:	15 Pa
Gas flow:	100 sccm

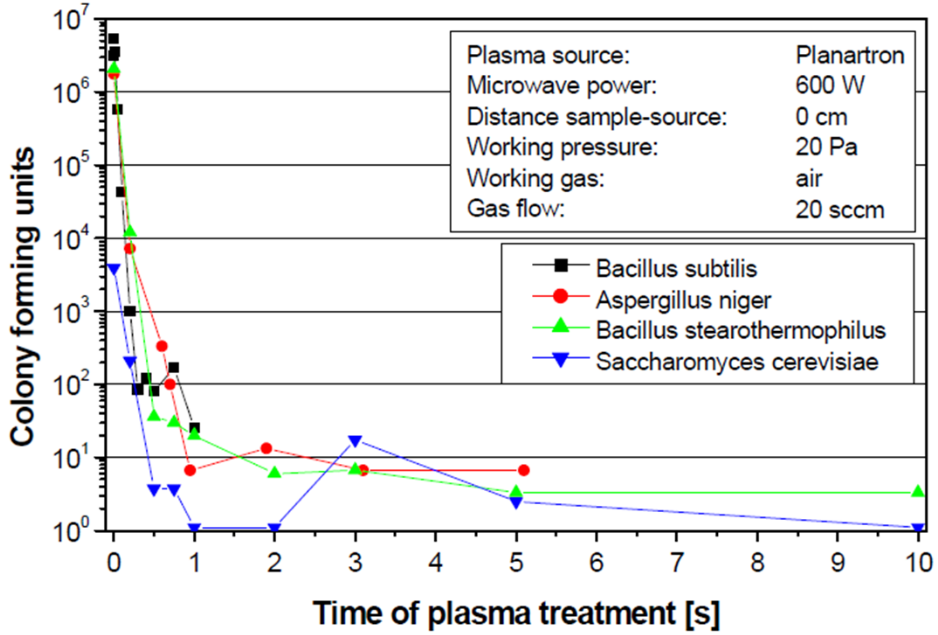
→ Air and H_2 plasmas produce most UV.

Sterilisation effect of various working gases



Plasmas producing much UV light show the best sterilisation effect

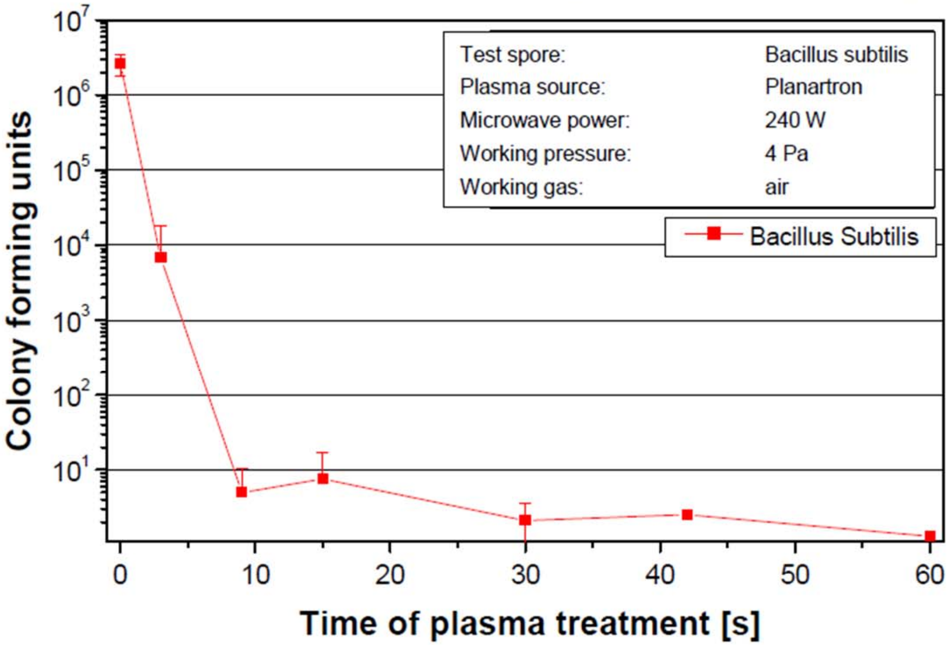
Sterilisation effect of various working gases



Synergy of the inactivation effects of UV light and radicals produced by the plasma leads to short and efficient plasma sterilisation results.

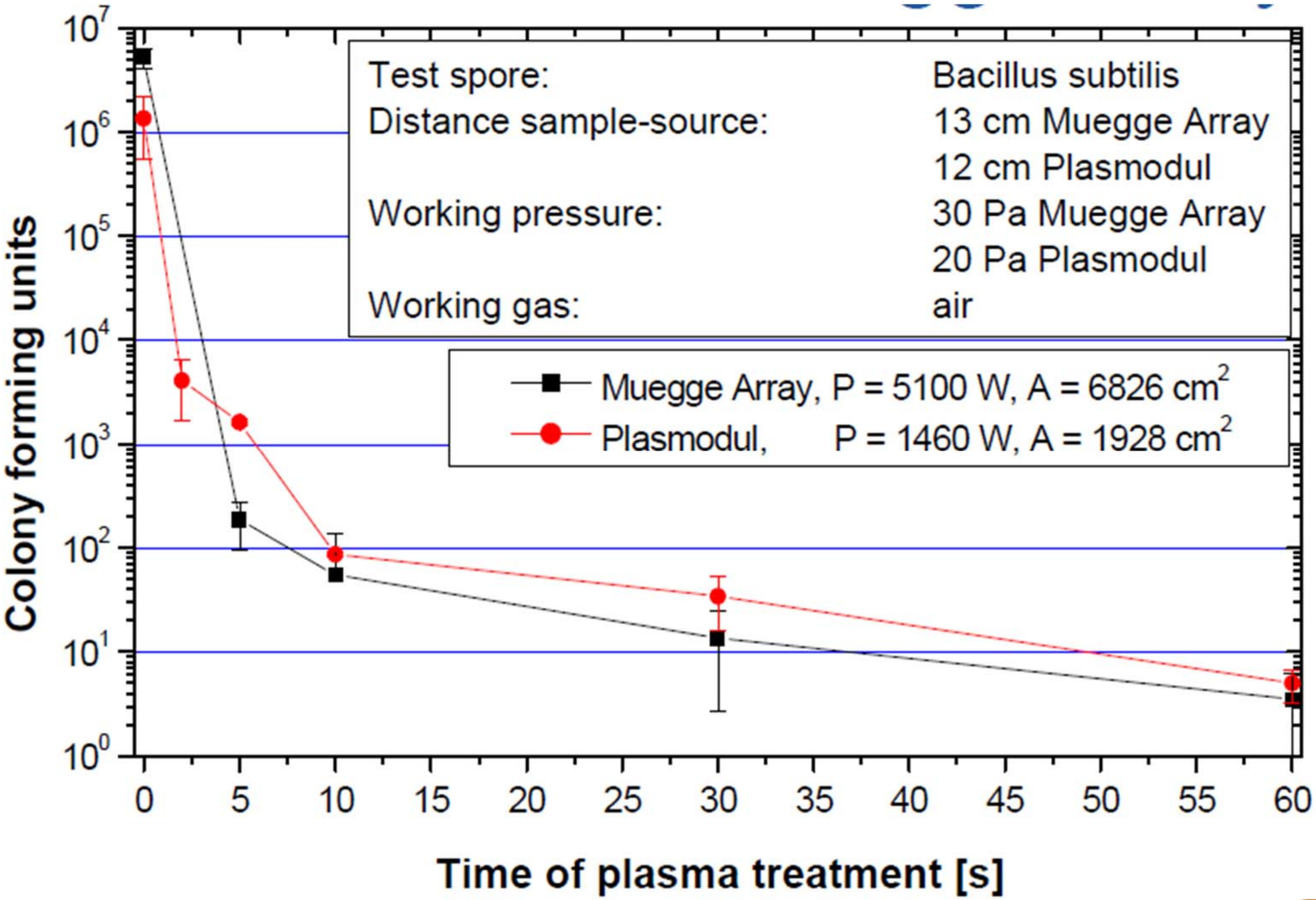
spore reduction of **4-5 orders of magnitude in < 1 s**

Plasma sterilisation of hollow bodies using an ECR plasma



Inactivation of the test spores by **6 orders of magnitude within < 10 s.**

Plasma sterilisation scalability



Summary of Plasma sterilisation:

Requirements for efficient sterilisation:

- ✓ short spore inactivation time
- ✓ low thermal loads
- ✓ no dangerous or even toxic agents used
- ✓ no formation of dangerous or even toxic products during sterilisation
- ✓ properties of the food packaging materials kept unchanged or even improved
- ✓ no follow-up treatment necessary

⇒ **sterilisation by plasma meets all requirements**

Final comments:

(Low-pressure microwave) plasma treatment of (polymer) packaging materials provides

- selective and tunable surface energy
  - ✓ for adhesion improvement
  - ✓ for easy printability
  - ✓ for anti-mist properties
- barrier properties by deposition of barrier layers towards
  - ✓ gases (oxygen, carbon dioxide, water vapour, …)
  - ✓ chemical solvents
- efficient inactivation of microbes (spores, germs, …)

at short treatment times.

Thank you for your attention