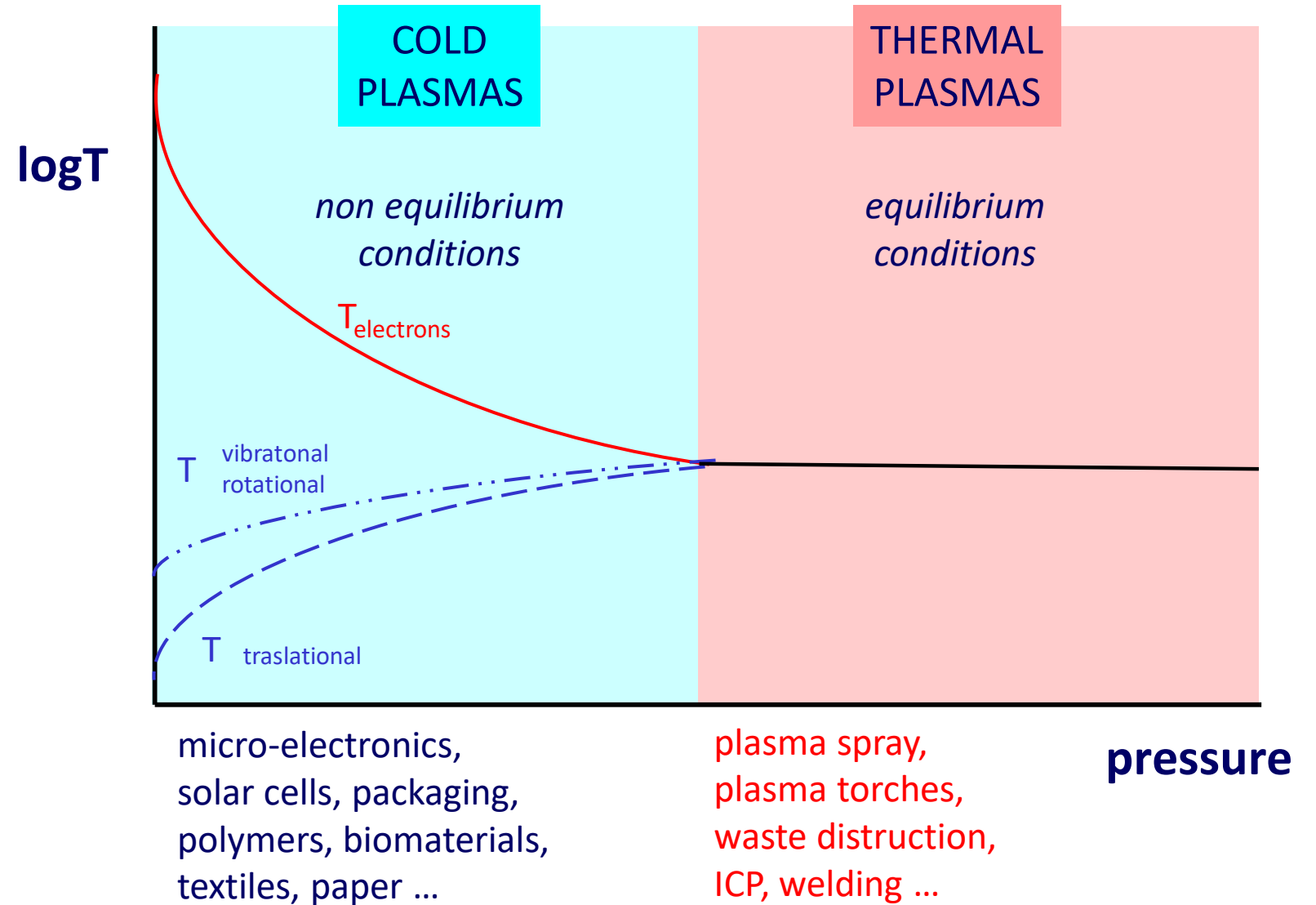
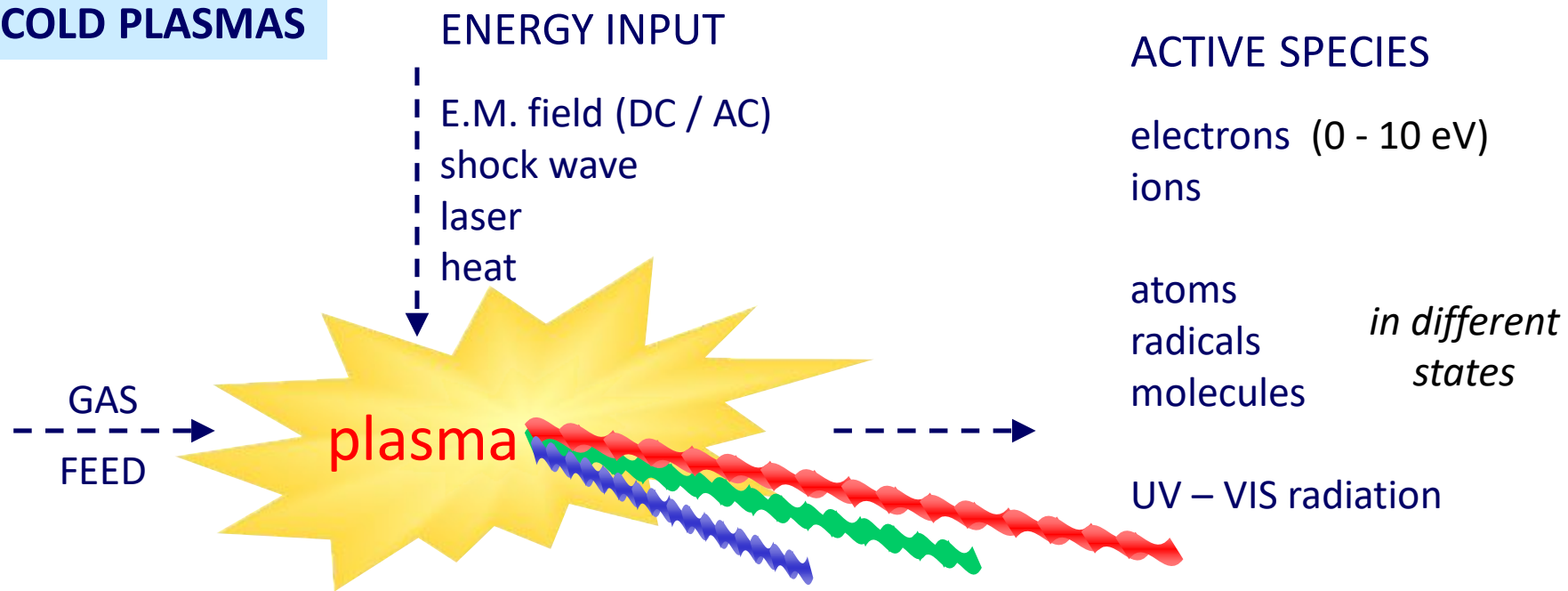


# REACTORS & PROCESSES



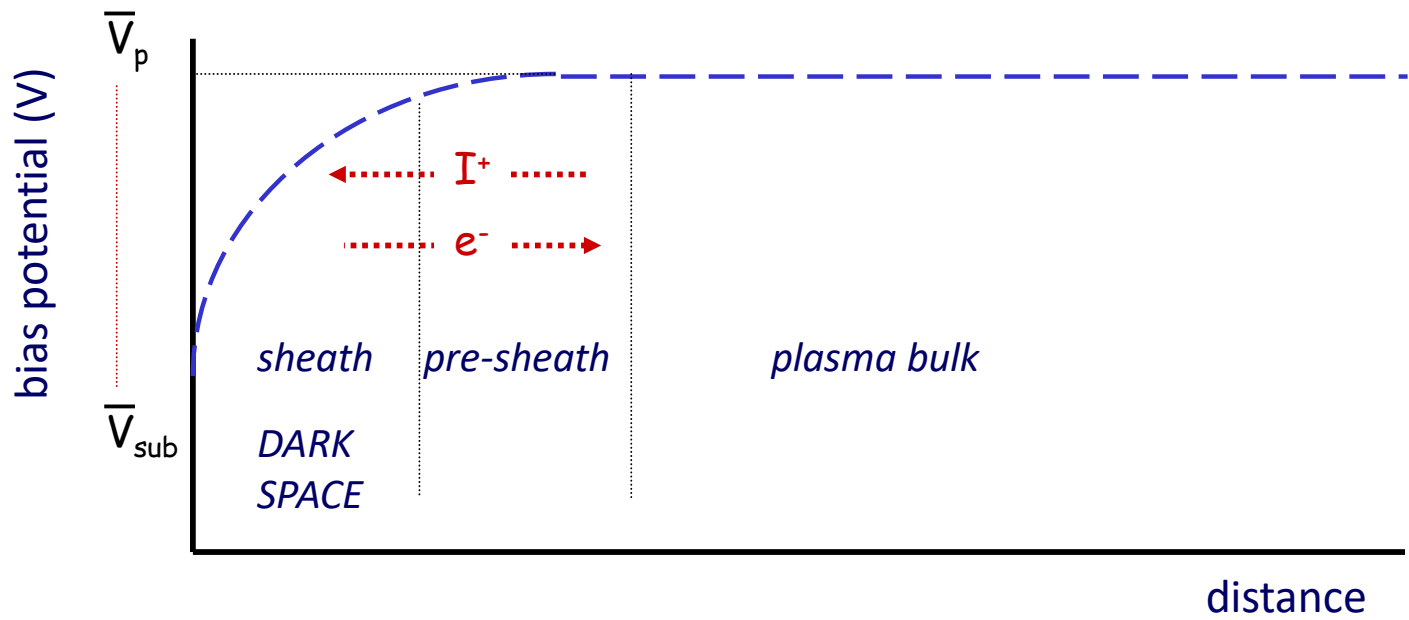
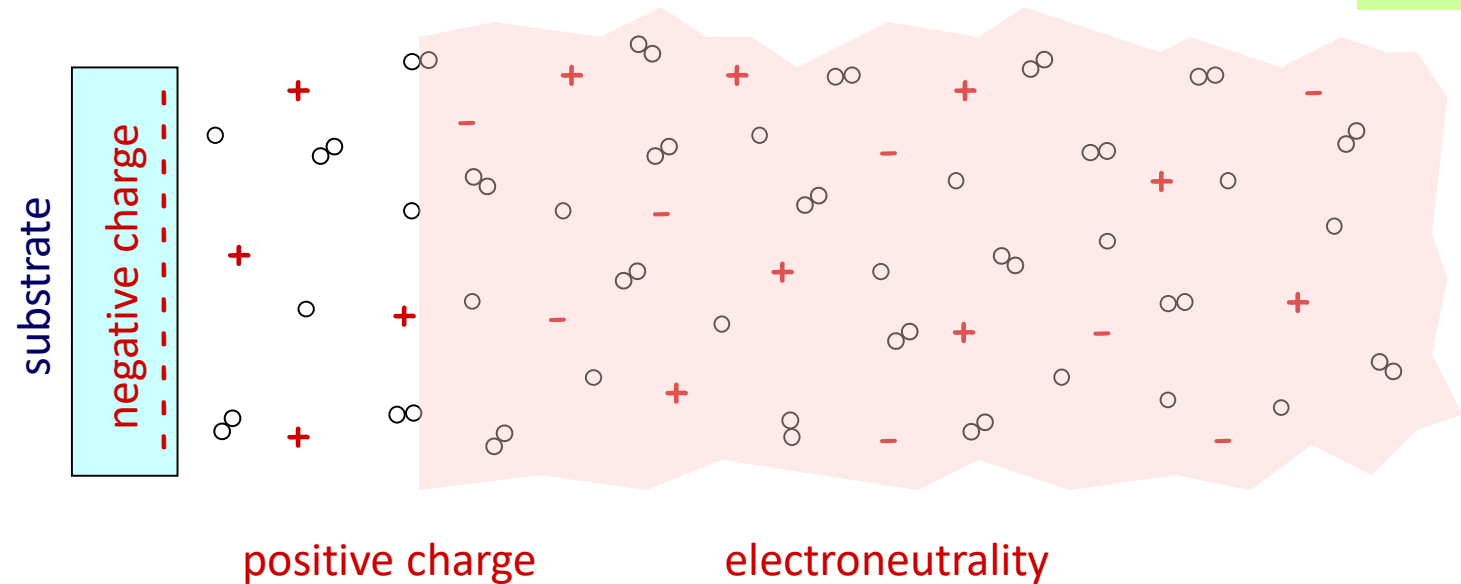
**non eq. conditions can exist also at atmospheric pressure  
e.g., APGD, DBD plasmas**

## COLD PLASMAS



**pressure,  
feed flow rate  
power input, frequency, pulsation,  
residence time,  
substrate temperature, bias, ...**

bias potential



DC plasmas are not suitable for dielectrics, need internal electrodes, are not stable, offer a low plasma density.

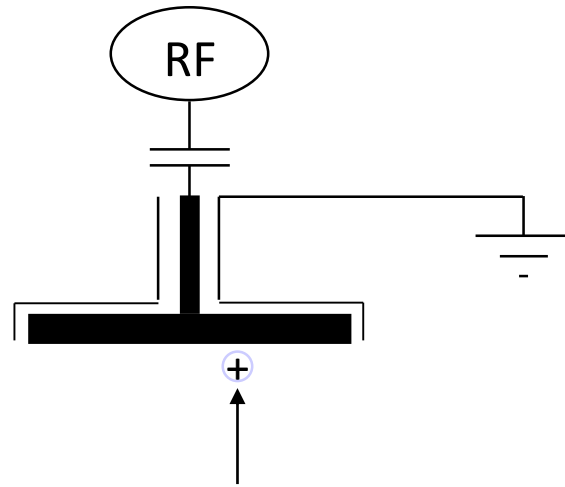
Most plasma sources in LP regimes use radiofrequency (13.56 MHz) or microwaves (2.54 GHz).

Audiofrequency (KHz) plasmas in LP regimes are characterized by an intense ion bombardment of the substrate (radiation damage), quite difficult to control.  
In AP regimes KHz sources are most utilized

LP, Low Pressure  
AP, Atm Pressure



# SPUTTERING

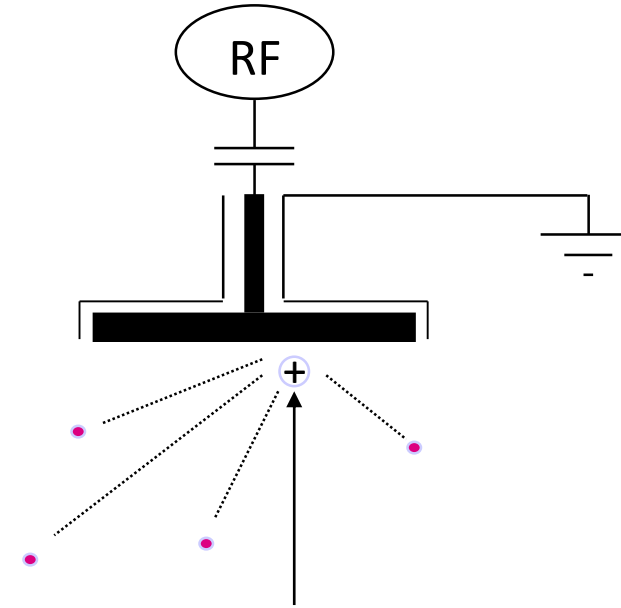


## Low Energy Bombardment

activation of treatments

activation of PE-CVD

no surface damage



## High Energy Bombardment

de-activation of PE-CVD

sputter-etching

surface damage

ejection of material  
from the electrode

contamination

# LOW-PRESSURE PLASMA CHEMISTRY

the arena

## GAS PHASE

(0.01 – 10 Torr)

electroneutrality

$$n_+ = n_- \rightarrow n_{i+} = n_{e-}$$

ideal gas approximation

$$PV = nRT$$

mean free path 10  $\mu\text{m}$  – 1mm

low number of  $e^-$  – neutral  
elastic collisions:

non equilibrium conditions

$$T_e \gg T_{el} > T_{rot}, T_{vib} > T_{trasl}$$

## PLASMA – SURFACE INTERACTIONS

Surfaces develop a negative charge  
respect to the plasma bulk:

electroneutrality does not hold  
near surfaces, and a “sheath” develops

positive ions bombard surfaces

+

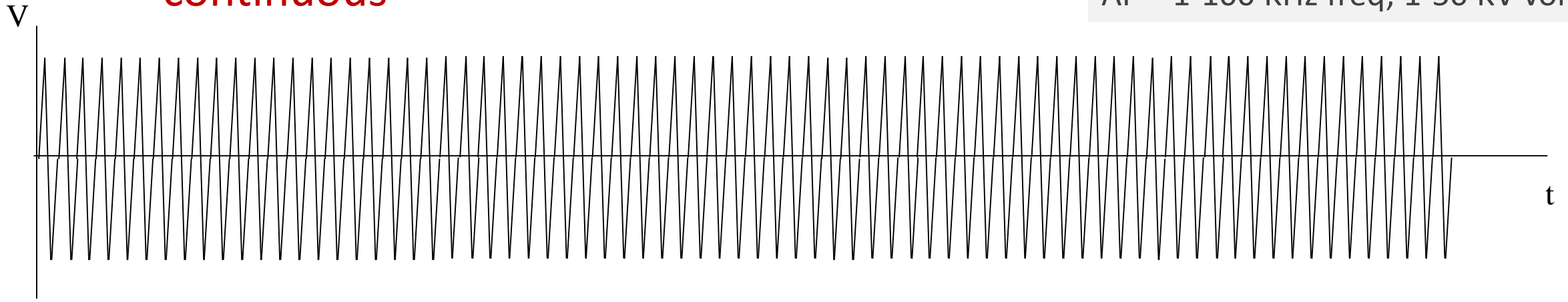
neutrals react with surfaces

Most applications of non equilibrium plasmas requires that the gas remains at room T. Since the low efficiency and number of elastic collisions at low P limit the energy transfer from free electrons to heavier species, it is quite easy to produce cold Low P gas discharges. With increasing pressure, however, the electron-species collision frequency increases, the energy transfer becomes more efficient, resulting in gas heating and plasma instabilities (e.g., sparks and arcs). **Many approaches are used to keep the gas cold in Atmospheric P discharges, namely:**

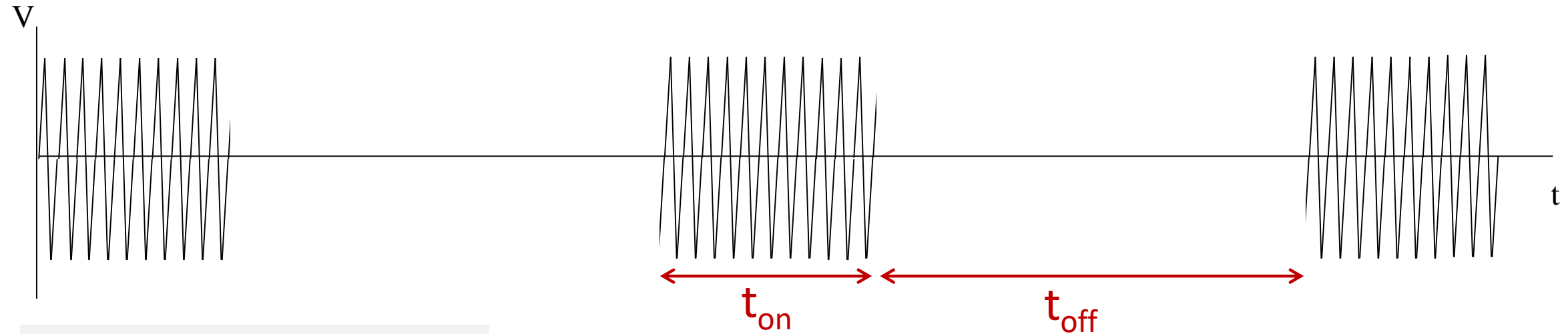
- **sharp electrodes, as in corona discharges;**
- **pulsing the plasma;  $\mu\text{s}$ -ns wide plasma pulses**
- **improved heat transfer;**
- **using gases (e.g., He) with high thermal conductivity;**
- **reduce the size of plasmas (e.g., micro-discharges);**
- **reduce the current with dielectric layers on the electrodes, as in Dielectric Barrier Discharges (DBD)**

continuous

AP 1-100 KHz freq; 1-50 KV volt.



pulsed



lower pulse width ( $\mu\text{m}$ ,  $\text{nm}$ )  
and higher V-rise speed  
are desired to keep the gas cold

milli  
micro  
nanoseconds

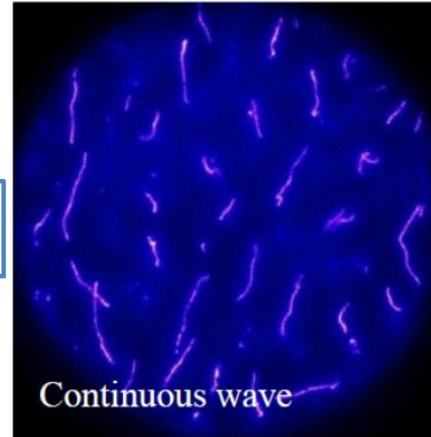


# FE-DBD: Sinusoidal, Micro-pulsed, Nano-pulsed

## Continuous (sinusoidal)

Rise time:  $\sim 1$  V / nsec  
Sinusoidal wave

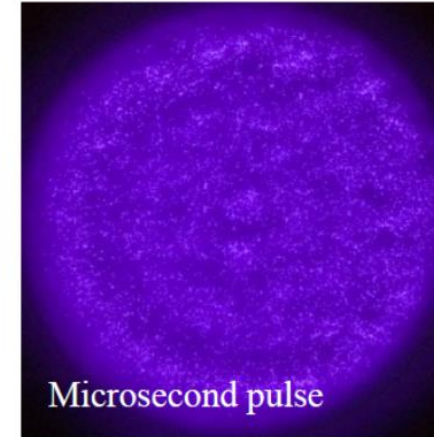
Filament temperature:  
350-450K



## Microsecond-pulsed

Rise time:  $\sim 5$  V / nsec  
Pulse duration:  $\sim 2$   $\mu$ sec

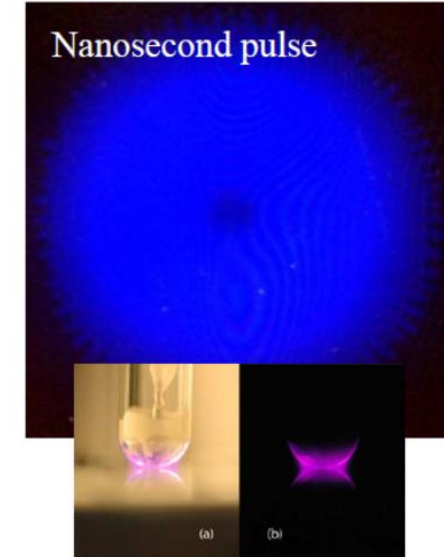
Filament temperature:  
320-420K



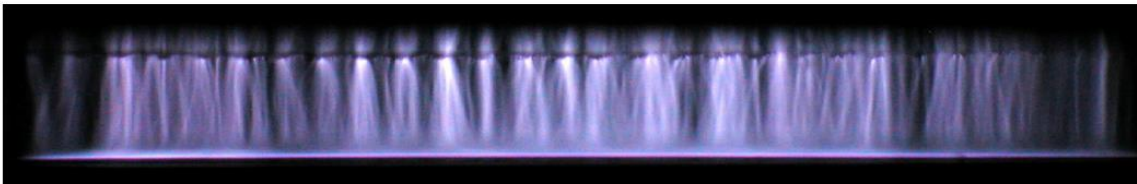
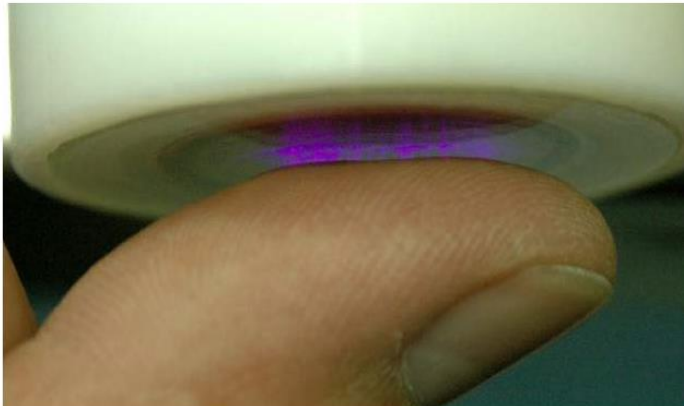
## Nanosecond-pulsed

Rise time:  $\sim 3,000$  V / nsec  
Pulse duration:  $\sim 40$  nsec

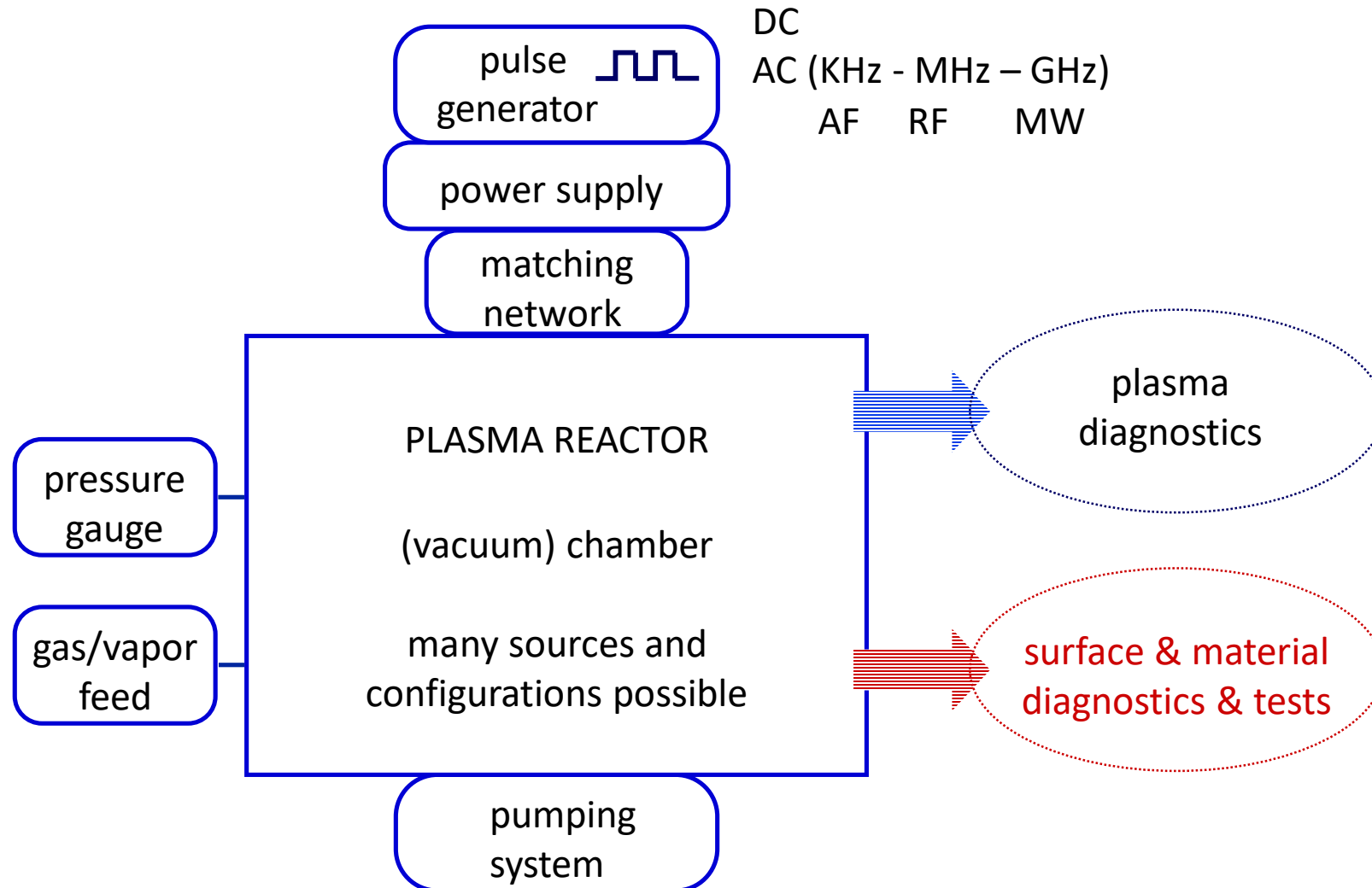
Rotational temperature:  
 $\sim 300$ K



## Microdischarge Interaction and Structuring in Dielectric Barrier Discharges



# PLASMA REACTORS LP/AP



# PLASMA PARAMETERS: external and internal

## “external” PARAMETERS

*imposed from the operator*

Pressure

Feed composition, flow rate, leaks

Field frequency, power density

Reactor configuration, materials,  
electrode geometry

Substrate position

*(e.g. glow vs. afterglow)*

Duty cycle %, *time on, time off*  
in pulsed plasmas

Substrate temperature

Substrate *bias* potential

## “internal” PARAMETERS

*output from diagnostics*

Fragmentation degree of the feed

Density and distribution of neutrals

Distribution energy (EEDF) and  
density ( $n_e$ ) of electrons

Ionization degree

Residence time of the species

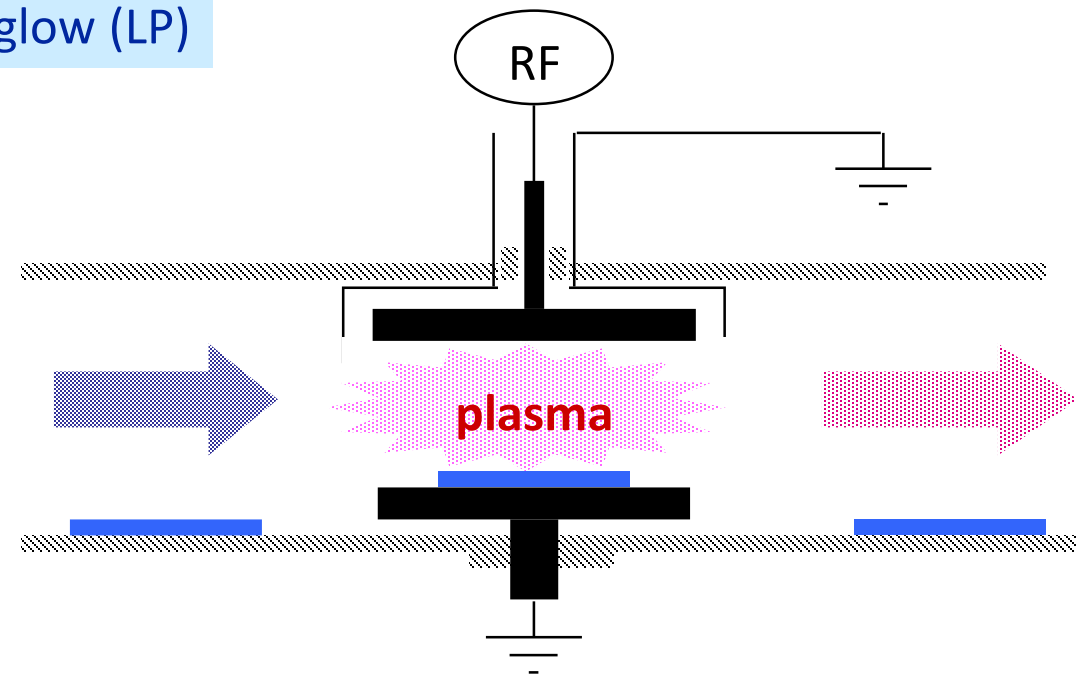
Process homogeneity

Positive-ion bombardment, sputtering

Deposition, etching, treatment rate

Contaminations

**SUBSTRATE POSITION**  
glow vs afterglow (LP)



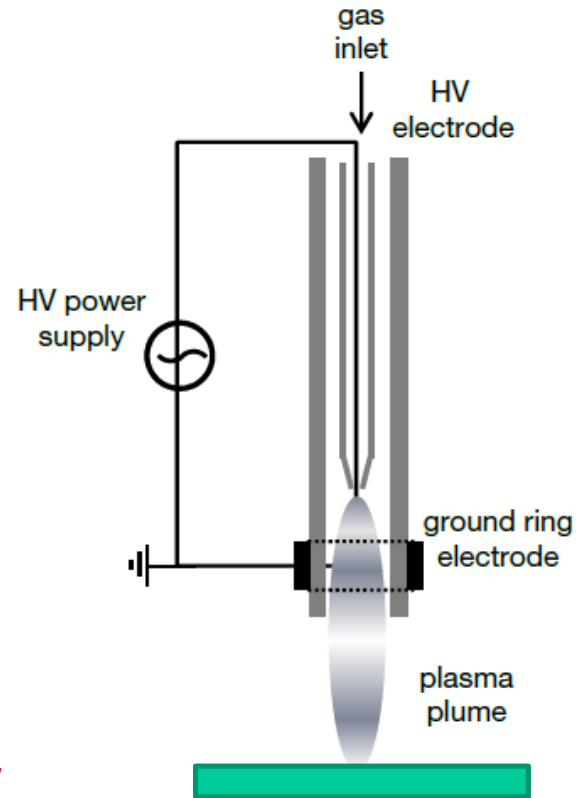
**Preglow**  
no treatment

**Glow**  
active species  
ion bombardment  
crosslinking  
high rates  
fragmentation

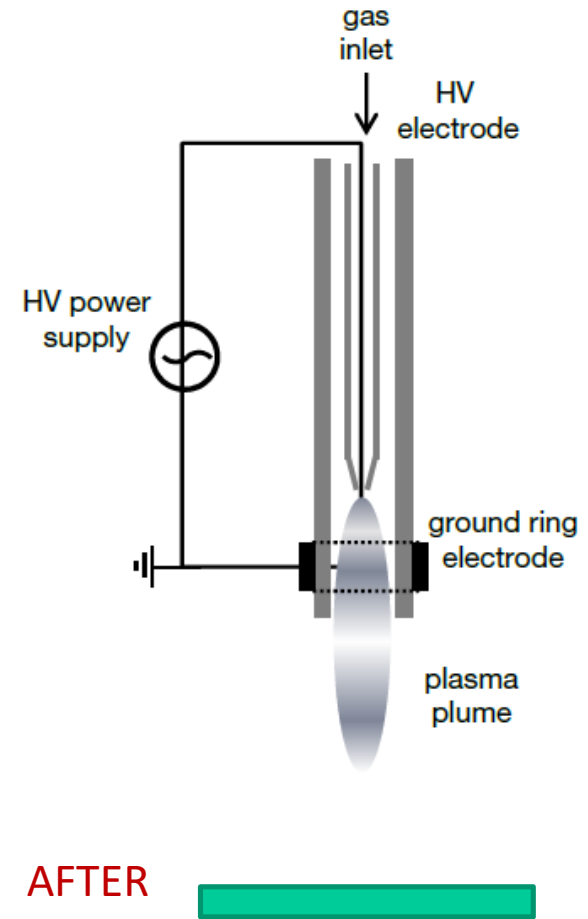
**Afterglow**  
no electrons  
no ions  
no bias  
long living species  
mild treatments  
selectivity  
structure retention

**SUBSTRATE POSITION**  
glow vs afterglow (AP)

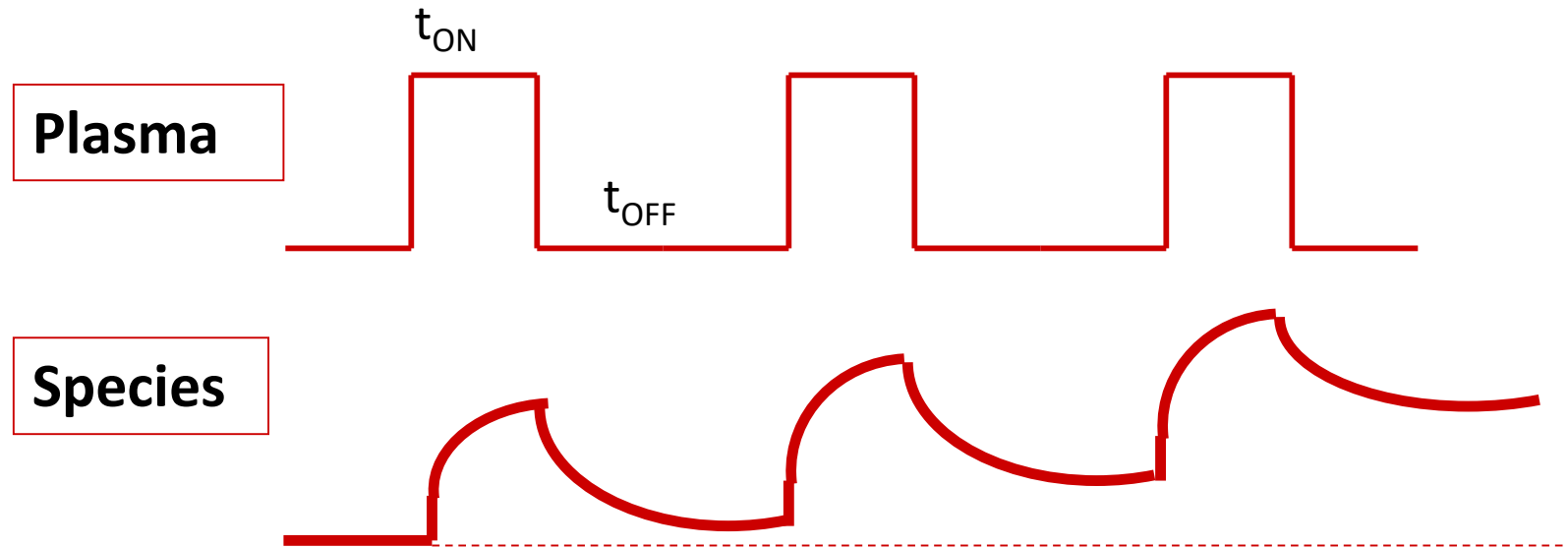
GLOW



AFTER  
GLOW



# POWER (bias) MODULATION



## Modulation Parameters

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

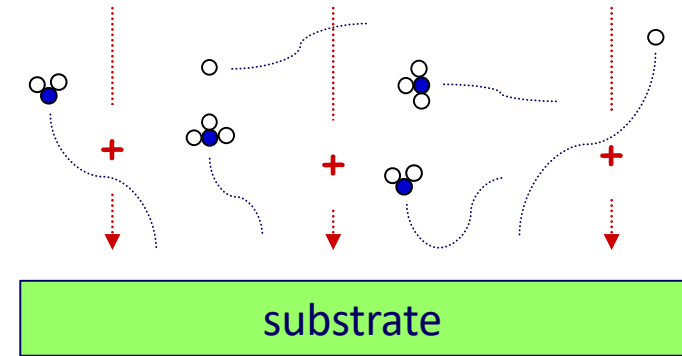
$$\text{Duty Cycle} = (t_{ON}/\text{period}) * 100$$

## Effective power

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

# PLASMA – SURFACE INTERACTIONS

**Low P** synergistic action of active species and ion bombardment



high density

low ionization degree

active species

+

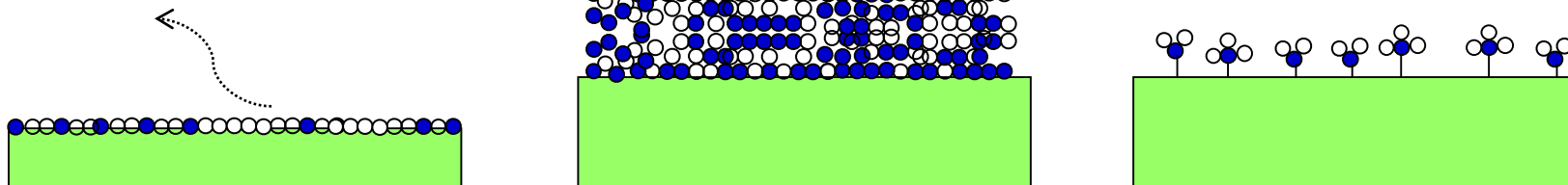
ion bombardment

etching

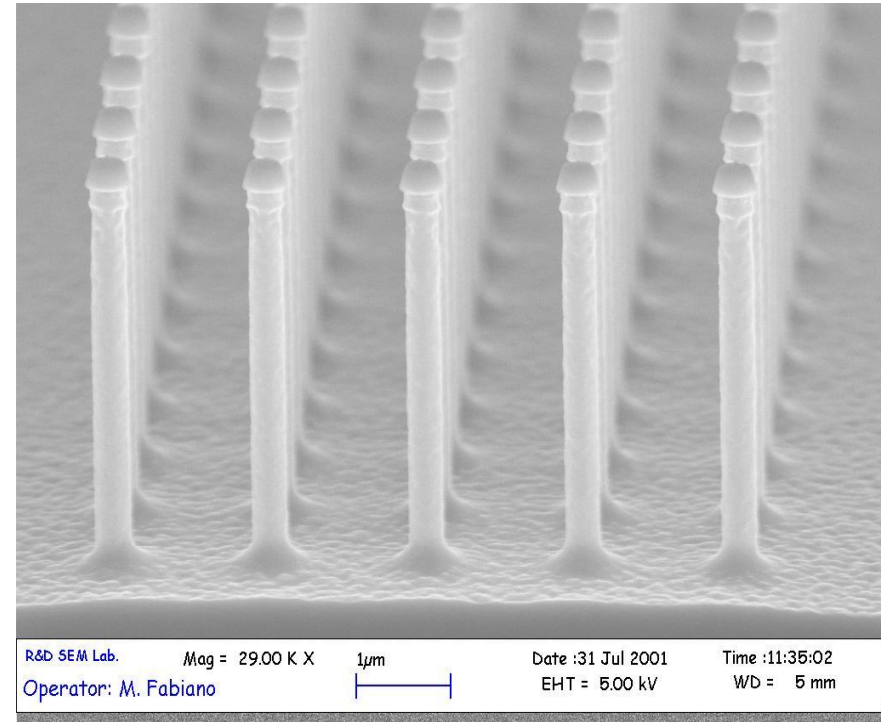
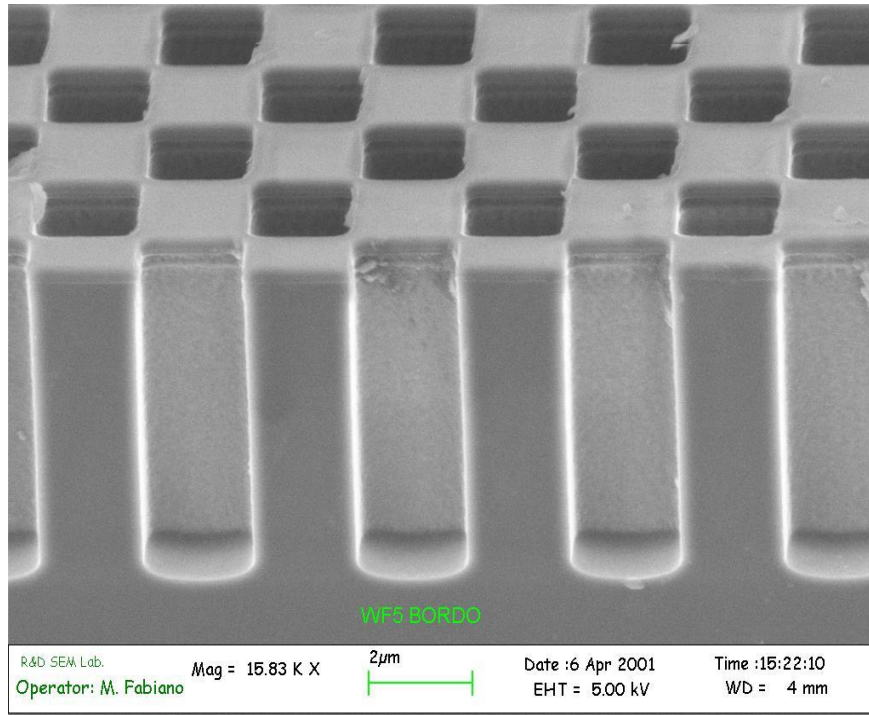
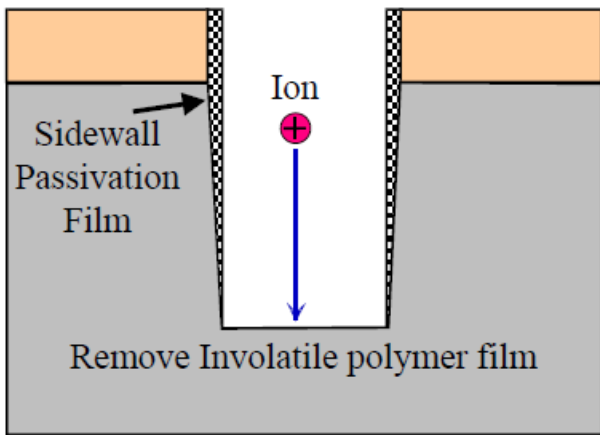
deposition

treatment

volatile products

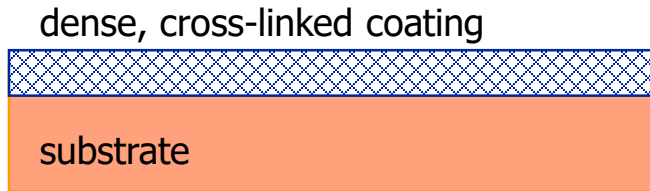


# DRY ETCHING

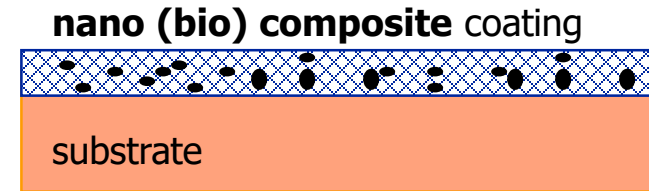




# PE-CVD

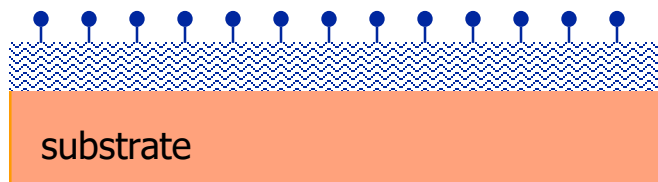


dense, cross-linked coating  
inorganic  
DLC, SiO<sub>x</sub>, ...



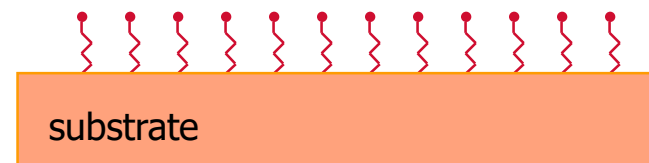
nano (bio) composite coating  
(bio) organic/inorganic  
metal/ceramic clusters  
embedded in a matrix

functional coating (-COOH, -NH<sub>2</sub>, -OH, >C=O, ...)



organic  
PEO-like, pdAA, teflon-like,  
silicone-like ...

high monomer structure retention



organic  
teflon-like

**modified thickness**  
**10 – 1000 nm**

## **CVD, Chemical Vapor Deposition**

The precursor of the coating is in the gas phase.

The deposition/polymerization process can be initiated by an initiator molecule and/or by a hot filament, or by heating the substrate. (e.g., pyrolysis, i-CVD, etc)

## **PE-CVD, Plasma-Enhanced CVD**

The precursor of the coating is in the gas phase.

The deposition process is initiated by fragmenting the “*monomer*” with an electric field (glow discharge). In case of organic monomers the jargon term *plasma polymerization* is utilized

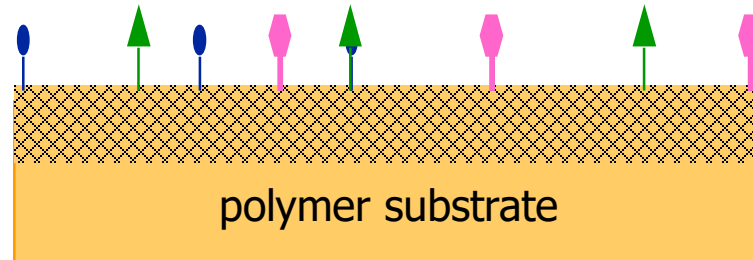
## **PVD, Physical Vapor Deposition**

The precursor of the coating is in the solid phase (filament, electrode).

The deposition process is initiated by heating a filament (evaporation) or by sputtering from an electrode bombarded by positive ions (glow discharge, ion gun, etc).

# PLASMA TREATMENTS

*grafting of functional groups*

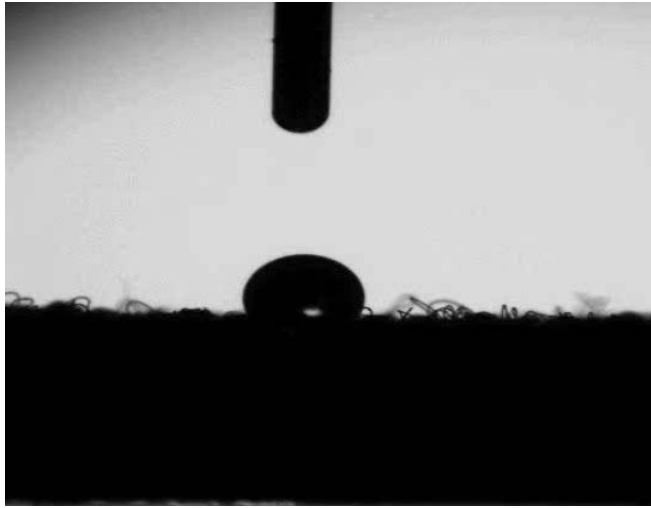


**modified thickness**  
**1 – 10 nm**

*surface modification (deposition, etching, grafting) plasma processes  
can be considered nanotechnologies for the z axis*

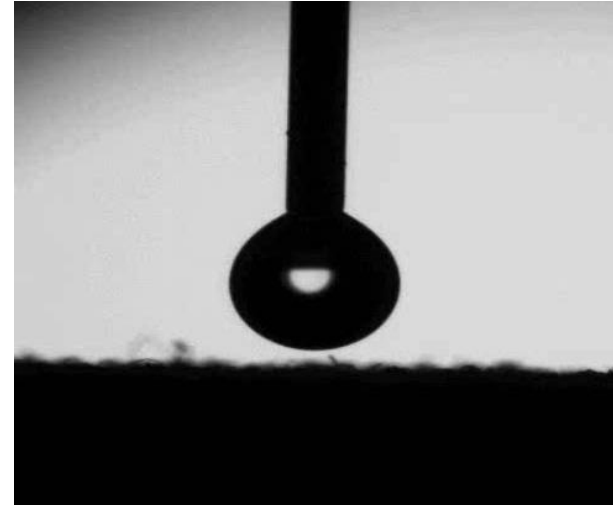
# HYDROPHILIC TEXTILE

untreated

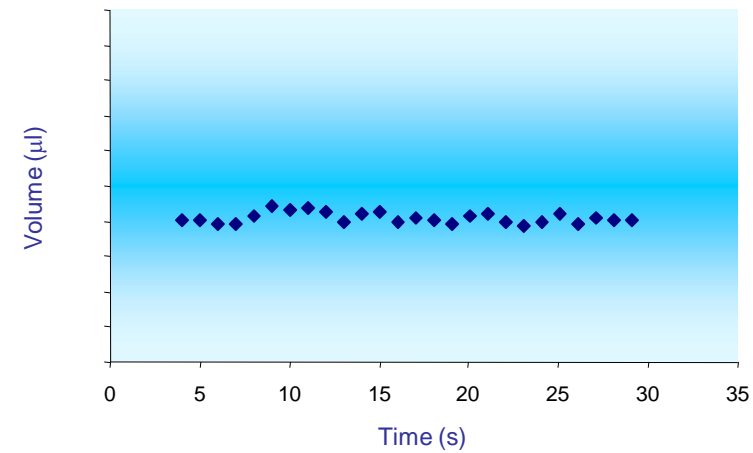
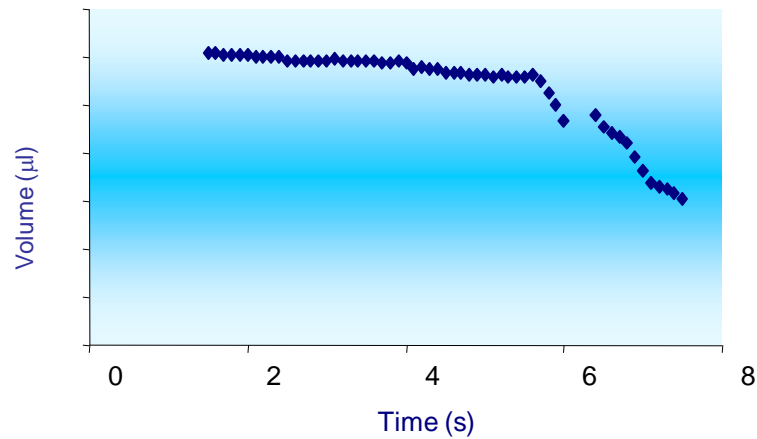


CF<sub>4</sub> plasma treated

WCA  
122±3°



water adsorption kinetics





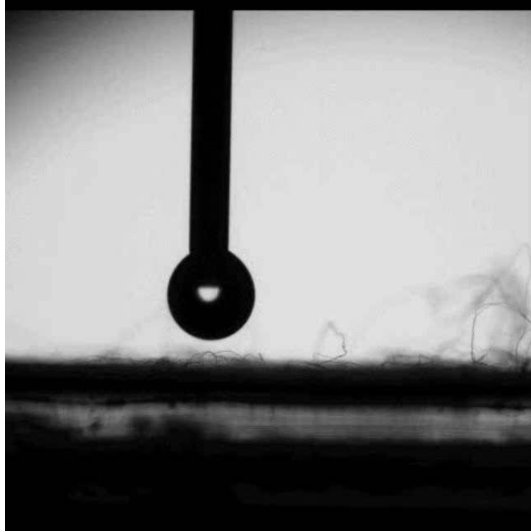
F atoms + pol. surf.  $\rightarrow$  fluorinated (grafted) pol. surf.

$\text{CF}_x$  radicals + pol. surf.  $\rightarrow$  fluorinated (coated) pol. surf.

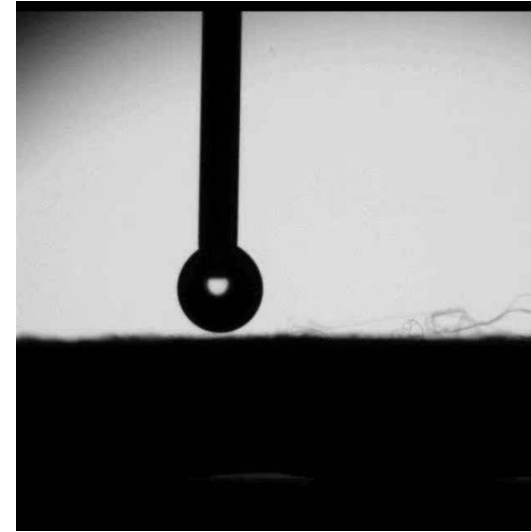
# HYDROPHOBIC PBT WNW

untreated

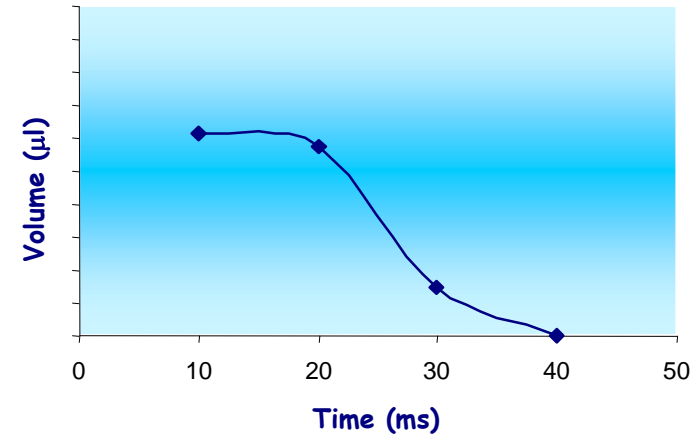
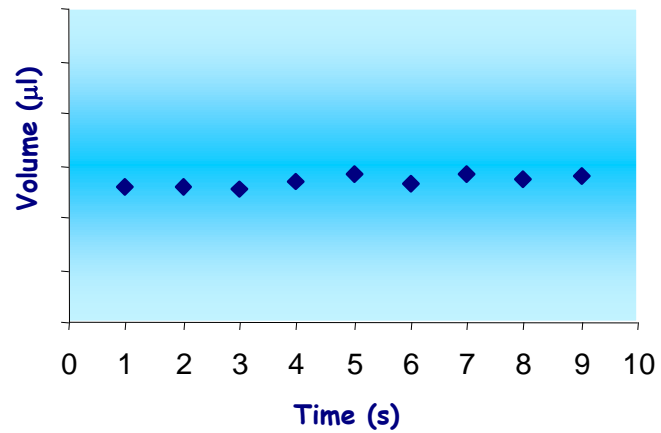
WCA  
 $142 \pm 4^\circ$



O<sub>2</sub> plasma treated



water adsorption kinetics





$\text{O}_2^* + \text{O}_{\text{atoms}} + \text{pol. surf.} \rightarrow \text{oxidized (grafted) pol. surf.}$

$\text{O}_2^* + \text{O}_{\text{atoms}} + \text{pol. surf.} \rightarrow \text{oxidized (etched) pol. surf.} + \text{CO, CO}_2, \text{H}_2\text{O}$

# SURFACE MODIFICATION OF MATERIALS WITH LOW PRESSURE PLASMA TECHNIQUES

*active species interact with surfaces in three different processes*

## PLASMA (Dry) ETCHING

Ablation of materials (Si, SiO<sub>2</sub>, III-V, II-VI, resists, polymers, metals, etc.) through reactions with active species forming volatile compounds.

ASHING: etching of polymers in O<sub>2</sub> plasmas.

## PE-CVD PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

Inorganic (SiO<sub>2</sub>, DLCs, diamond, a-Si:H, etc.) and organic (silicone-, PEO- teflon-like, etc.) coatings can be deposited.

**PLASMA POLYMERIZATION** is jargon name for PE-CVD of organic coatings; where a **MONOMER** is used to feed the discharge.

## PLASMA TREATMENTS

Modification of the topmost layers of materials (polymers) by grafting chemical groups (-NH<sub>2</sub>, -COOH, -F, -OH...) and/or crosslinking surfaces with reactive (NH<sub>3</sub>, CF<sub>4</sub>, O<sub>2</sub>, ...) or inert (Ar, He,..) gases (CASING).



# TECHNOLOGICAL APPLICATIONS OF COLD PLASMAS

## **Gas phase reactions**

Production of Ozone; abatement of pollutants; vehicle exhaust gas treatments.

## **Light sources**

Neon lights; High Intensity Discharge (HID) car lights; TV plasma displays.

## **Aerospace**

Plasma-based space propulsion technologies; plasma-aided combustion; plasma actuators for airplane wings.

## **Surface modification processes of materials**

### **Etching processes**

Si, SiO<sub>2</sub> and other materials in Microelectronics for production of Ultra Large Scale (ULS) Integrated Circuits (IC);

### **Deposition of thin films**

gas/vapor barrier layers in Food Packaging; protective anti-corrosion coatings on metals

hydrogenated amorphous Silicon (a-Si:H) photovoltaic coatings for solar cells;

diamond and diamond-like (DLC) hard coatings;

functionalization of very large area substrates (polymer webs, textiles, displays).

### **Treatments**

grafting of polar groups on polymers for printing;

improving hydrophilicity and citocompatibility of polystyrene cell-culture plates.

## **Plasma sterilization of materials**

## **Plasma synthesis/functionalization of micro/nanoparticles**

Synthesis of semiconductor nano-crystals; synthesis of carbon nanotubes;

functionalization of micro/nanoparticles.

## **Therapeutic uses of plasmas (Plasma Medicine)**

Plasma-aided surgery; wound healing; cancer treatments; disinfection of teeth cavities in dentistry.

# SURFACE PROPERTIES OF MATERIALS

## TUNABLE

### WITH PLASMA PROCESSES

adhesion

wettability/hydrophobicity

oleophobicity

gas/vapor barrier

permeability

biocompatibility

resistance to bacterial adhesion

chemical inertness

non fouling character

electrical conductivity

hardness (anti-scratch)

roughness, texture

refractive index

dyebility

color

corrosion protection

...

# WHY NON EQUILIBRIUM PLASMAS ?

LOW TEMPERATURE PROCESSES FOR THERMOLABILE MATERIALS

SURFACE MODIFICATIONS, NO BULK ALTERATIONS

*polymers, paper, textiles, ...*

ADAPTABLE TO ANY SHAPE AND MATERIAL SUBSTRATE

*webs, inside of small tubes, powders, granules, fibers, ...*

HIGH DENSITY OF ACTIVE SPECIES

*comparable with high  $T$  gases and flames*

TUNEABLE ION BOMBARDMENT

DRY TECHNOLOGY, NEGLIGIBLE IMPACT TO THE ENVIRONMENT

ATMOSPHERIC PRESSURE PROCESSES

SYNTHESIS OF AN ENTIRELY NEW CLASS OF SURFACES

TRANSFER TO INDUSTRIAL SCALE

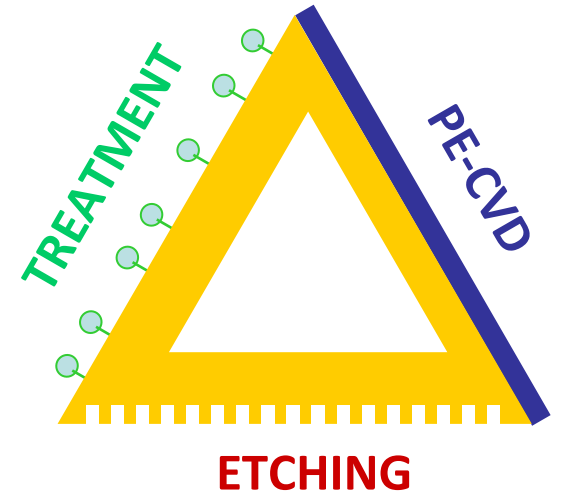
PROCESS CONTROL POSSIBLE

# INDUSTRIAL AREAS of COLD PLASMAS

**MICROELECTRONICS**  
**SEMICONDUCTORS**  
**SOLAR CELLS**  
**LIGHT SOURCES**  
**OZONE PRODUCTION**

AUTOMOBILE  
FOOD PACKAGING  
TEXTILE  
BIOMATERIALS  
MICROFLUIDICS  
MEMS  
CLEANING  
STERILIZATION  
BIOLOGY  
ENVIRONMENT

CATALYSIS  
MEDICINE  
POLYMERS  
PAPER  
WETTABILITY  
ADHESION  
METALLIZATION  
PRINTING, DYEING  
CORROSION PROTECTION  
CULTURAL HERITAGE  
COMPOSITES  
SENSORS  
OPTICS  
BUILDINGS



## LOW T PLASMA PROCESSES: APPLICATIONS

### ETCHING

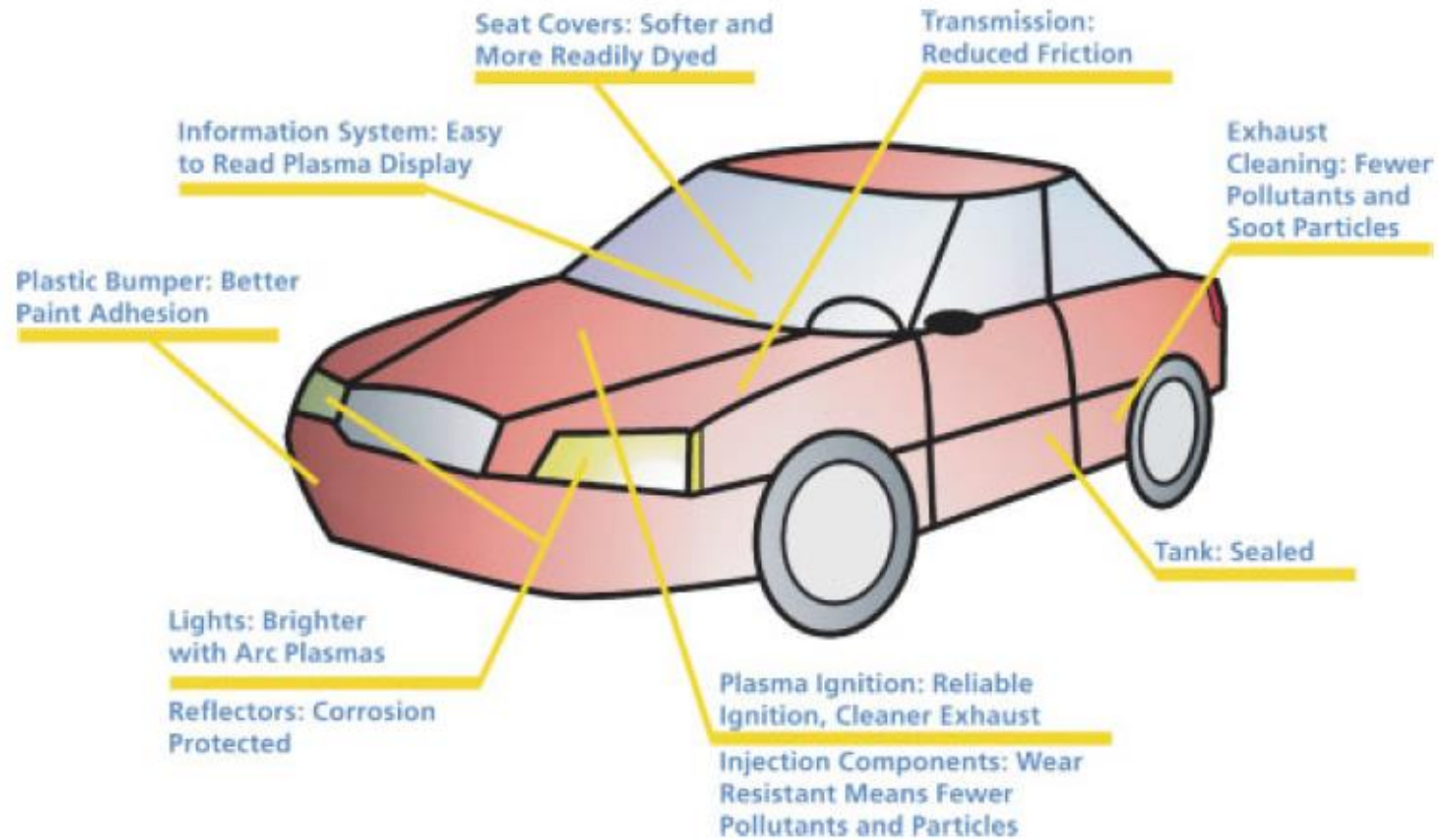
Si, SiO<sub>2</sub>, III-V & II-VI SC, resists, dielectrics, Al ... for VLSI circuits; cleaning; bioMEMS; sterilization; glass, PMMA for microfluidics, soft lithography ....

### PE-CVD (coatings)

Gas barrier in food packages (webs, bottles, ... ) and OLED; corrosion protection on metals (car, ...); protective for cultural heritage; low-k and high-k dielectrics for microelectronics; semiconductors for solar cells; anti-scratch, anti-reflective, colored for optics; water- oil-proof for paper and textiles; cell-adhesive, blood-compatible, protein and cell repulsive, bacterial-resistant for biomaterials; hydrophilic/hydrophobic; functional for (bio)molecule (enzymes, peptides, ...) immobilization on biomedical surfaces and sensors; nanocomposite and bio-nanocomposite coatings, ....

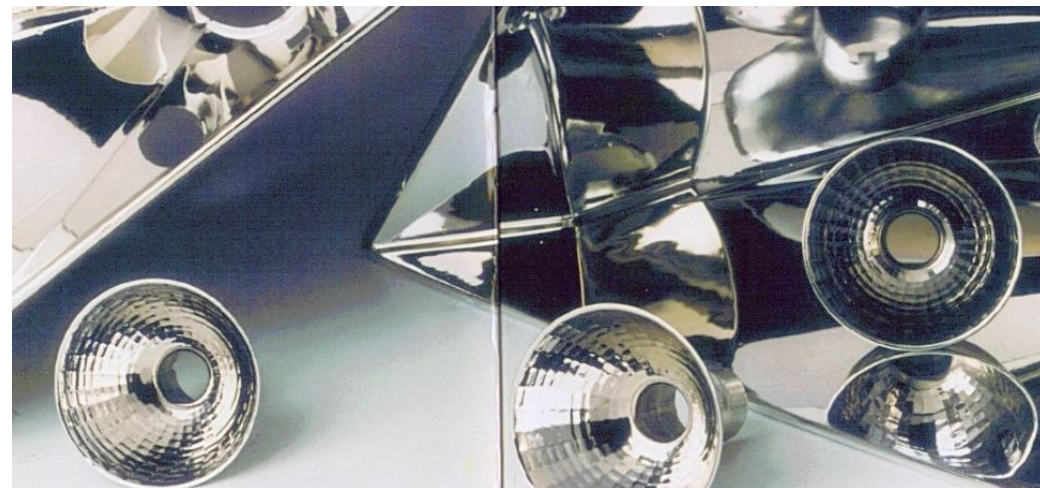
### TREATMENTS (grafting)

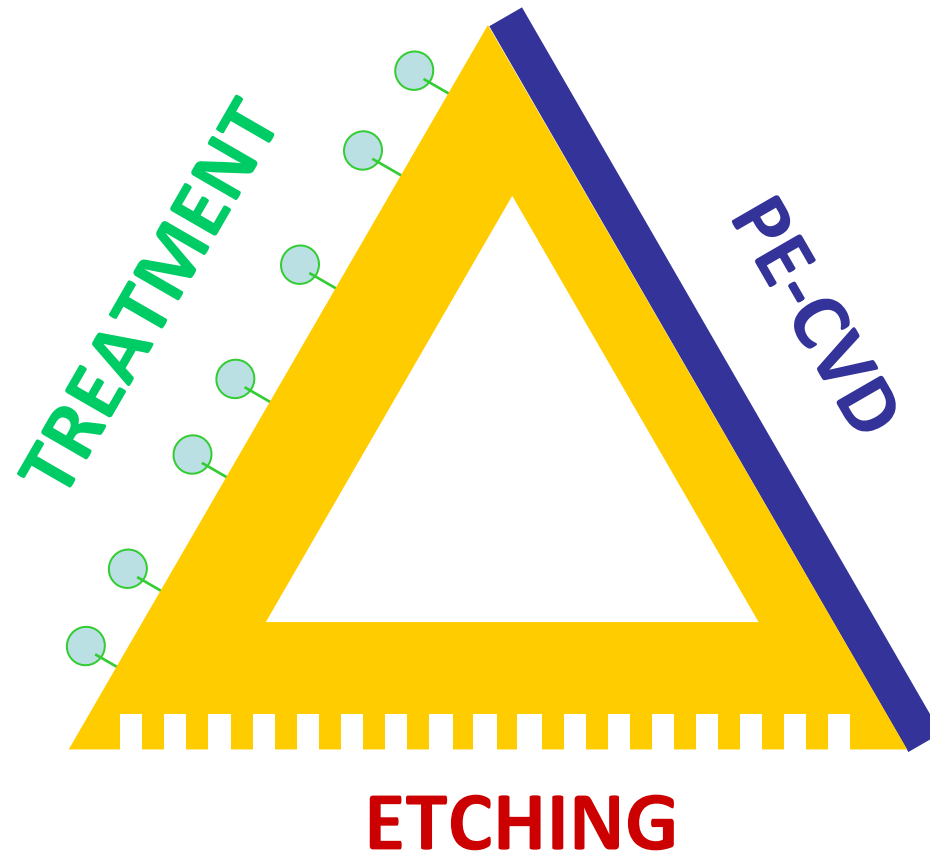
Improved adhesion of inks, dyes, glues, metals on polymers and textiles; anti-felting, anti-shrinking for wool; improving fiber- and particle-matrix adhesion in composite materials or scaffolds; hydrophilic/hydrophobic; cell-adhesive, grafted groups to immobilize (bio)molecules on biomedical surfaces and sensors; ...

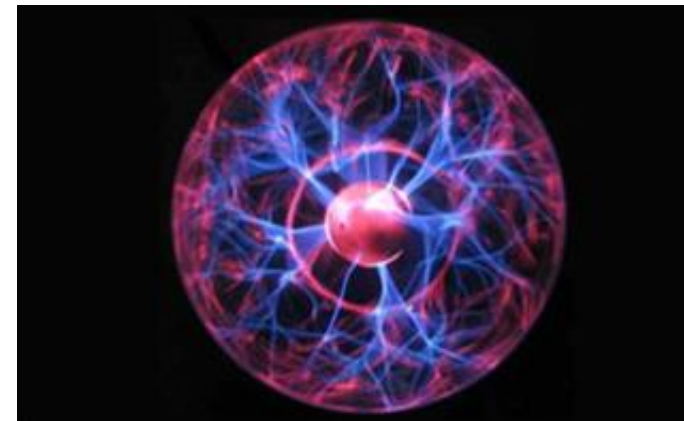


**plasma  
for the car**

**PE-CVD SiO<sub>x</sub>  
“protecting seal” coatings  
on Al-evaporated plastic car lights**

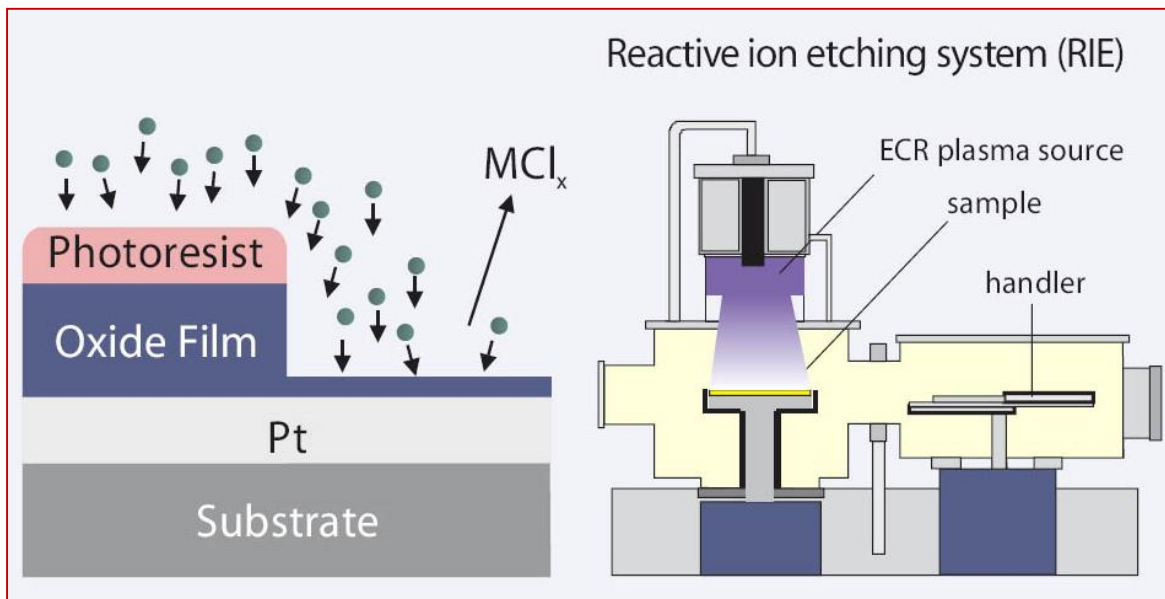






# REACTOR CONCEPTS

Pietro Favia



<http://www.ion-med.com/how.asp>

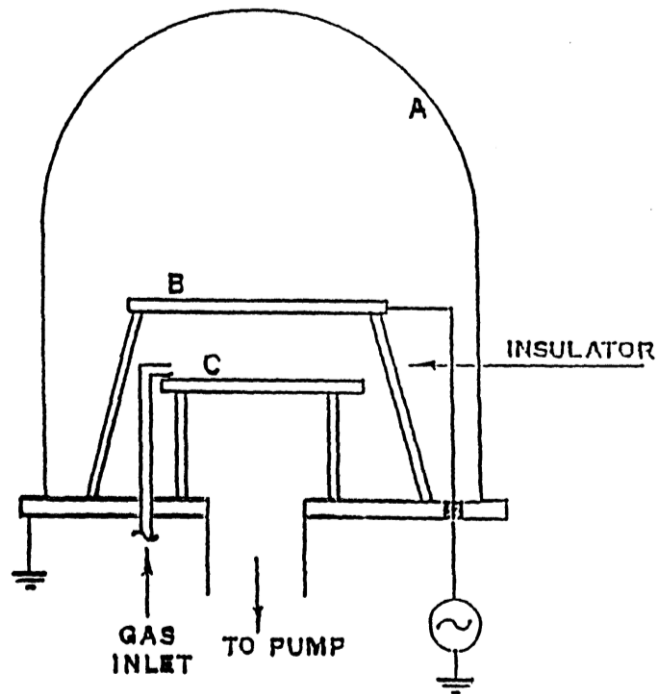




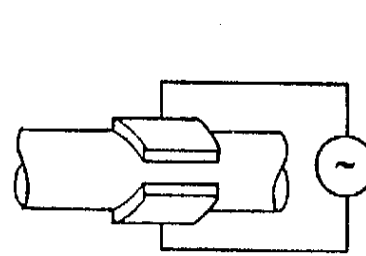
# LOW P PLASMA REACTORS: popular configurations



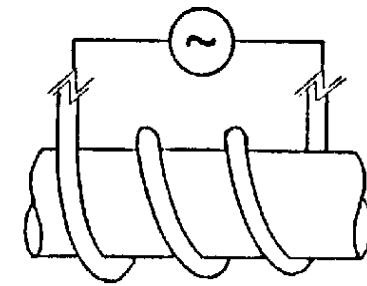
**INTERNAL  
ELECTRODES**  
*bell jar reactor*



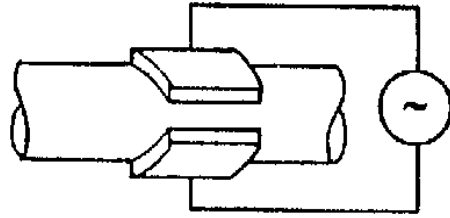
## EXTERNAL COUPLING



**CAPACITIVE**

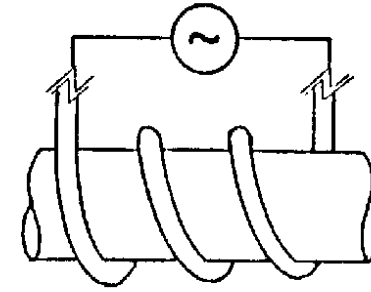


**INDUCTIVE**



**CAPACITIVE**

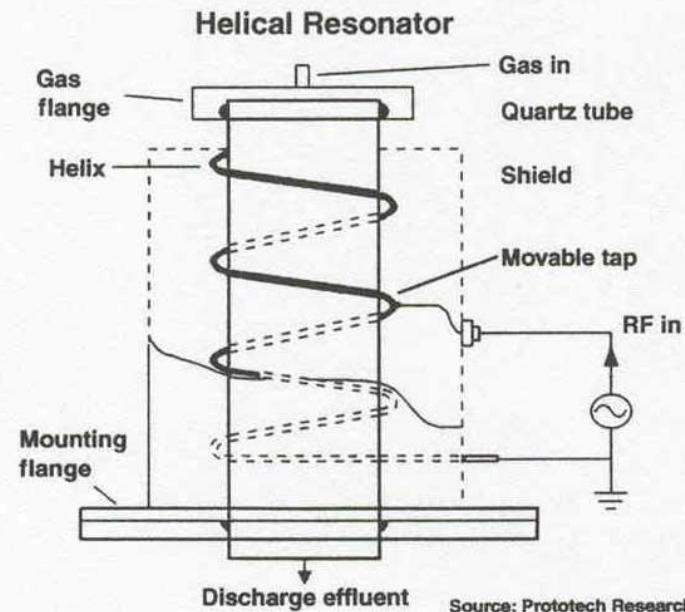
## EXTERNAL COUPLING

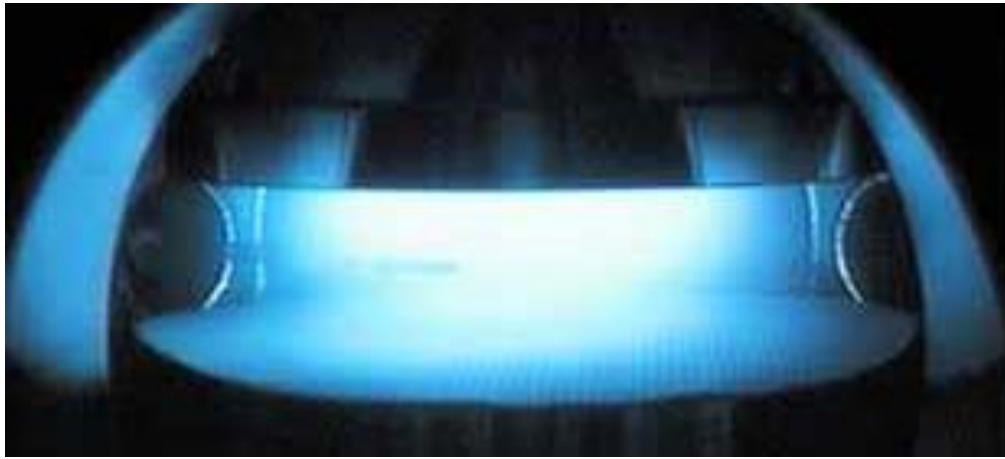


**INDUCTIVE**

### *Inductively coupled plasma*

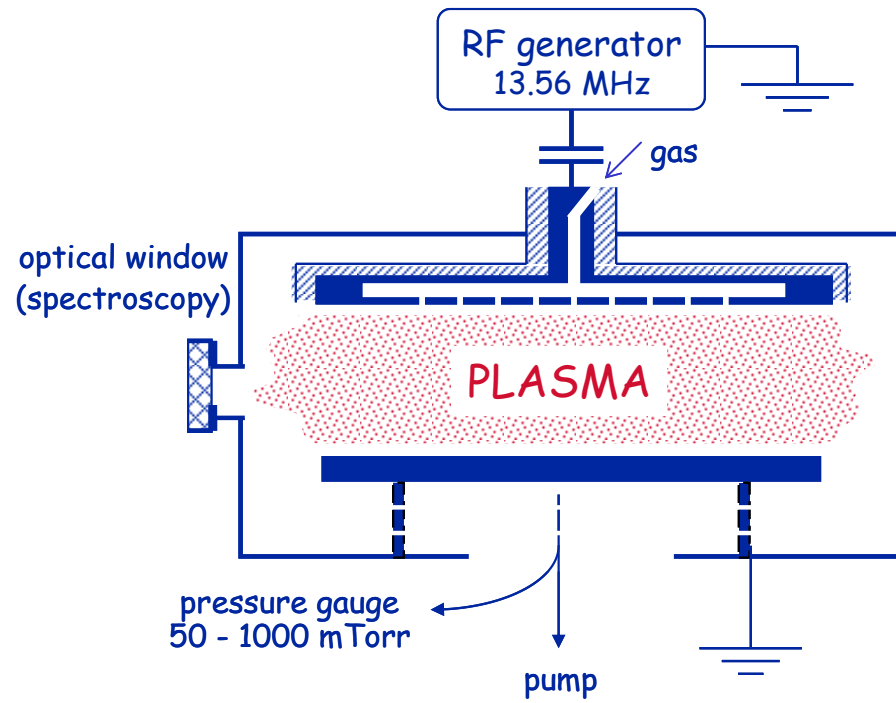
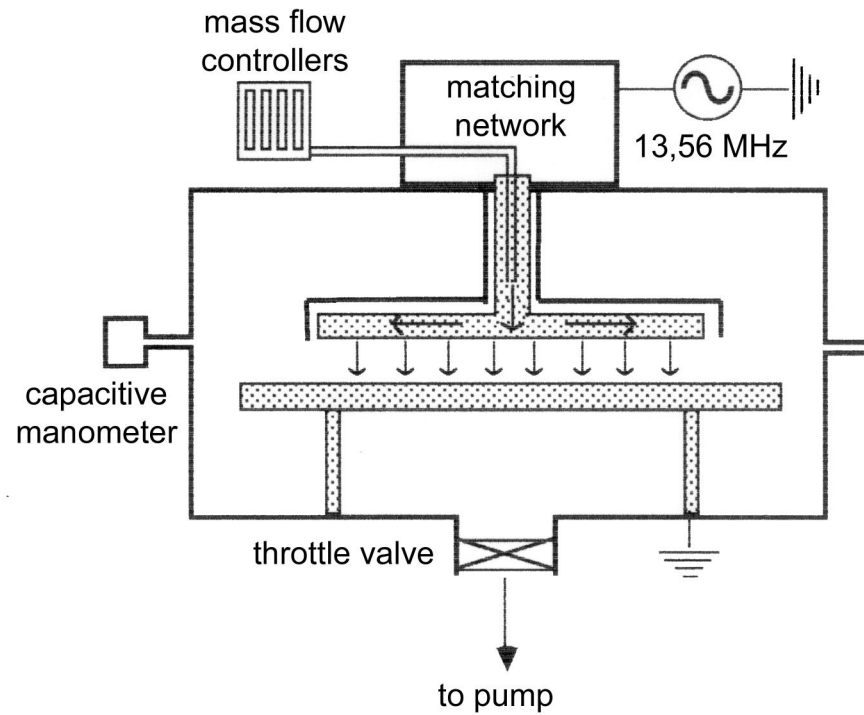
This electrostatic, shielded, inductively coupled plasma source produces electric field lines from a helical resonator combined with an electrostatic shield to produce electric field lines that are circumferential in response to the axial RF magnetic field.



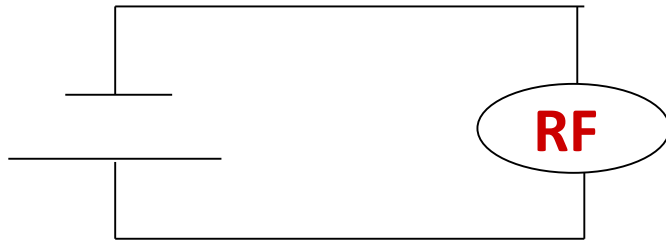


# PARALLEL PLATE PLASMA REACTOR

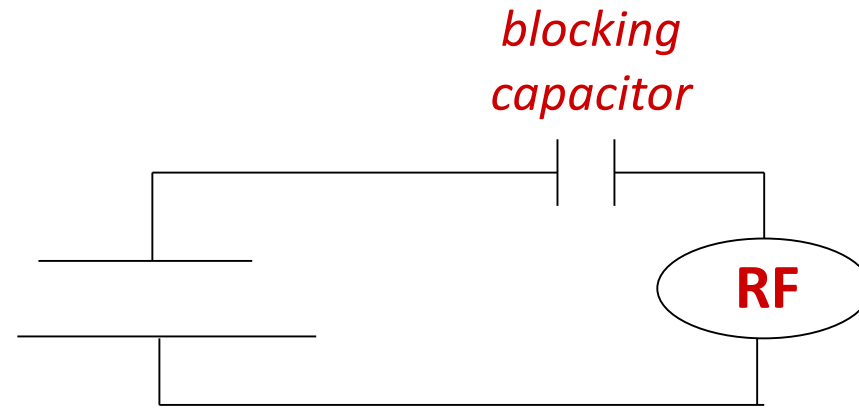
*internal electrodes*



## POTENTIALS IN A GLOW DISCHARGE (oversimplified picture)



**DIRECT COUPLING**

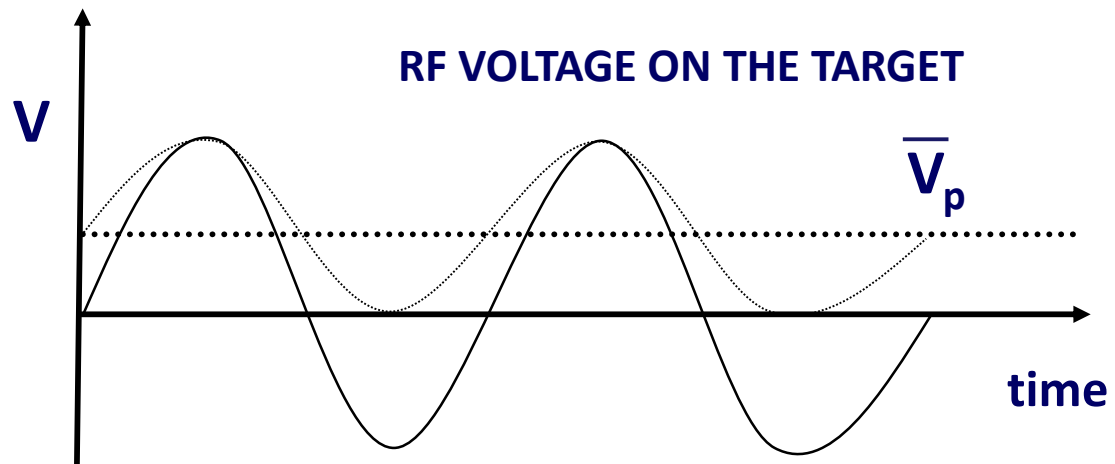
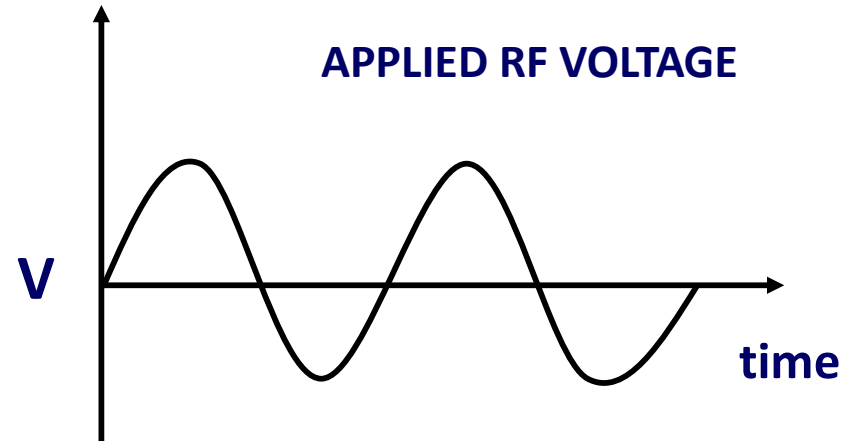
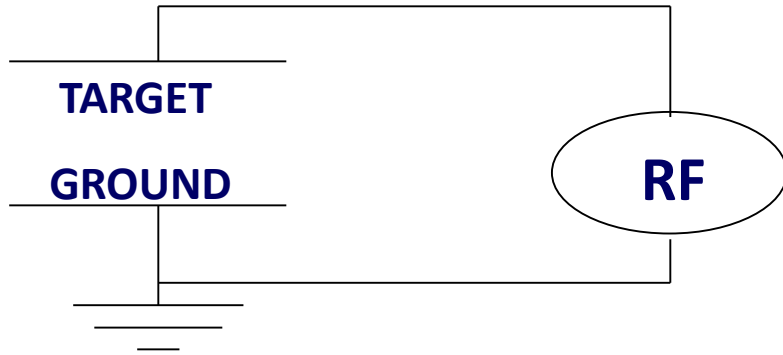


**CAPACITIVE COUPLING**

**WITH THE BLOCKING CAPACITOR  
NO NET CURRENT CAN FLOW IN THE CIRCUIT IN ONE RF CYCLE**

$$I_{\text{tot}} = 0$$

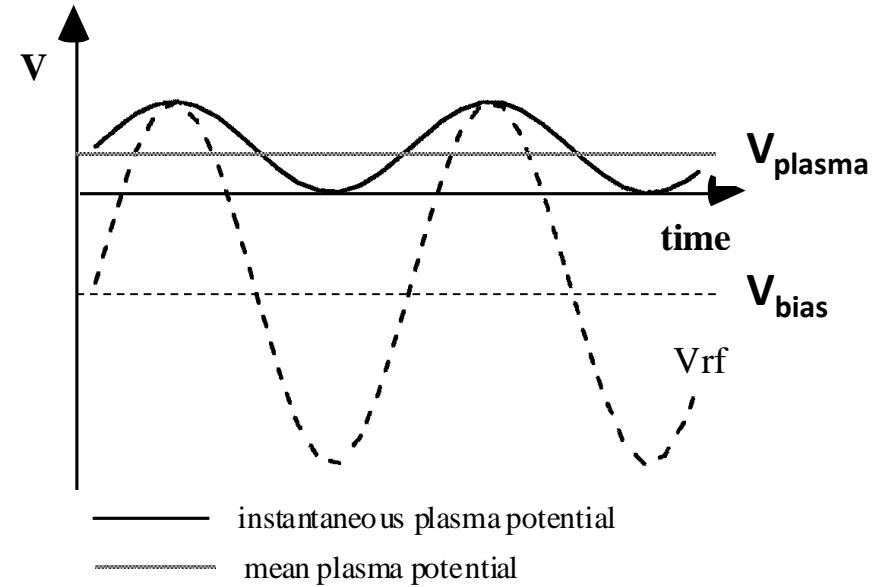
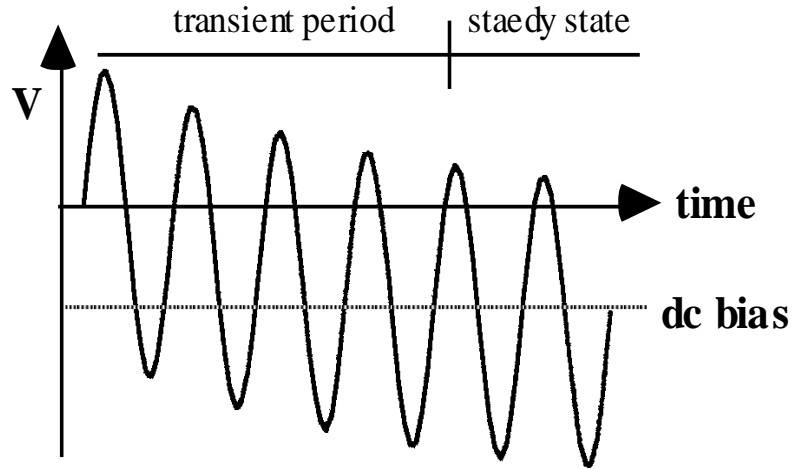
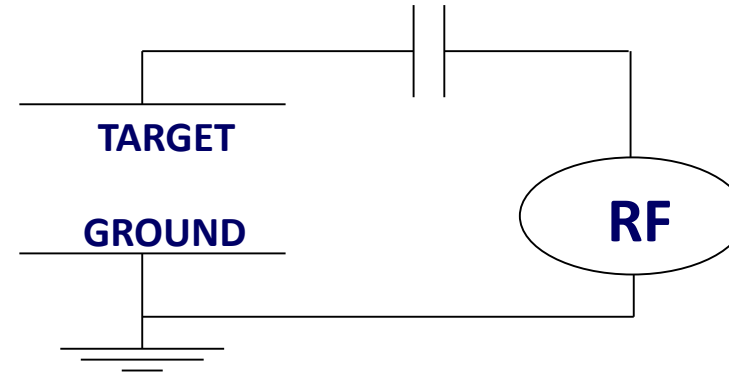
## DIRECT COUPLING



**AVERAGE PLASMA POTENTIAL  $> 0$  (e.g.  $V_p/2$ )**

**AVERAGE TARGET POTENTIAL = 0**

# CAPACITIVE COUPLING



**THE SITUATION IS SIMILAR  
FOR A FLOATING SUBSTRATE**

## **FLOATING POTENTIAL**

**AVERAGE POTENTIAL  
ON AN ELECTRICALLY INSULATED SUBSTRATE**

## **BIAS (or SELF) BIAS POTENTIAL**

**AVERAGE POTENTIAL OF A SUBSTRATE (ELECTRODE)  
CONNECTED TO A RF POWER SUPPLY**

## **AVERAGE PLASMA POTENTIAL**

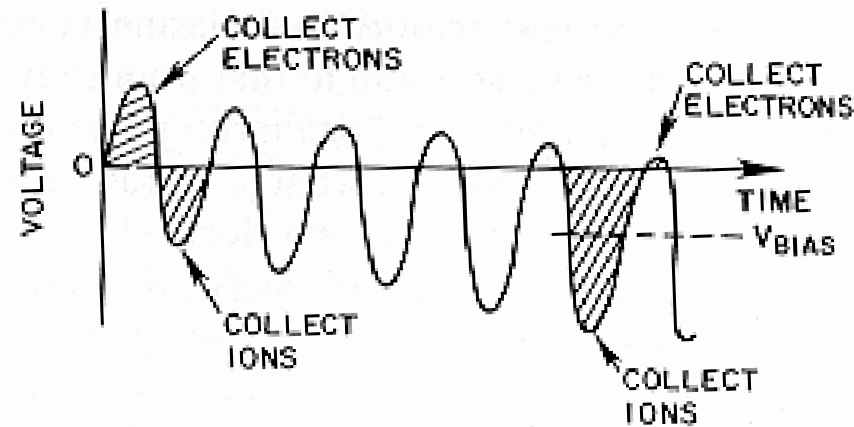
**AVERAGE POTENTIAL OF THE BULK OF THE PLASMA**

1. AC voltage overcomes the problem of charge which accumulates on a dielectric in the DC system.

The positive charge which accumulates due to ion bombardment during one half of the AC cycle can be neutralized by electron bombardment during the next half cycle. The frequency of AC must be high enough so the half period will be shorter than the charge-up time of the dielectric. Although this time will vary due to conditions and dielectric materials, for most applications the frequency must be above **100 KHz**.

2. Although there are a number of differences in the practical operation of AC plasmas, the principles of DC glow discharges can be applied to AC. One simply considers the AC as a rapidly reversing DC plasma.

At low frequency both electrons and ions can follow the field, so that a glow discharge is the same as DC, except that the polarity reverses twice each cycle. At high frequency the massive ions cannot respond to the frequency changes, whereas electrons can. By far the most common RF frequency used is 13.56 MHz, allowed by the FCC.



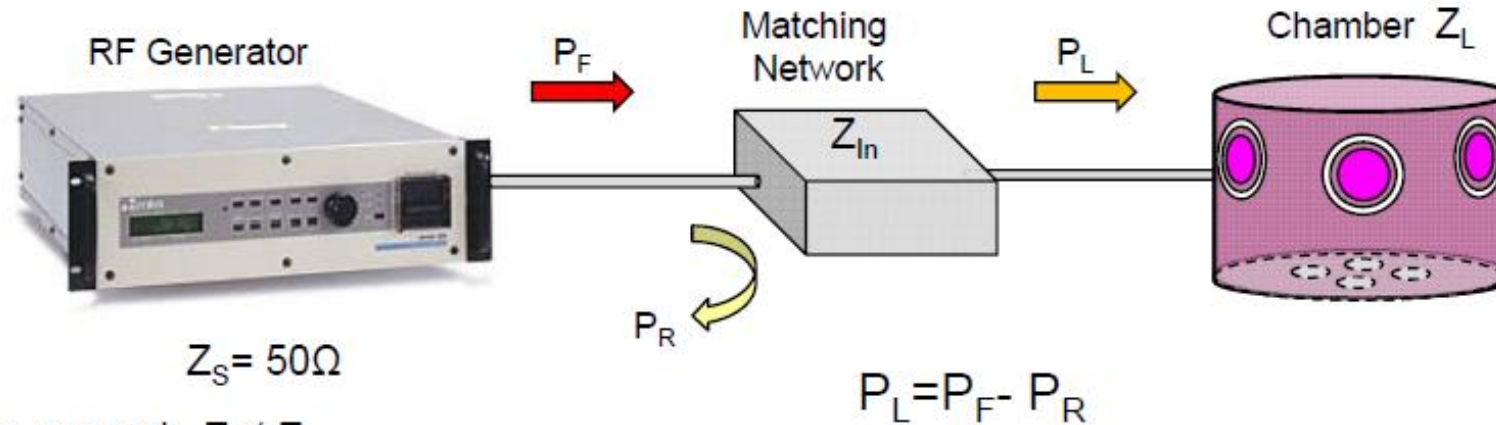
*Fig. 9.* The potential on the powered electrode of Fig. 8b as a function of time for the first several rf cycles.



# MATCHING NETWORK

The matching network (manual/automatic) maximizes the power delivered to the plasma, reduces reflected power (standing waves) and protects the power supply.

A reactor could be operated also without the matching network; in practice the requested power density cannot be maximized without matching.

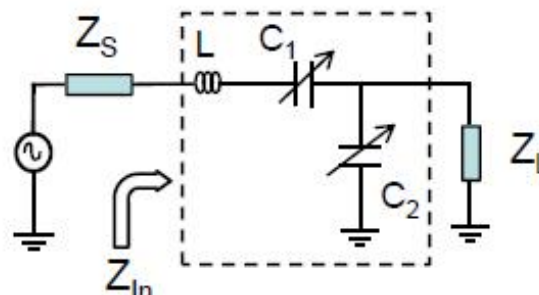


In general:  $Z_L \neq Z_S$

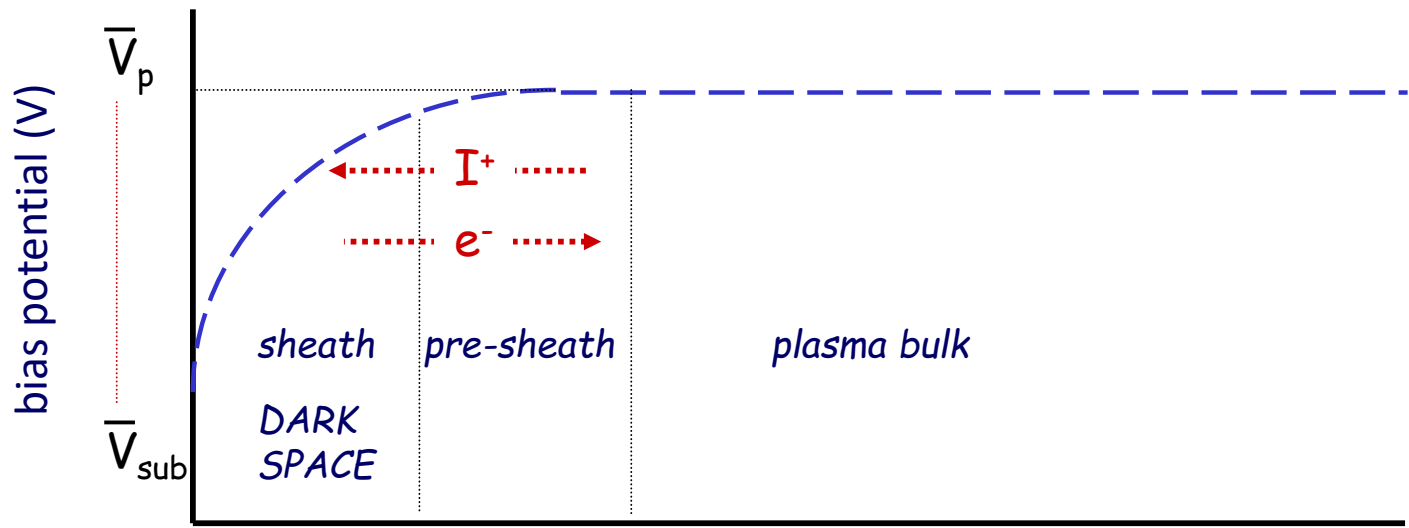
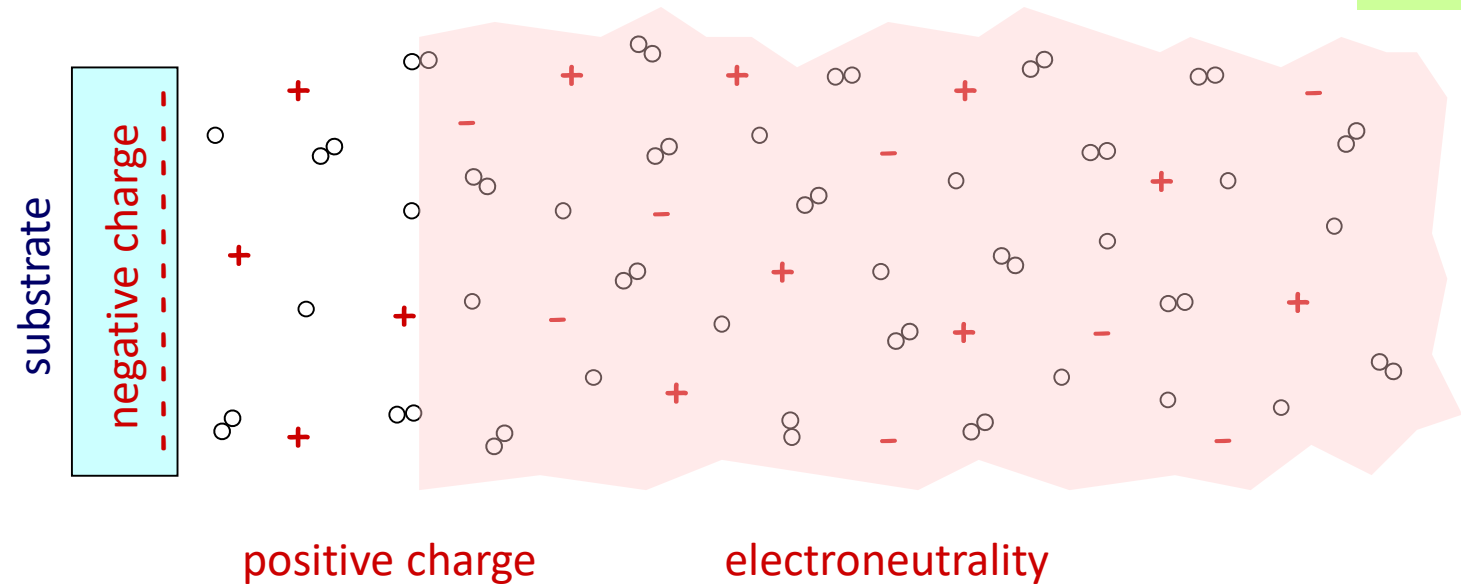
Purpose of Matching Network:  $Z_{in} = Z_S$  to maximize power delivery from source.

Manual or Automatic  
Matching Network

L-type



bias potential



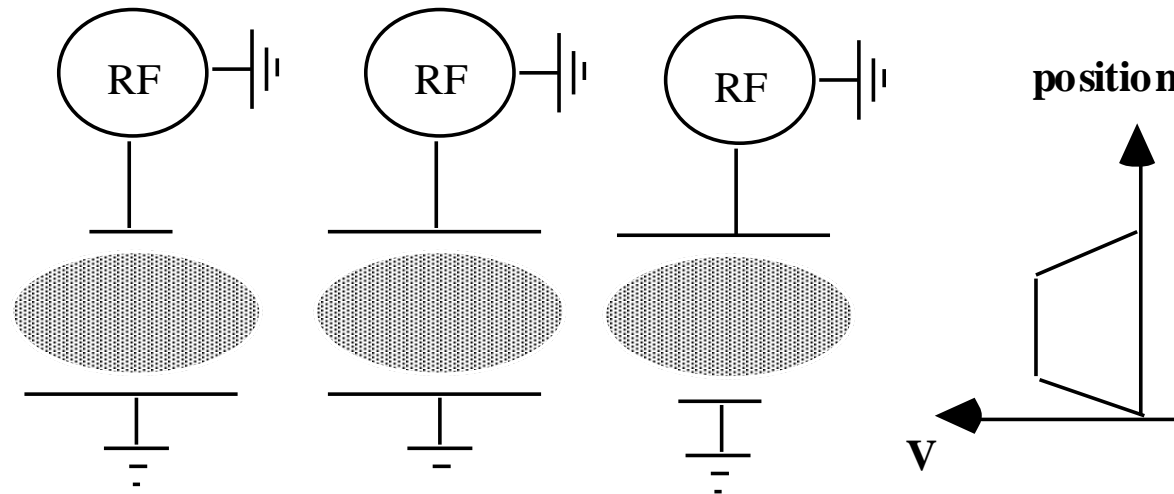
the thickness of the sheath increases with surface potential

distance

- **at 13.56 MHz ions are affected by average potentials since, during the period they cross the sheath, RF polarity changes several times.**
- **the surfaces in contact with the plasma are interested by positive ion bombardment because plasma bulk is the most positive region in the system.**
- **positive ion energy depends on system geometry, pressure, frequency, and a.c. peak-to-peak voltage.**
- **electrons reach surfaces with low energy for the decelerating effect of the sheaths.**

# ION BOMBARDMENT INSIDE A PLASMA REACTOR

## DIRECT COUPLING



**PERFECT SIMMETRY**  
**NO DIFFERENCE BETWEEN THE TWO ELECTRODES**

# CAPACITIVE COUPLING

the higher average potential drop (plasma-substrate) is experienced by the electrode with lowest area

## Koenig & Meissel Law

$$\frac{V_1}{V_2} = \left( \frac{A_2}{A_1} \right)^n \quad n = 1 - 4$$

### Assumptions

(strong deviation at high P):

- ion current density equal at both electrodes;
- collisionless sheaths
- uniform plasma density

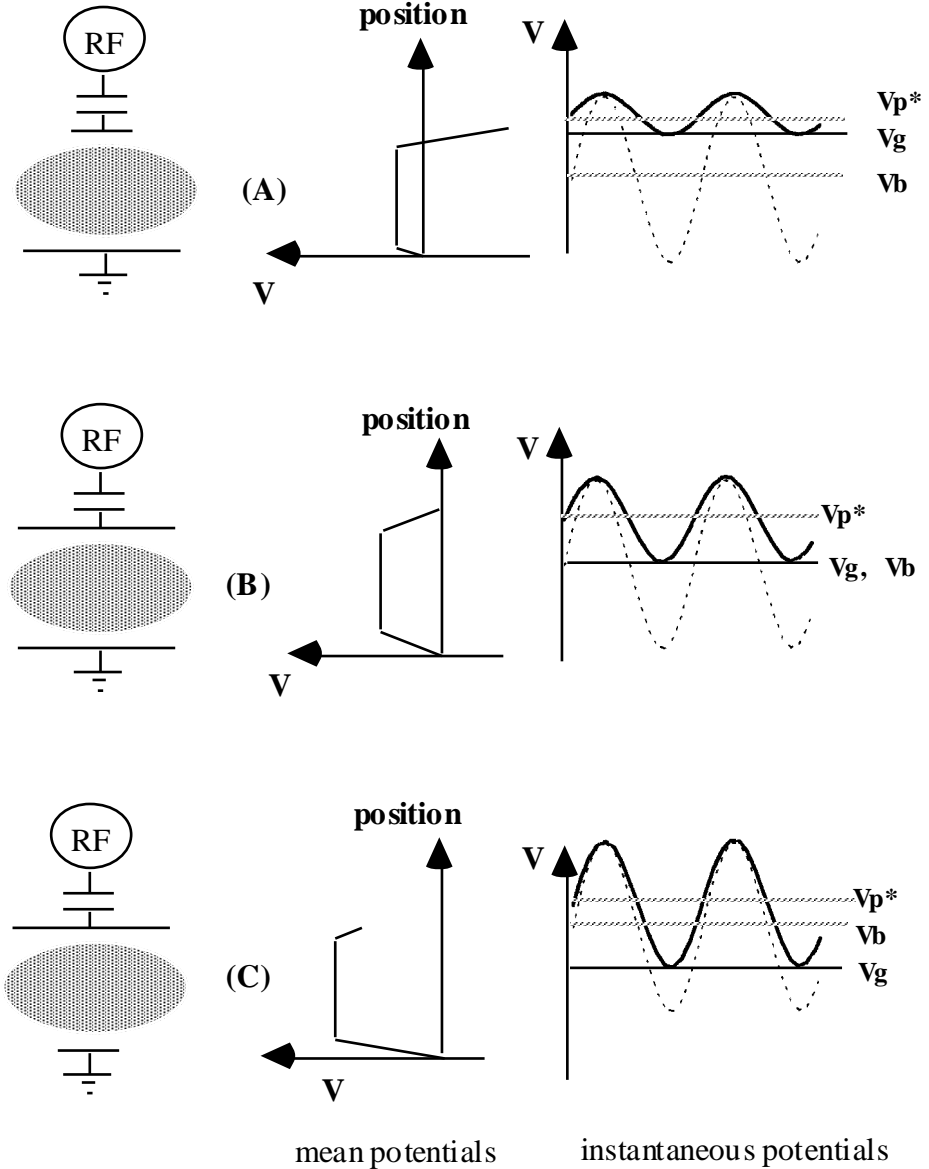
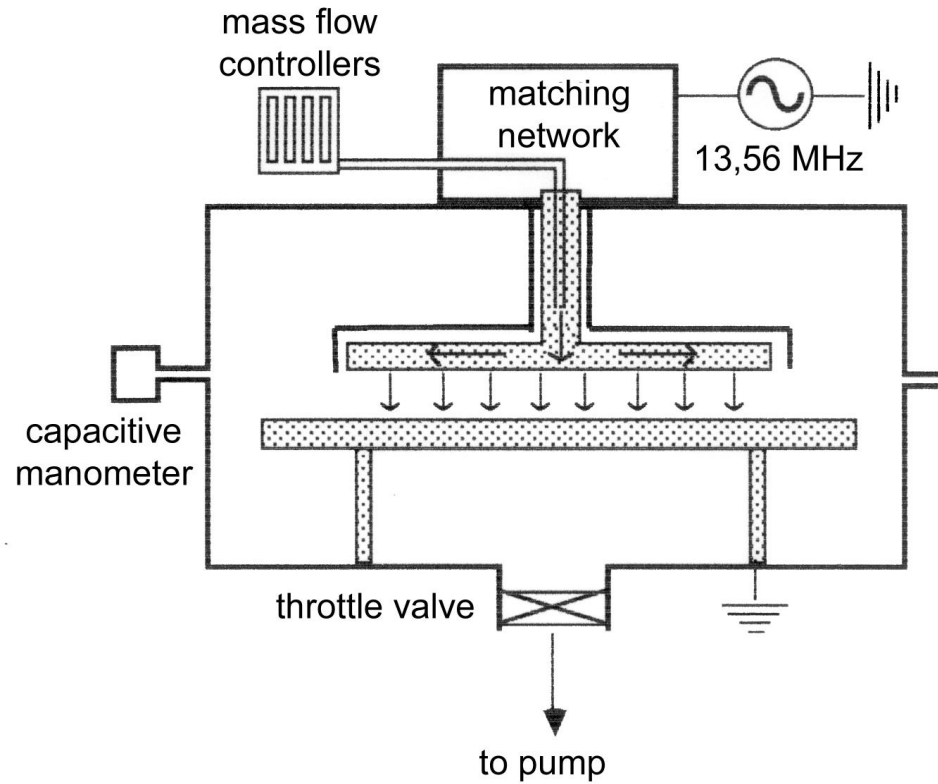


Figure 12. instantaneous and averaged potentials as a function of reactor geometry

# PARALLEL PLATE “DIODE” REACTOR

**INTERNAL  
COUPLING**



**THE SYSTEM IS ASYMMETRIC  
DUE TO THE REACTOR WALLS**

walls put one of the many  
scale up problems

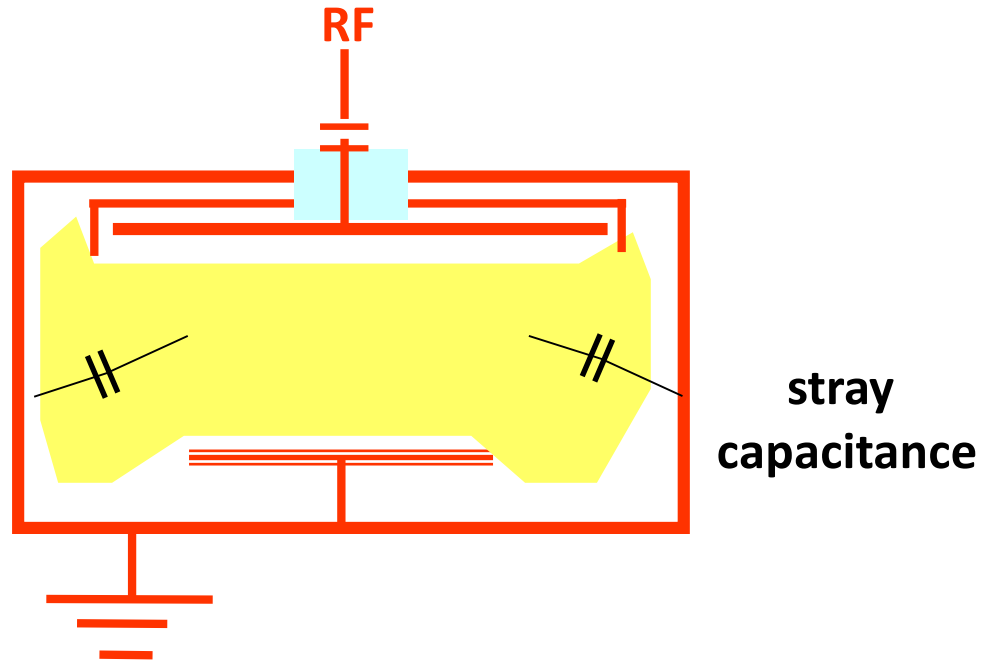


lab scale

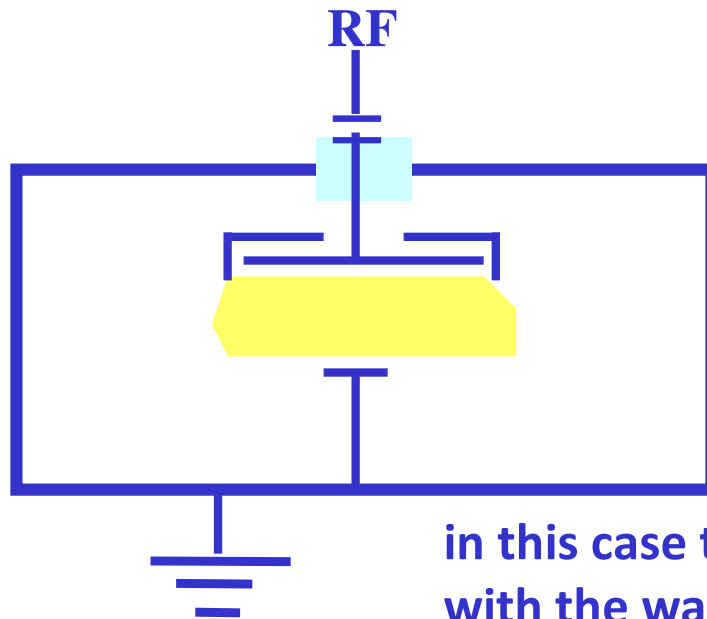
walls affect  $A_1/A_2$   
in a different way



large scale



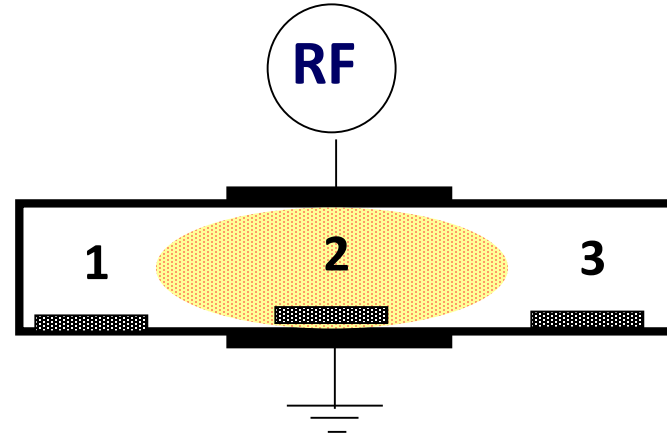
stray  
capacitance



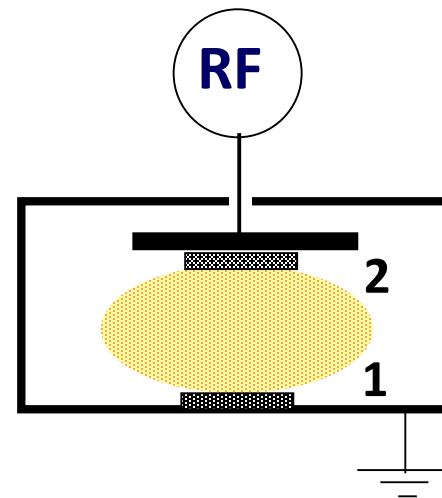
in this case the interactions  
with the walls are reduced

# REACTOR GEOMETRY AND CHARACTERISTICS

## CONTROL THE PHYSICAL CONTRIBUTION TO THE PROCESS



substrate  
position

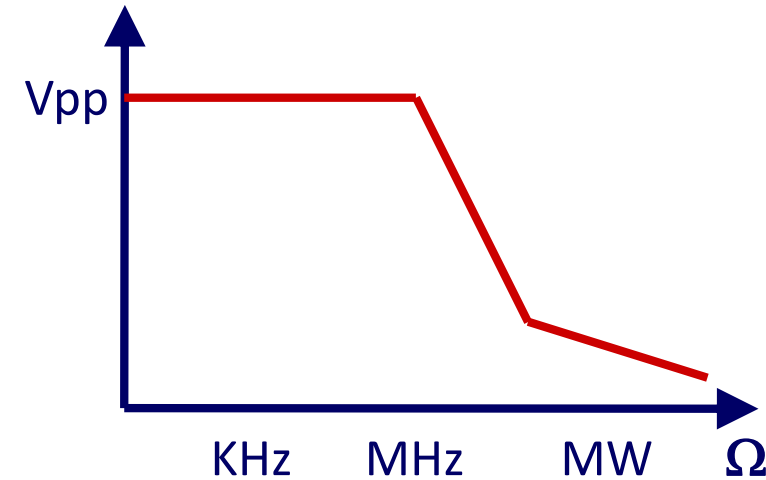




## EFFECT OF RF FREQUENCY ( $\omega$ ) ON THE ION BOMBARDMENT

$V_{pp}$ ,  $V_p$  and  $V_{bias}$  increase by decreasing  $\omega$   
KHz > MHz > GHz

Ion Transit Frequency (ITF, 0.9-2 MHz)  
is the frequency above which ions can't  
cross the sheath in less than half RF cycle



above ITF       $I^+$  are influenced by average potentials

below ITF       $I^+$  are influenced by instantaneous potentials

when  $\omega < ITF$   
(es KHz)

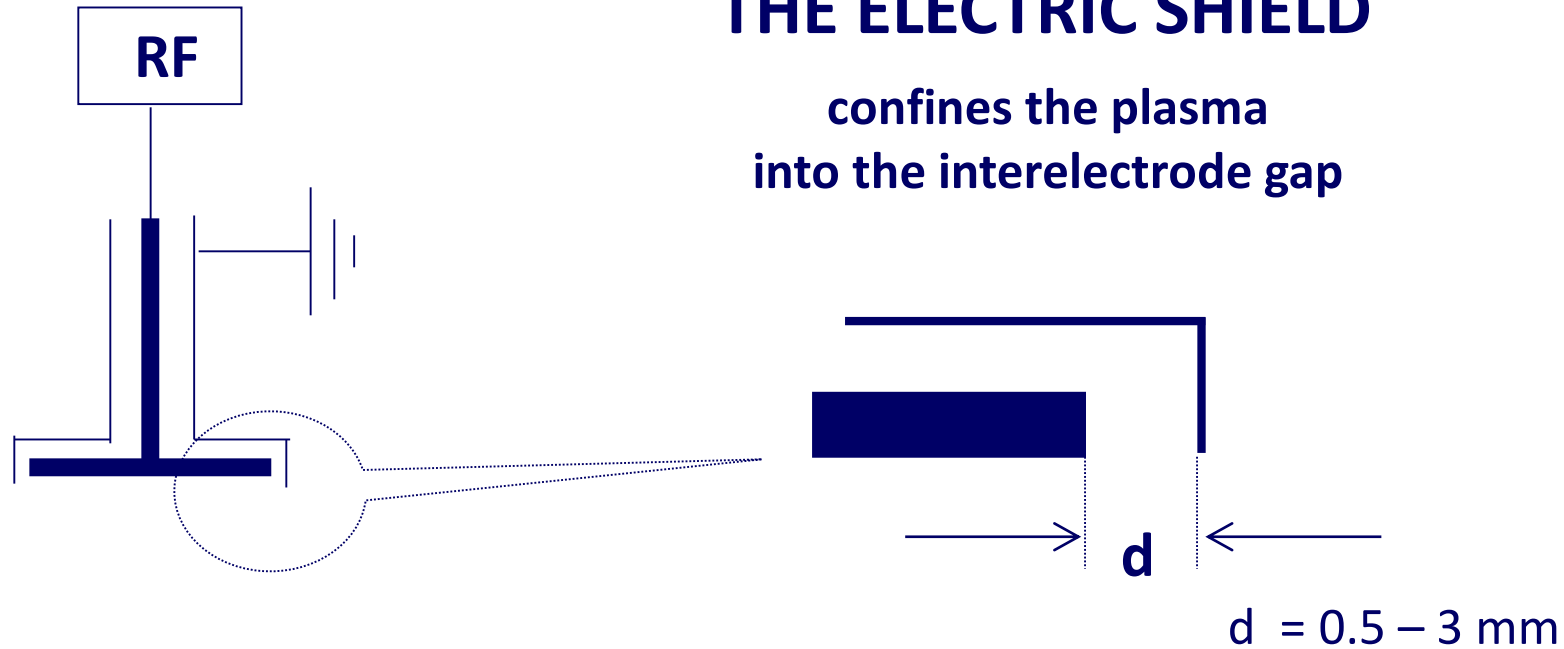
the ion bombardment becomes more energetic

the ion energy distribution function becomes broader

In the GHz, also electrons become unable to follow the oscillations  
of the electric field and are affected by average potentials

# THE ELECTRIC SHIELD

confines the plasma  
into the interelectrode gap



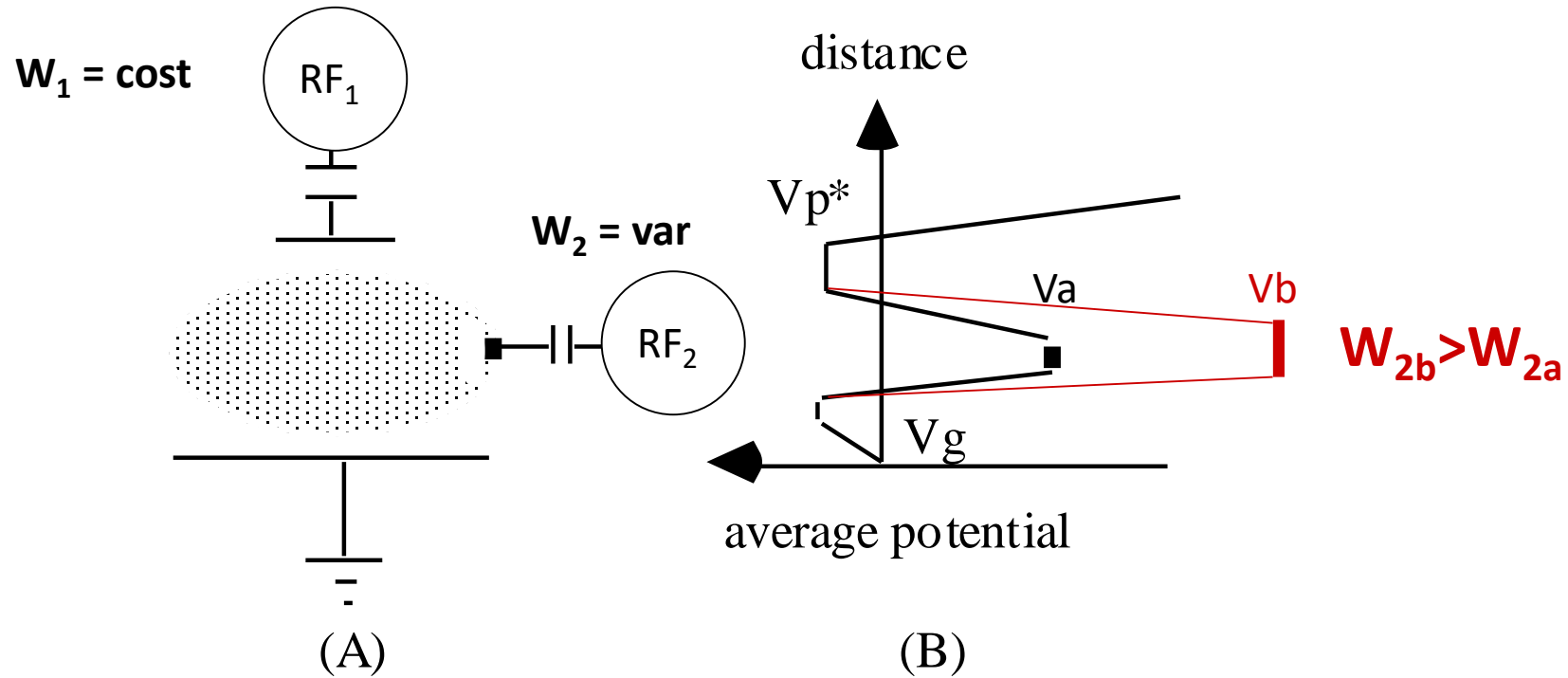
**d (macroscopic, Paschen) is related to the Debye length (microscopic)**

**d must avoid discharge ignition with arcs and sparks**

**$P \uparrow$     $d \downarrow$**

**$w \uparrow$     $d \downarrow$**

the surface potential of insulators can be tuned  
with an additional RF power supply

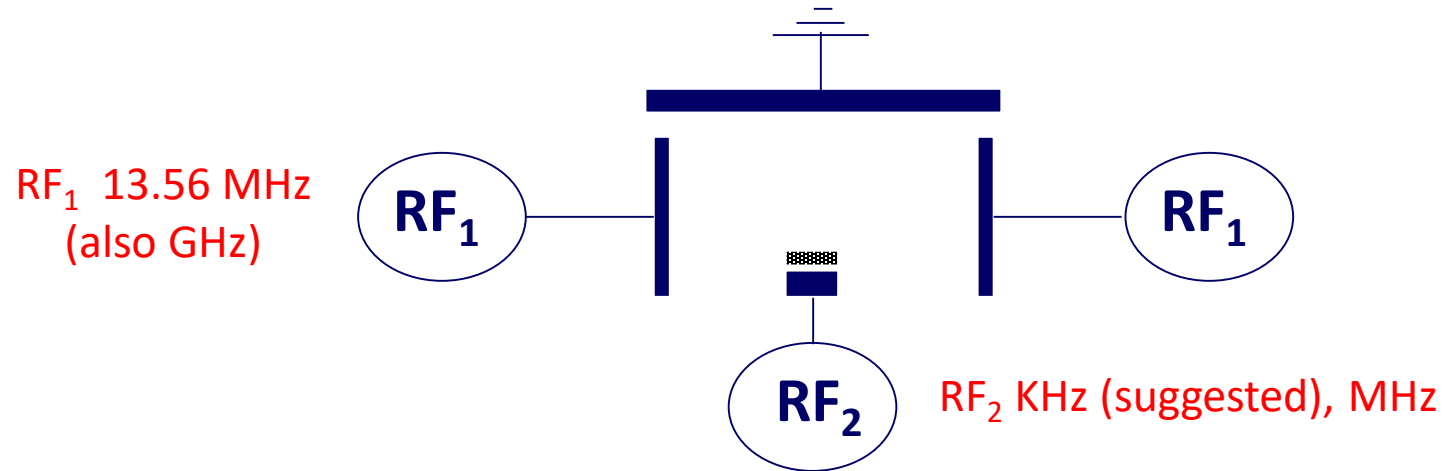


$$W_1 \gg W_2$$

**TRIODE  
REACTOR**

# DUAL FREQUENCY TRIODE REACTORS

THE ION BOMBARDMENT CAN BE TUNED INDEPENDENTLY FROM OTHER PARAMETERS



to reduce plasma perturbations the substrate electrode must be as small as possible

higher frequency  
RF MW



Plasma generation  
(low V<sub>p</sub>, high I, high n<sub>e</sub>, N)

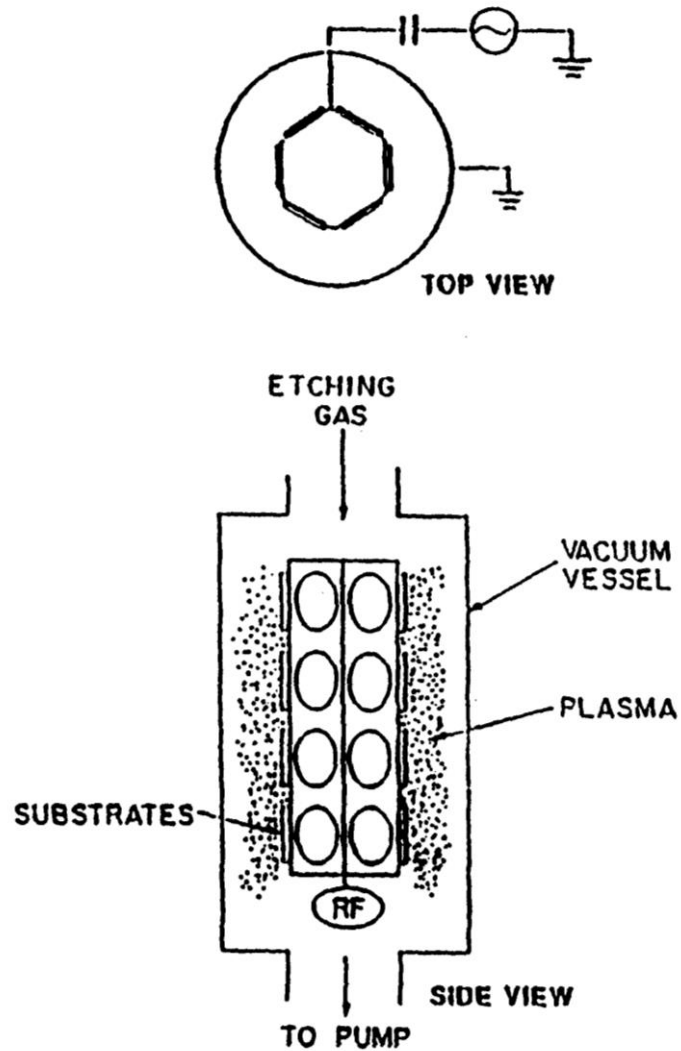
Lower frequency  
AF



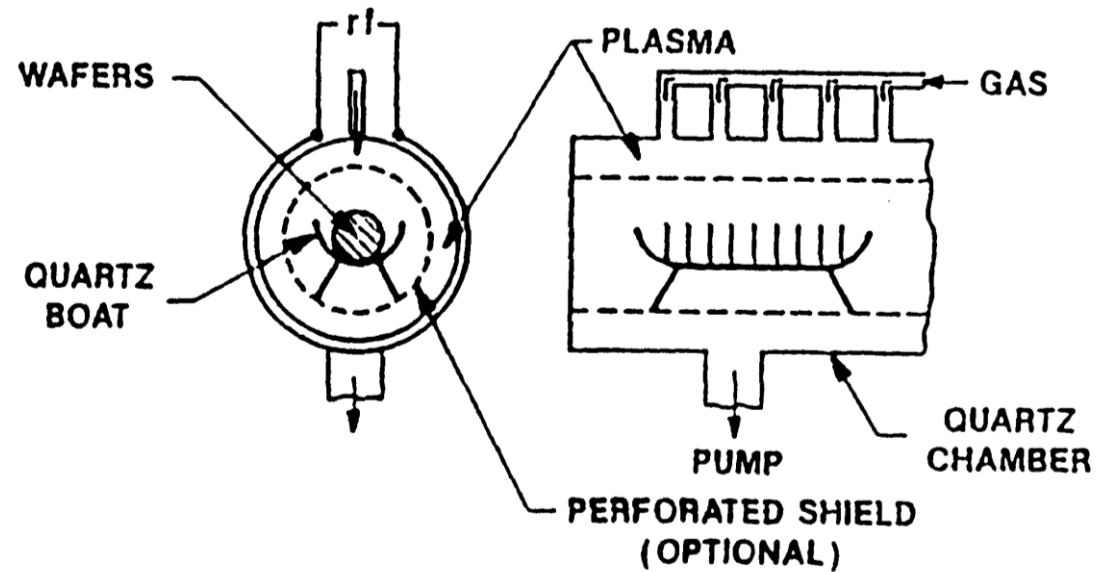
Ion bombardment  
(high V<sub>p</sub>, high V<sub>b</sub>, low I)

# THE HEXODE

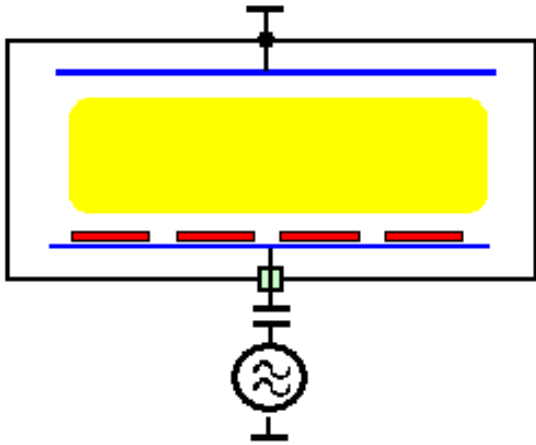
etching processes  
in the 80s



# BARREL REACTORS

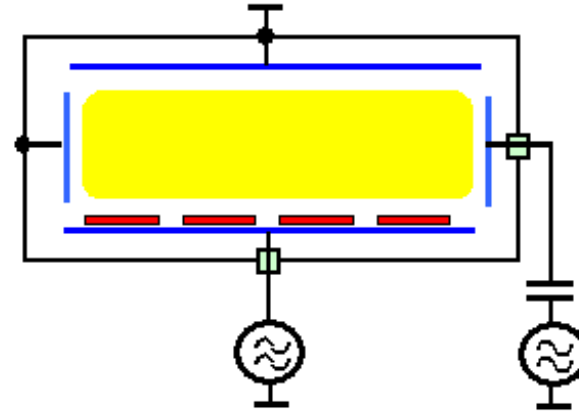


**RIE**

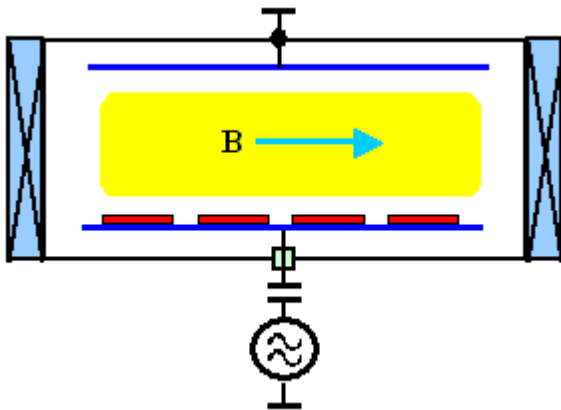


triode

**TRIE**

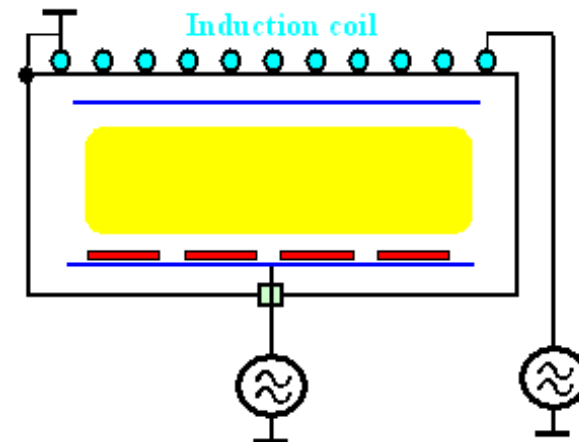


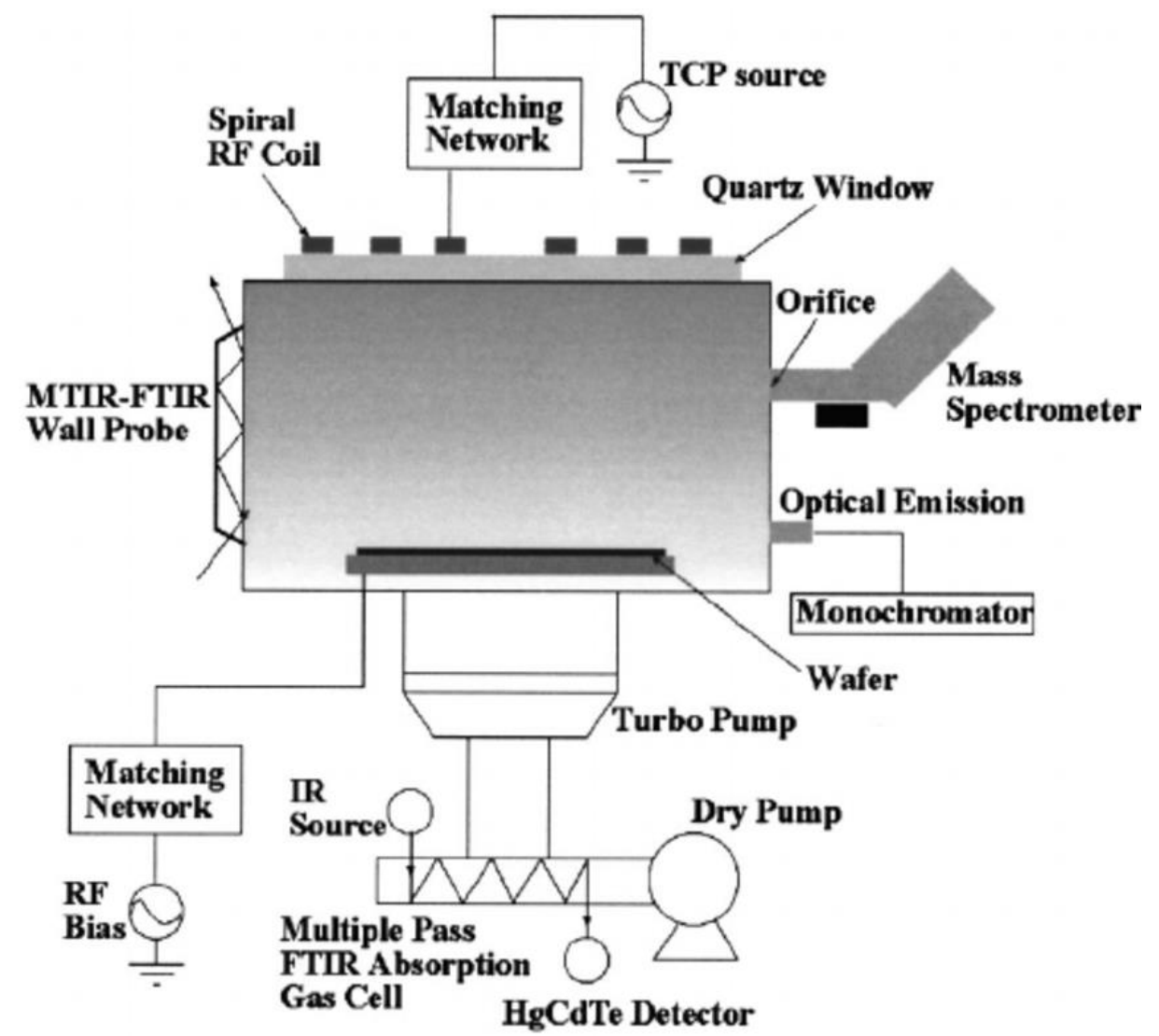
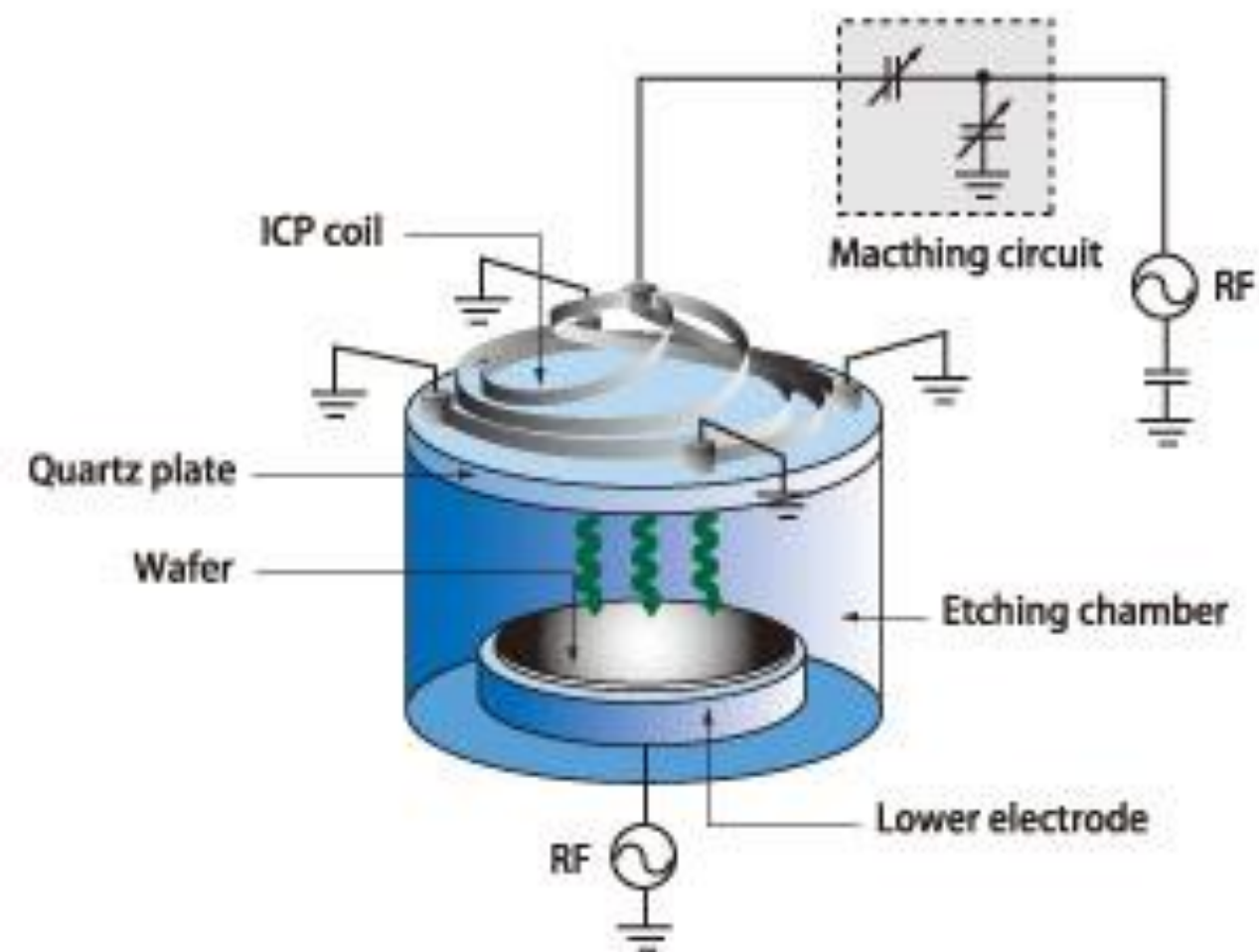
**MRIE**



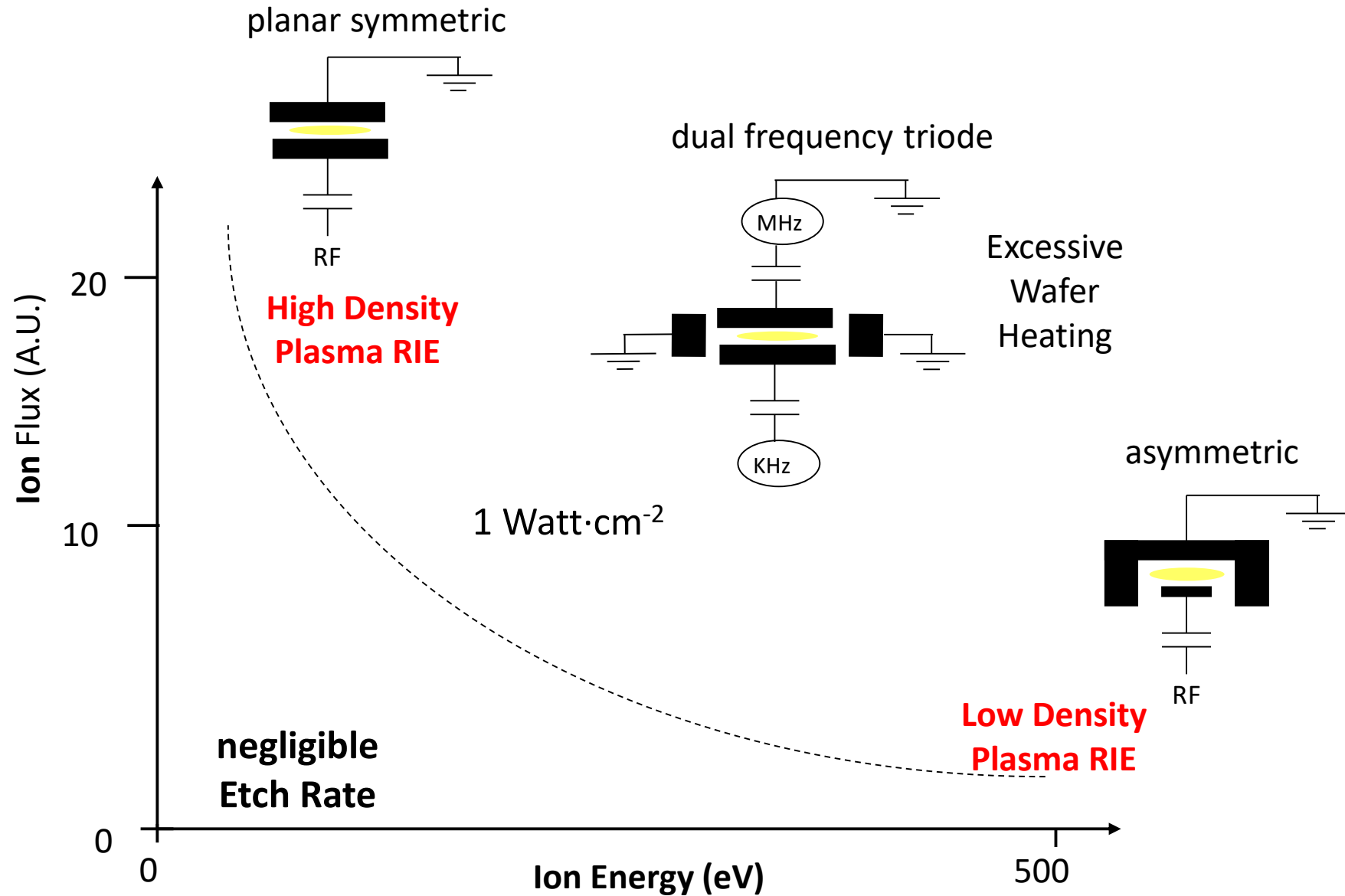
triode

**ICPE**





# ION ENERGY / FLUX POSSIBILITIES IN RIE





## ECR PLASMA (Deposition)

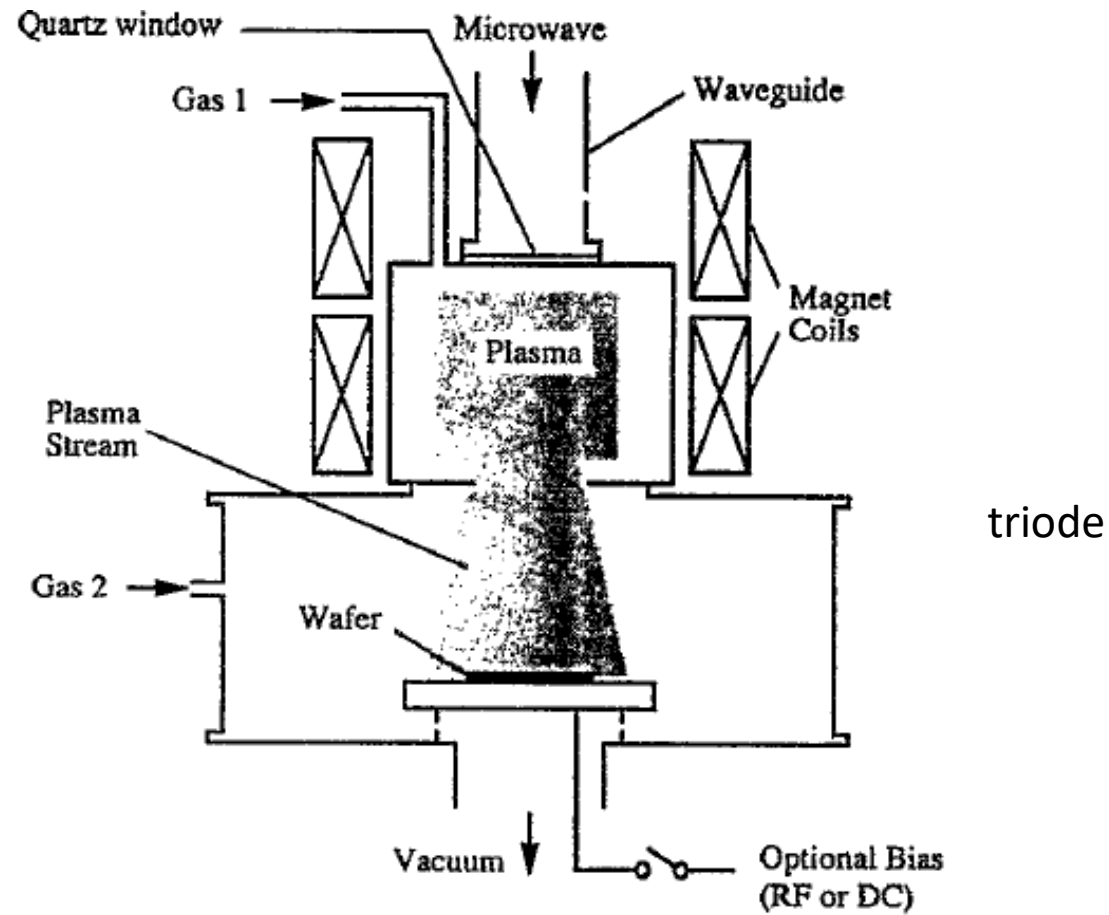
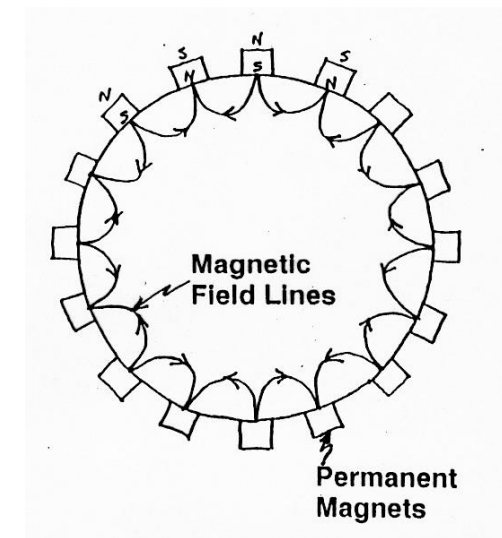
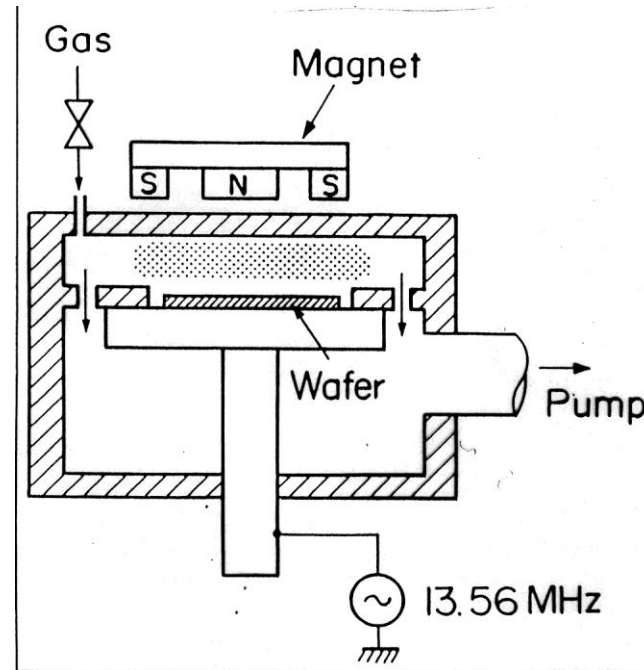


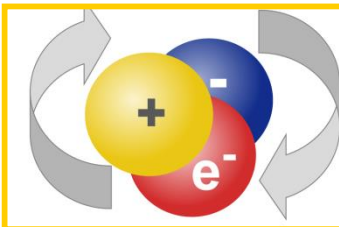
FIG. 7. Schematic of an ECR plasma source (reprinted with the permission of Plenum Press).

### Industrial applications of low-temperature plasma physics\*

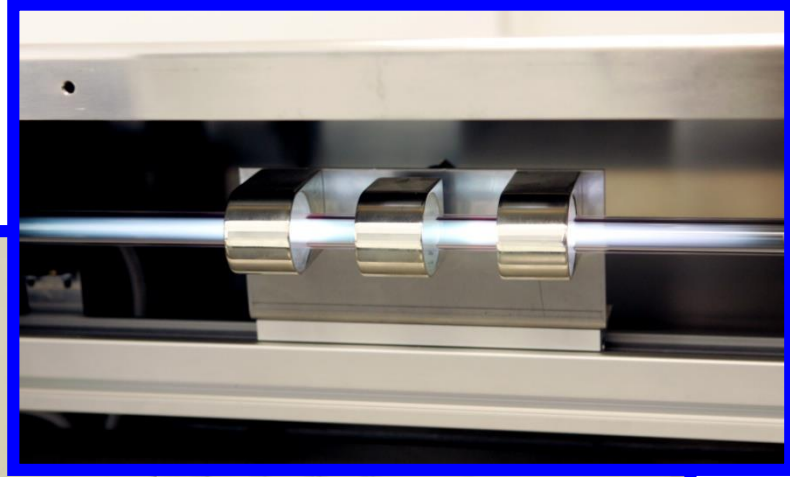
Francis F. Chen<sup>†</sup>  
*University of California, Los Angeles, California 90024-1594*

# MAGNETRON

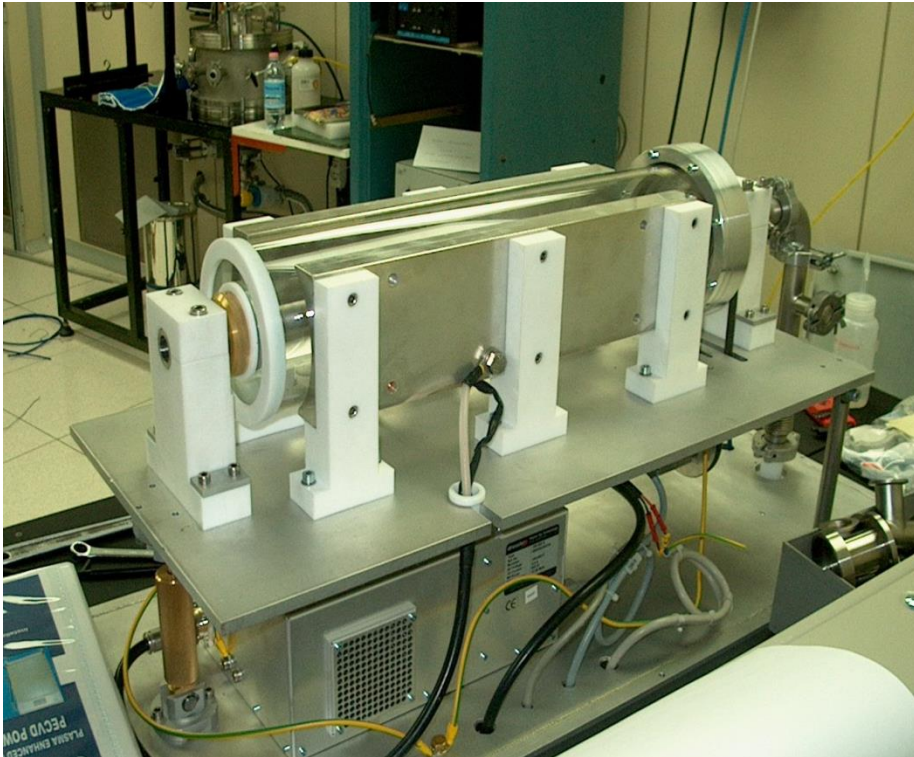




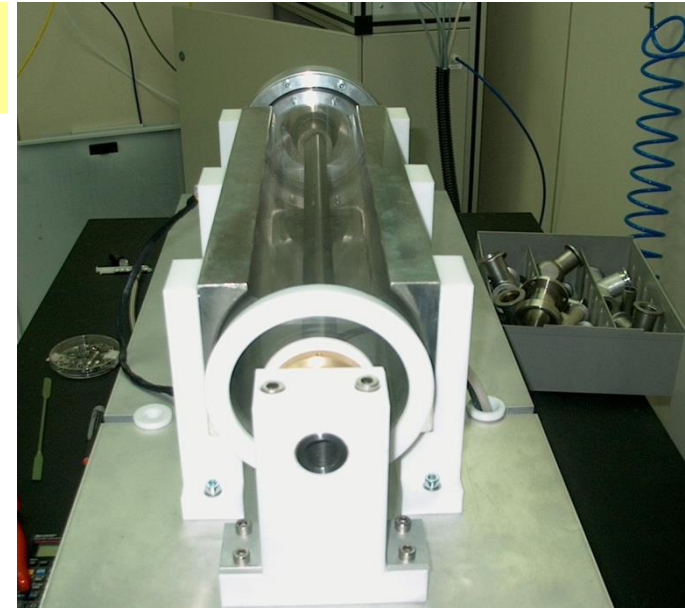
**PLASMA SOLUTION srl**  
spin off dell'Università di Bari



# ROTATING REACTOR FOR GRANULES

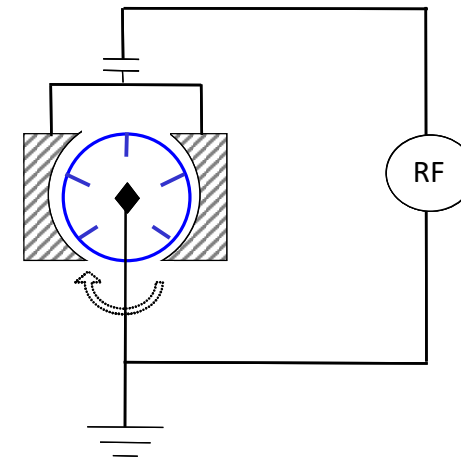


side view



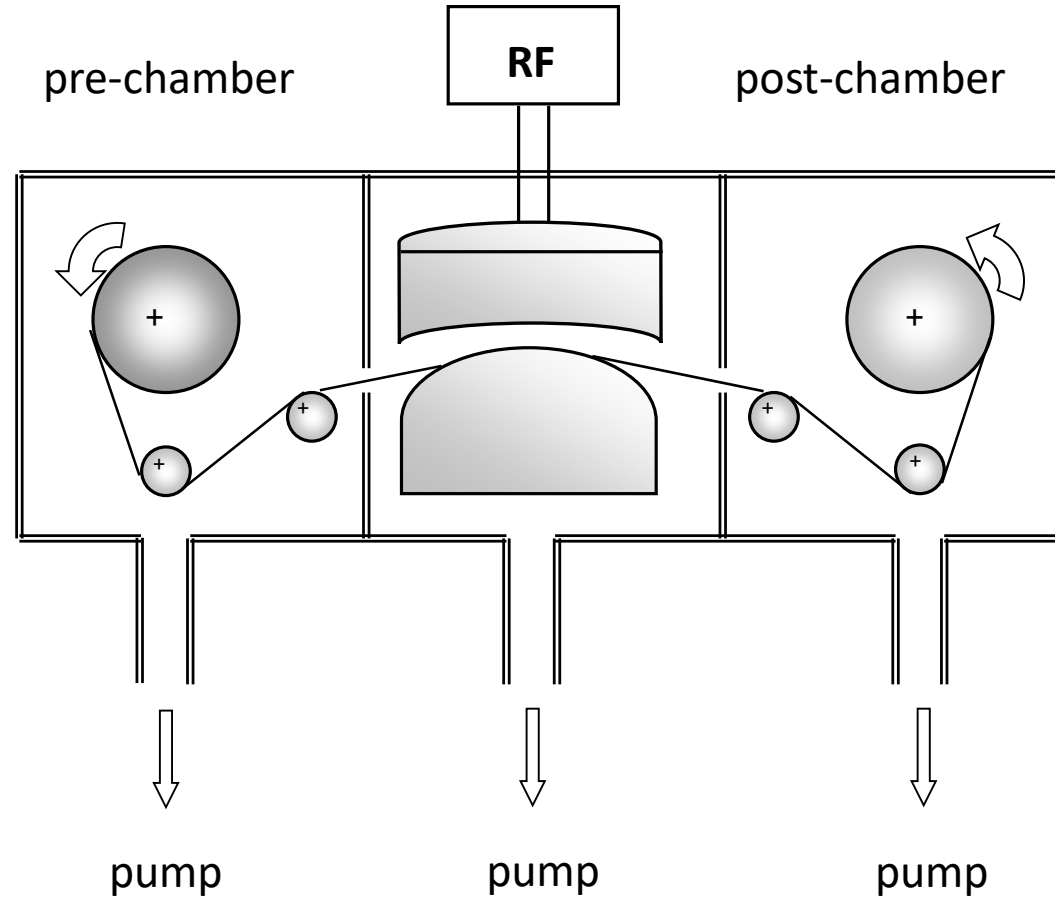
top view

Internal wing system to keep granules stirred during the process



# WEB COATING

## roll-to roll reactors



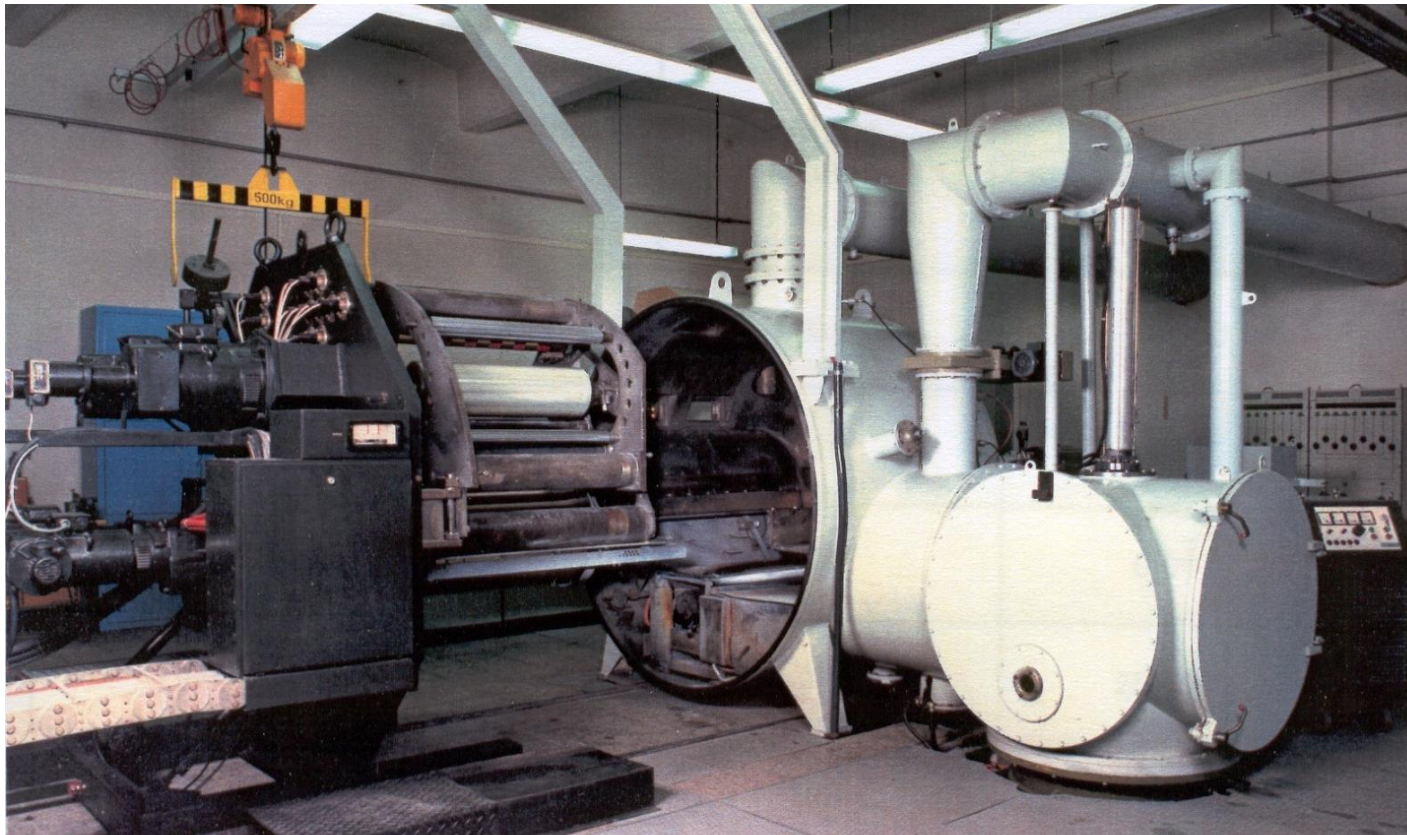
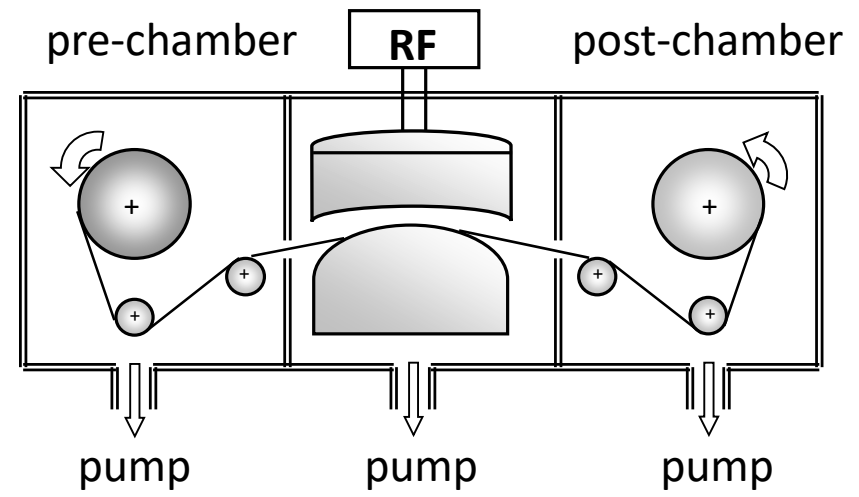
### ADVANTAGES

LOW COST PUMPS  
VERSATILITY OF TREATMENTS  
REDUCED MAINTENANCE

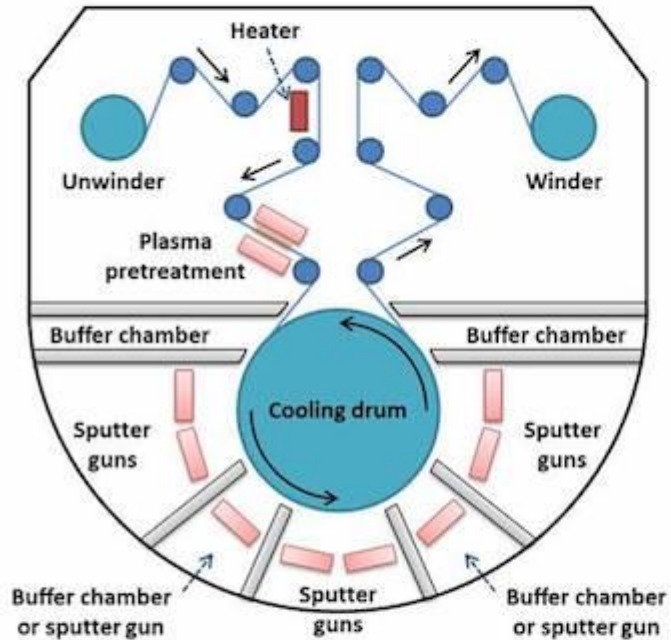
### DISADVANTAGES

LONG LOADING  
LONG WEB INSPECTION

# PLASMA REACTORS: industrial web coater

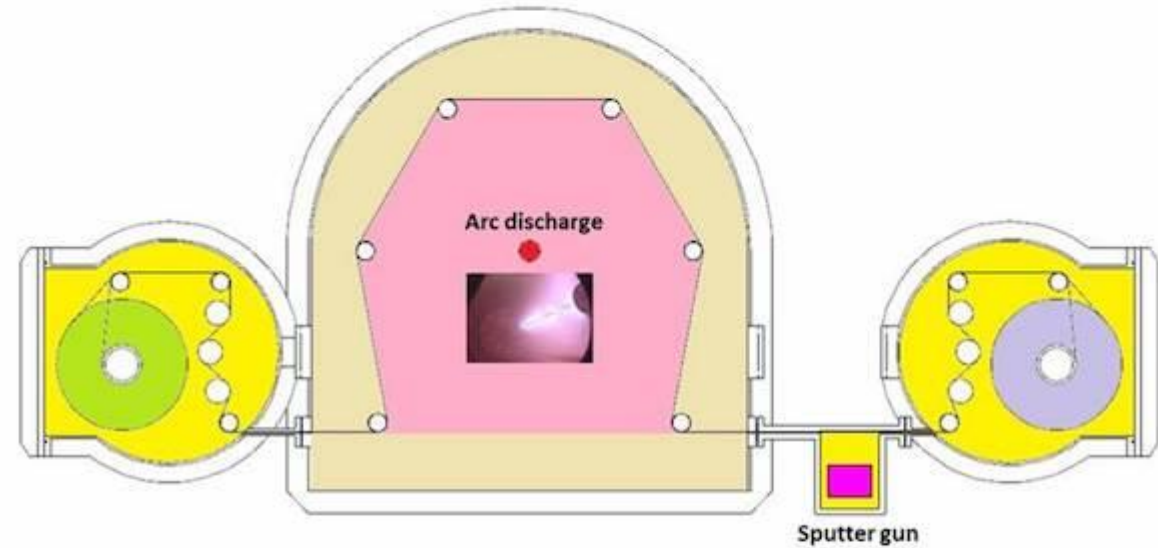


## Conventional



VS.

## RollInCoat

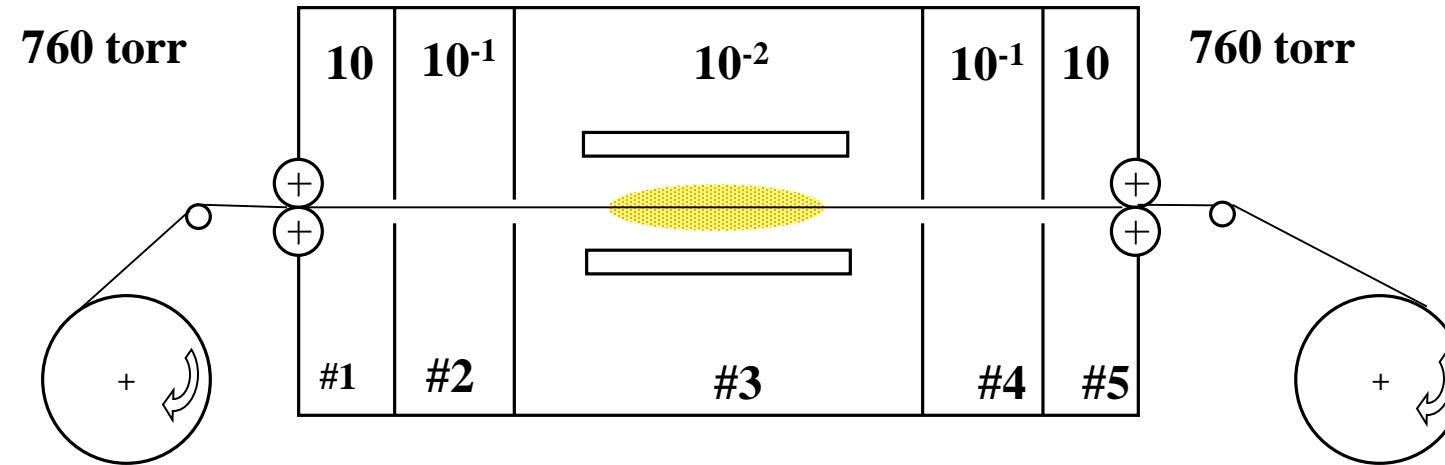


- Conventional magnetron sputtering
- Complicated structure, high cost > \$7,000,000
- Expensive target, low utility 30%
- Unstable reactive sputtering

- Patented hybrid plasma modular coating
- Simple structure, low cost ≈ \$1,200,000
- Cheap target, high utility 70%
- Stable reactive arc deposition

# WEB COATING AND TREATMENTS

# AIR-VACUUM-AIR



## ADVANTAGES

easy web inspection

loading without breaking vacuum

## DISADVANTAGES

degassing and leaking

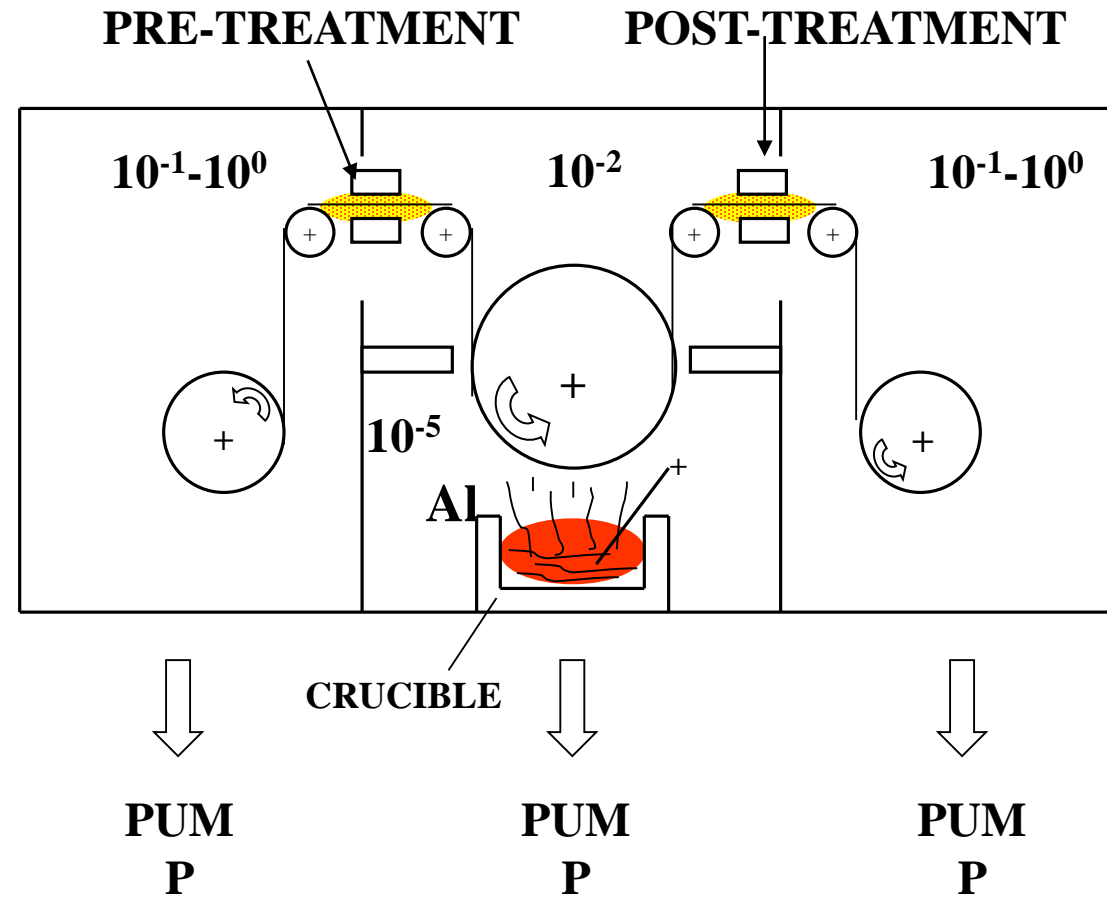
high pump cost

frequent maintenance

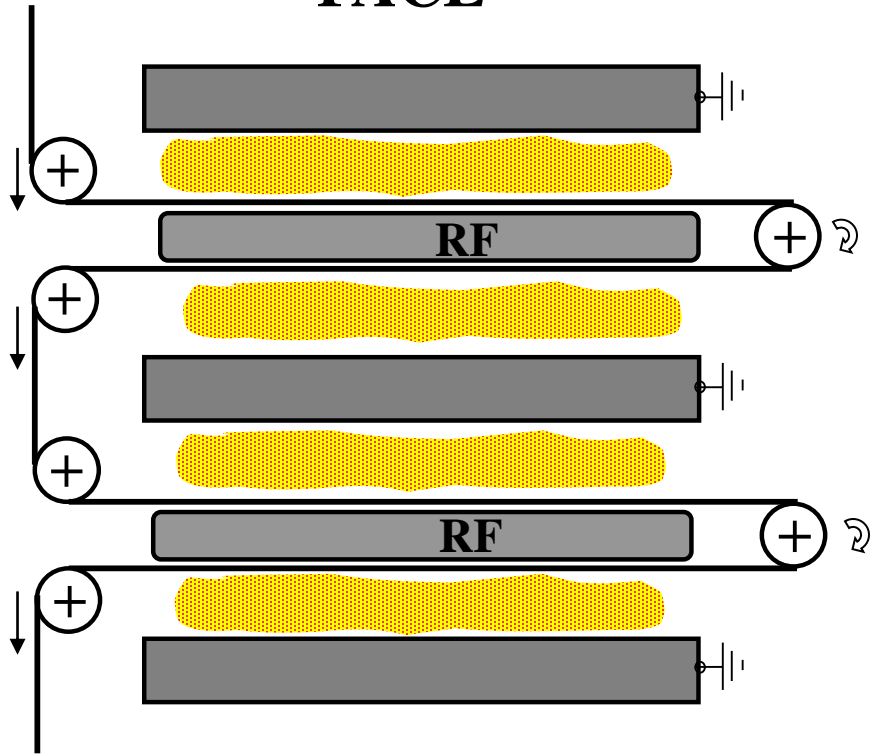
limited to air and O<sub>2</sub> treatments



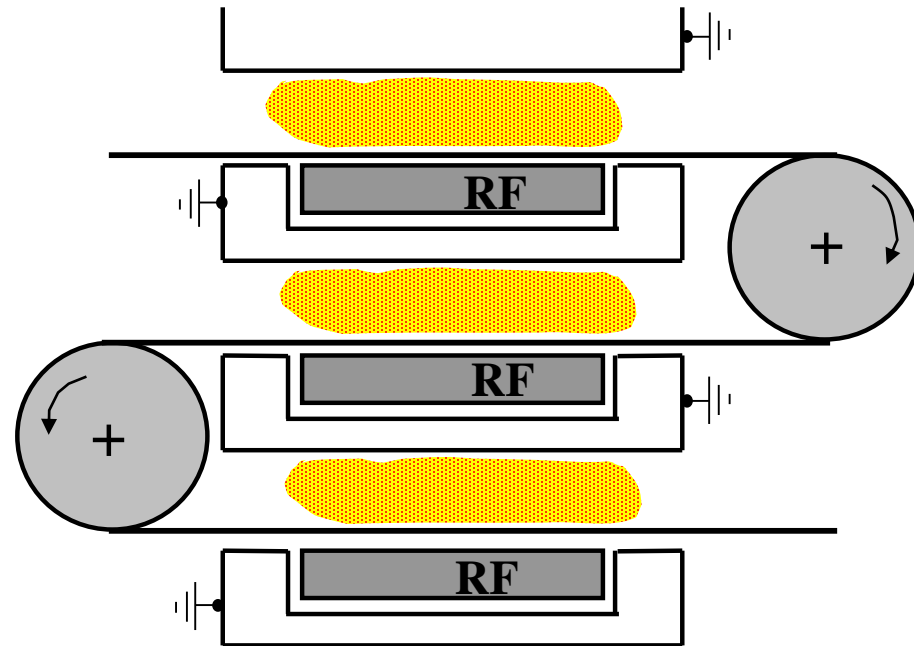
# PLASMA ASSISTED METALLIZATION



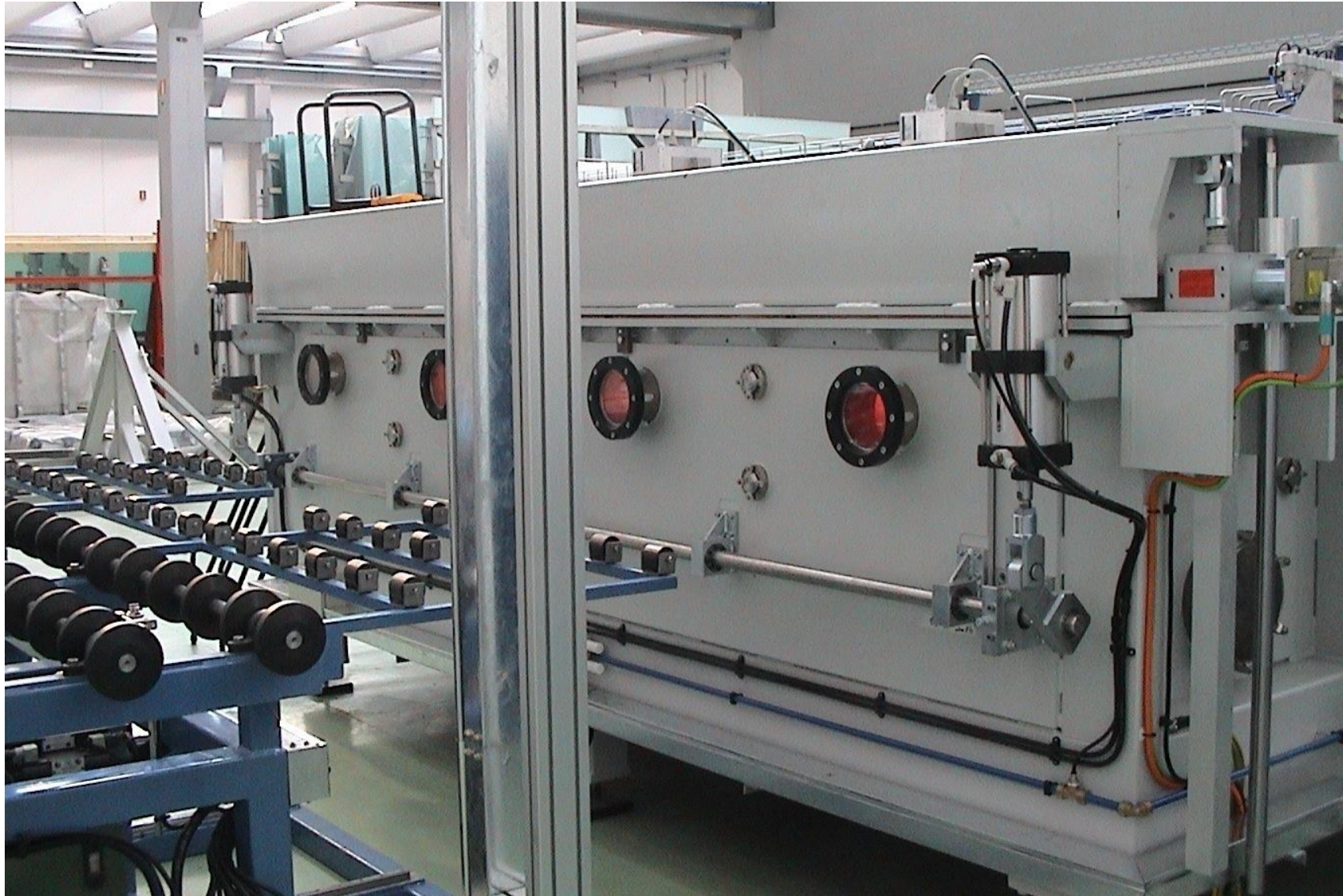
## MULTIPLE SINGLE FACE



## MULTIPLE DOUBLE FACE



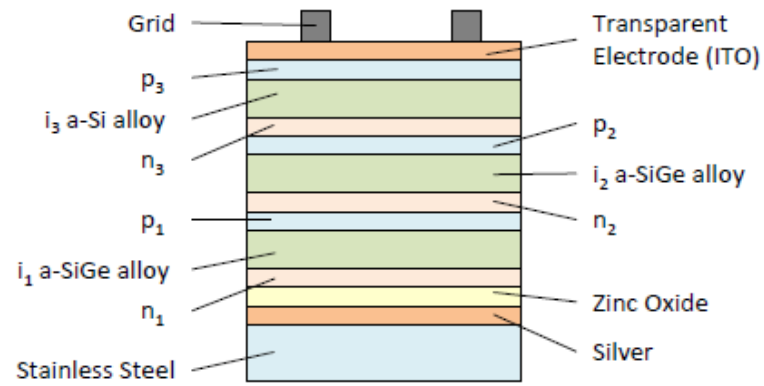
## LARGE SCALE PLASMA REACTORS



self-cleaning layers on glass → buildings



Industrial deposition system for the fabrication of DLC coatings for automotive parts and other applications. Each chamber contains six 1.6 m long electrodes.  
**(Courtesy of Hauzer Techno Coatings)**



**Triple-junction solar cell**  
 S. Guha, J. Yang, J. Non-Cryst. Sol. 2006



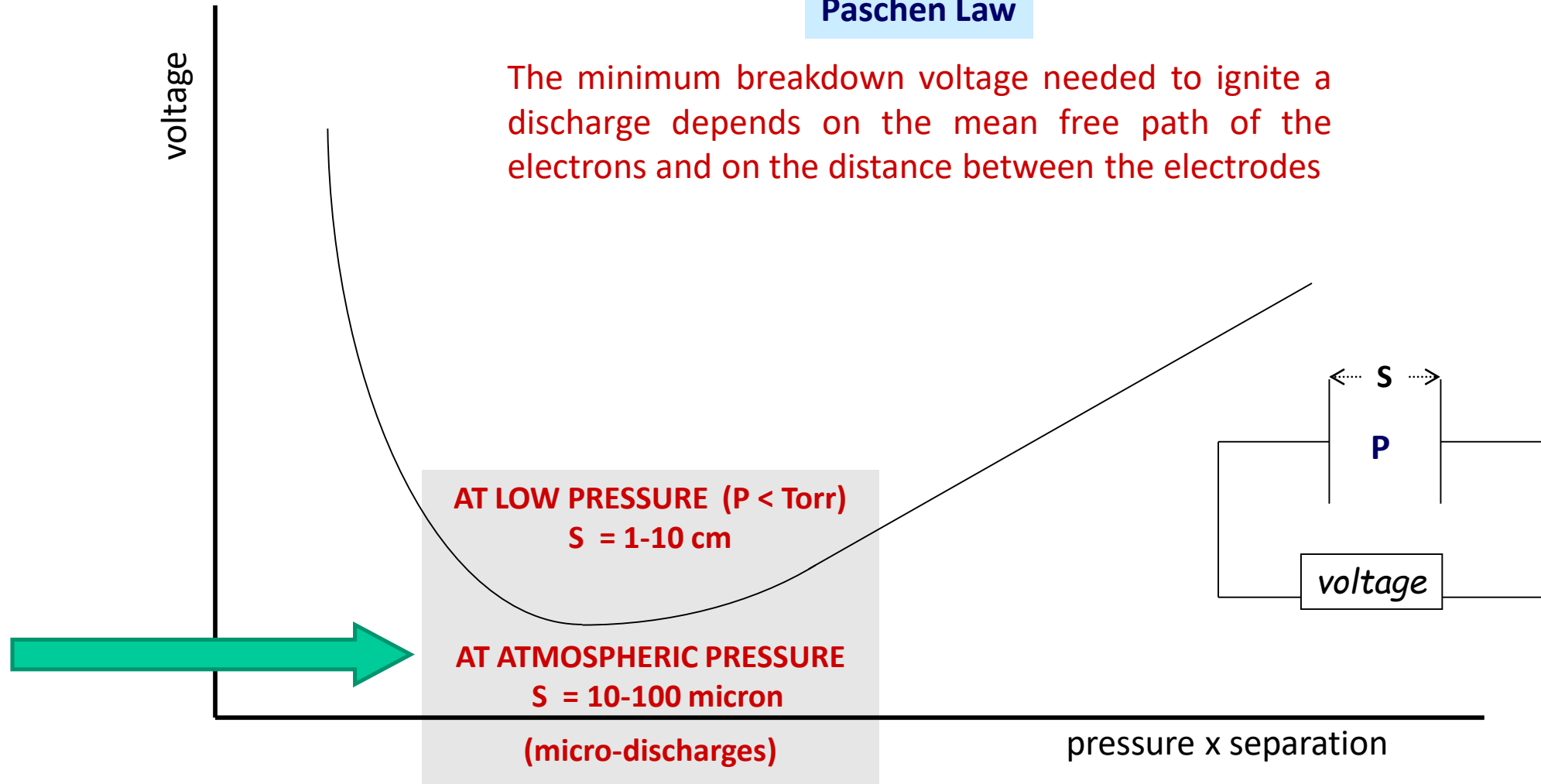
**Large area roll-to-roll deposition system for the fabrication of triple-junction photovoltaic cells: 2,500m long, 36 cm wide and 125  $\mu\text{m}$  thick SS foils; 4 compartments: a) washing, b) back reflector sputtering (Al, ZnO), c) PECVD of 9-layer triple junction – nc-Si and SiGe, d) AR coating – ITO.**

**System: 90m long, 3m tall, web speed 30 cm/min, 14,5 km of solar cells in 72 hrs.  
 (Courtesy of United Solar Ovonic, USA)**



## Paschen Law

The minimum breakdown voltage needed to ignite a discharge depends on the mean free path of the electrons and on the distance between the electrodes



### Low $PxS$

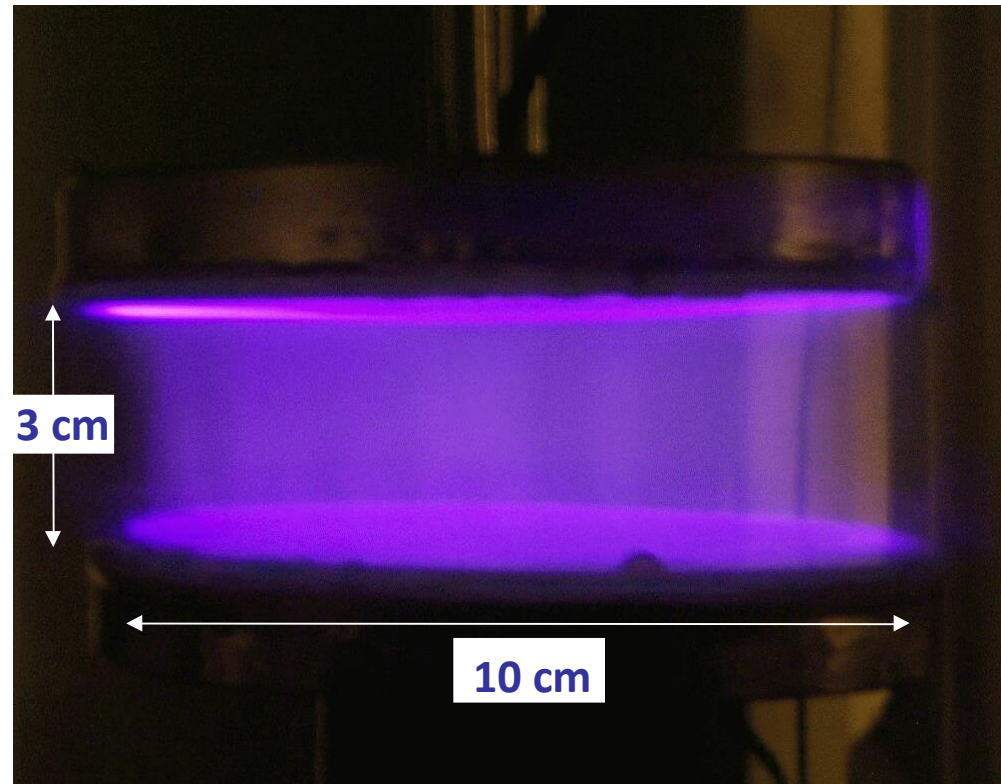
electrons experience not enough ionizing collisions while travelling between electrodes

### High $PxS$

due to the high collision frequency, electrons cannot accelerate enough to provide a minimum number of ionizing collisions

## Atmospheric Pressure REACTORS and SOURCES

M. Laroussi, ODU 1999  
He plus Air  
DBD,  $f = 20$  kHz

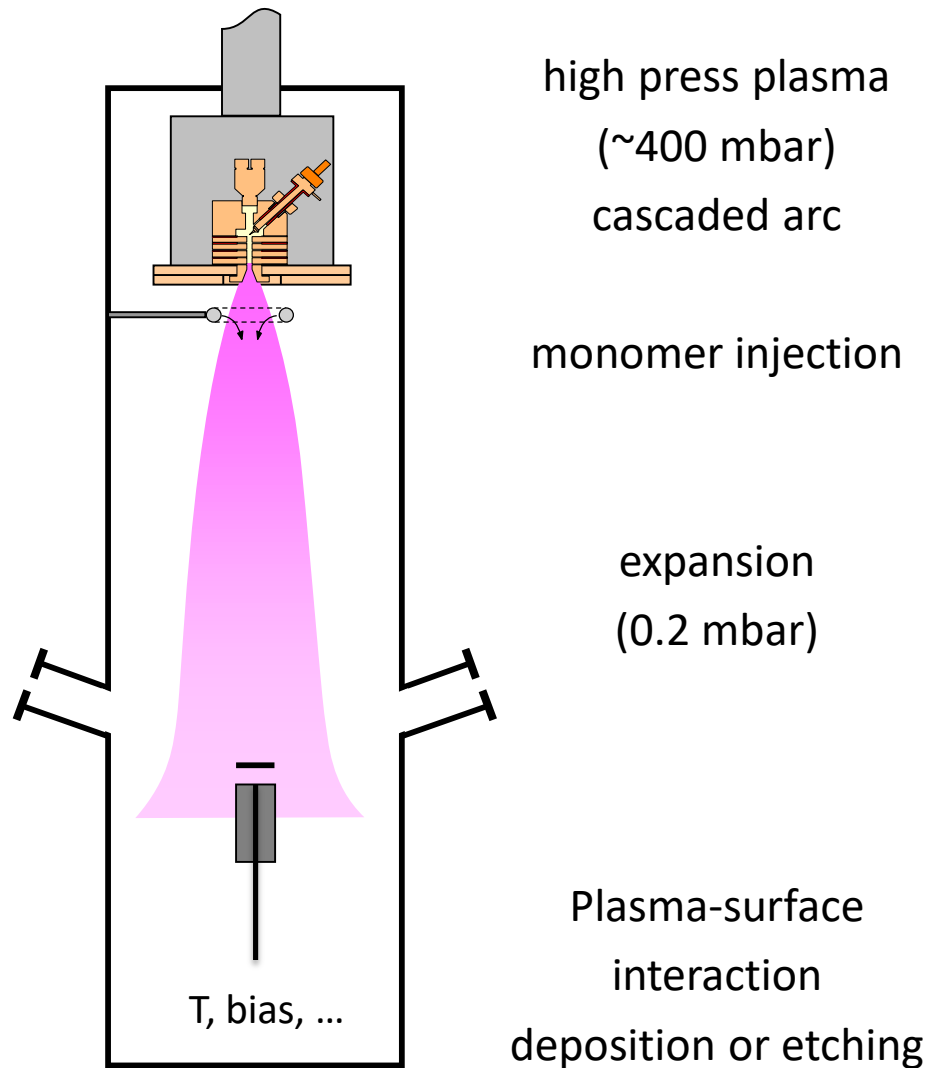




Most applications of non equilibrium plasmas requires that the gas remains at room T. Since the low efficiency and number of elastic collisions at low P limit the energy transfer from free electrons to heavier species, it is quite easy to produce cold Low P gas discharges. With increasing pressure, however, the electron-species collision frequency increases, the energy transfer becomes more efficient, resulting in gas heating and plasma instabilities (e.g., sparks and arcs).

**Many approaches are used to keep the gas cold in Atmospheric P discharges, namely:**

- **sharp electrodes, as in corona discharges**
- **pulsing the plasma;  $\mu\text{s}$ -ns wide plasma pulses;**
- **improved heat transfer; higher flow rates;**
- **using gases (e.g., He) with high thermal conductivity;**
- **reduce the size of plasmas (e.g., micro-discharges);**
- **reduce the current with dielectric layers on the electrodes, as in Dielectric Barrier Discharges (DBD)**



*Courtesy of Prof. M.C.M. "Richard" Van de Sanden, TUE, Eindhoven*

# The Expanding Plasma, PECVD of $\alpha$ -Si:H

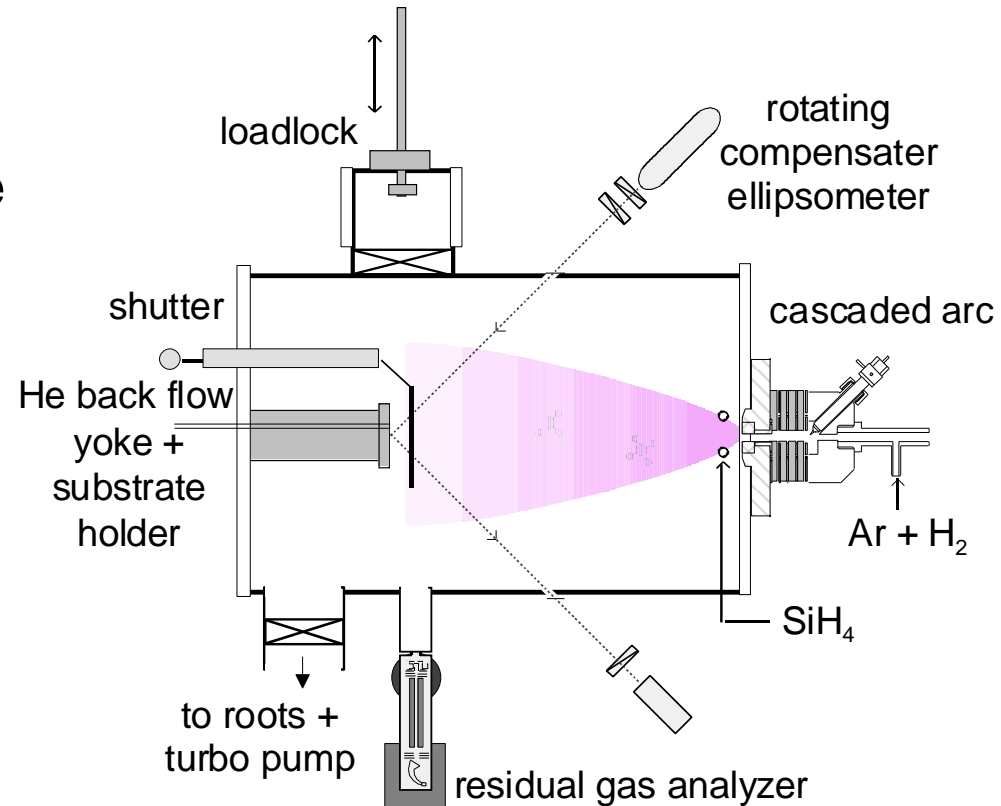
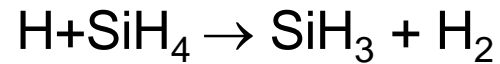
12

Real remote plasma:

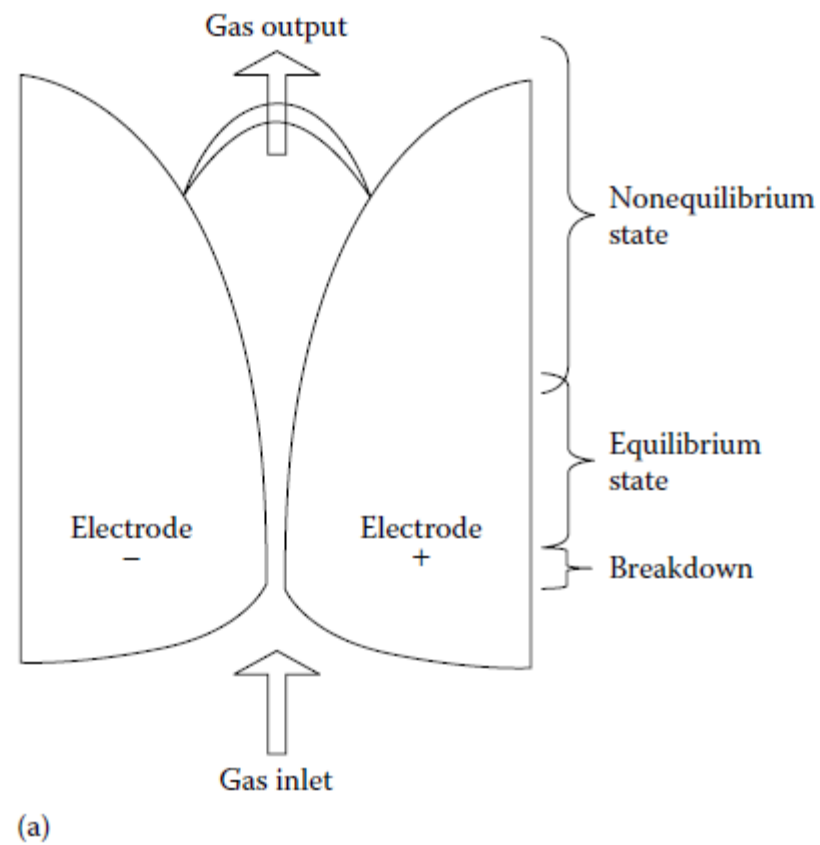
Expansion of high-pressure  
Ar-H<sub>2</sub> plasma into low-pressure  
reactor → SiH<sub>4</sub> dissociation

Large parameter range

Optimized conditions:

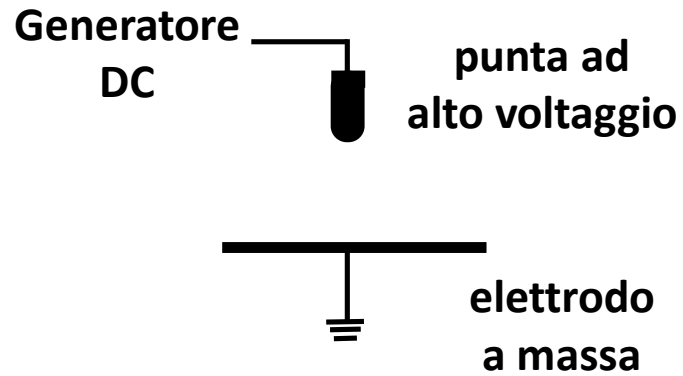


Very high deposition rates: 10 nm/s. 400 nm within 1 minute!



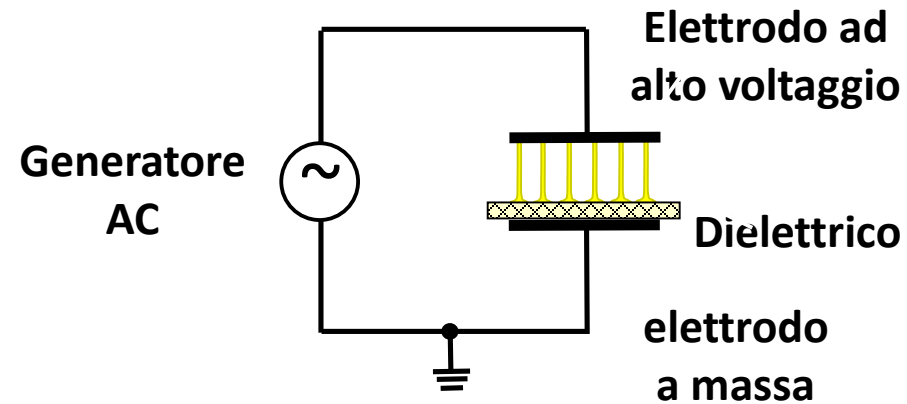
**FIGURE 2.10** (a) Gliding arc electrode configuration with indication of the LTE and non-LTE region. (b) Superposition of snapshot images of a gliding arc discharge that illustrates the dynamic movement of the arc. (Reprinted with permission from Fridman, A., *Plasma Chemistry*, Cambridge University Press, Cambridge, 2008, © Cambridge University.)

## Corona Discharges

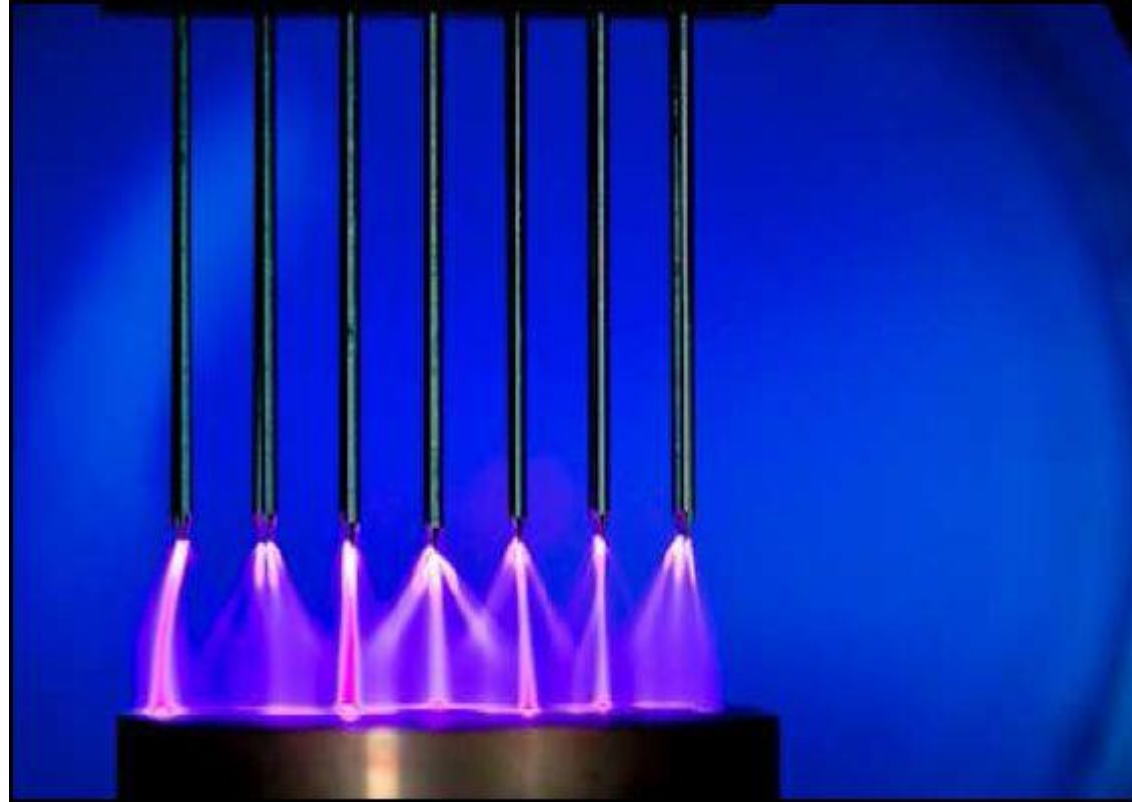


- **elettrodi asimmetrici** per stabilizzare la scarica.
- **alti voltaggi, corrente continua**
- scarica omogenea, localizzata all'elettrodo piccolo, ad alto voltaggio, estesa verso l'elettrodo a massa.  
**forte disomogeneità spaziale**

## Dielectric Barrier Discharges DBD



- almeno uno strato **dielettrico** fra gli elettrodi metallici.
- **alti voltaggi, corrente alternata**
- **microscariche** ( $\sim 10$  ns,  $r \sim 0.1$  mm) distribuite omogeneamente nello spazio e nel tempo su tutto l'elettrodo:  
**FILAMENTARY DBD**
- In opportune condizioni è possibile ottenere scariche omogenee come a bassa pressione: **GLOW DBD**



**multi-tip pulsed corona discharge tested at LAPLACE-PRHE Laboratory.**



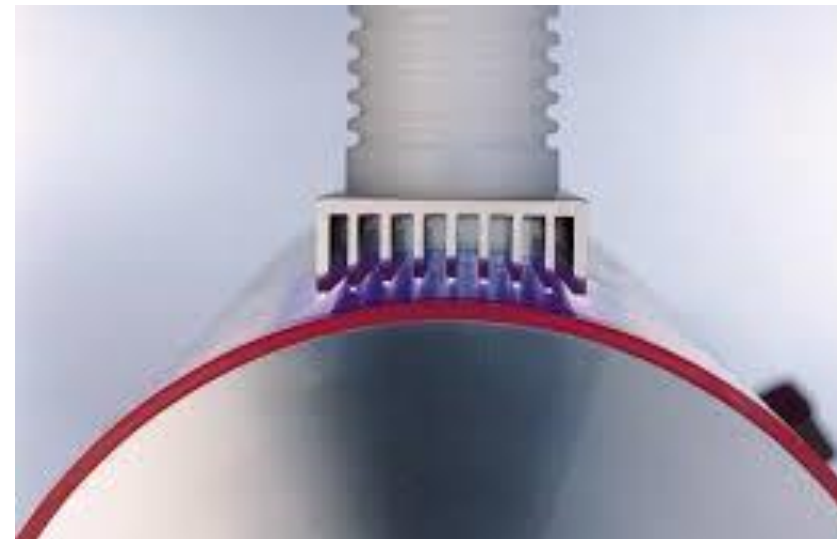
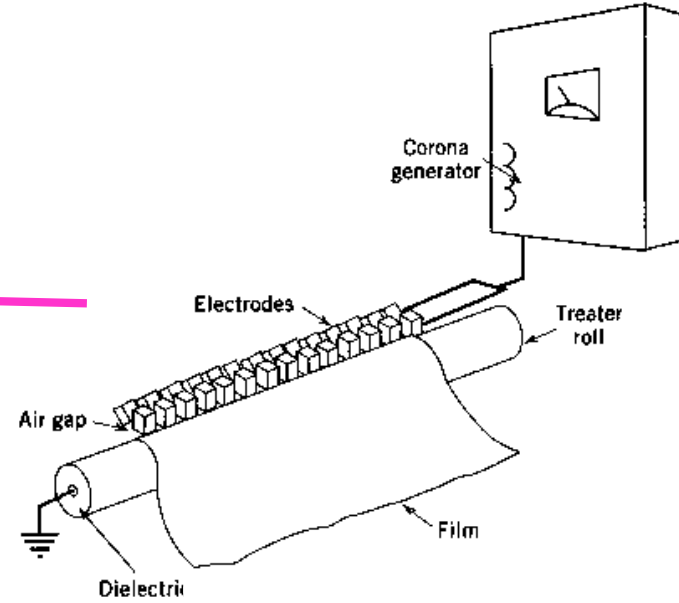
## **CORONA DISCHARGES IN AIR**

**ACTIVATION OF POLYMERS  
TO  
PRINTABILITY  
GLUEABILITY  
DYEABILITY  
WETTABILITY**



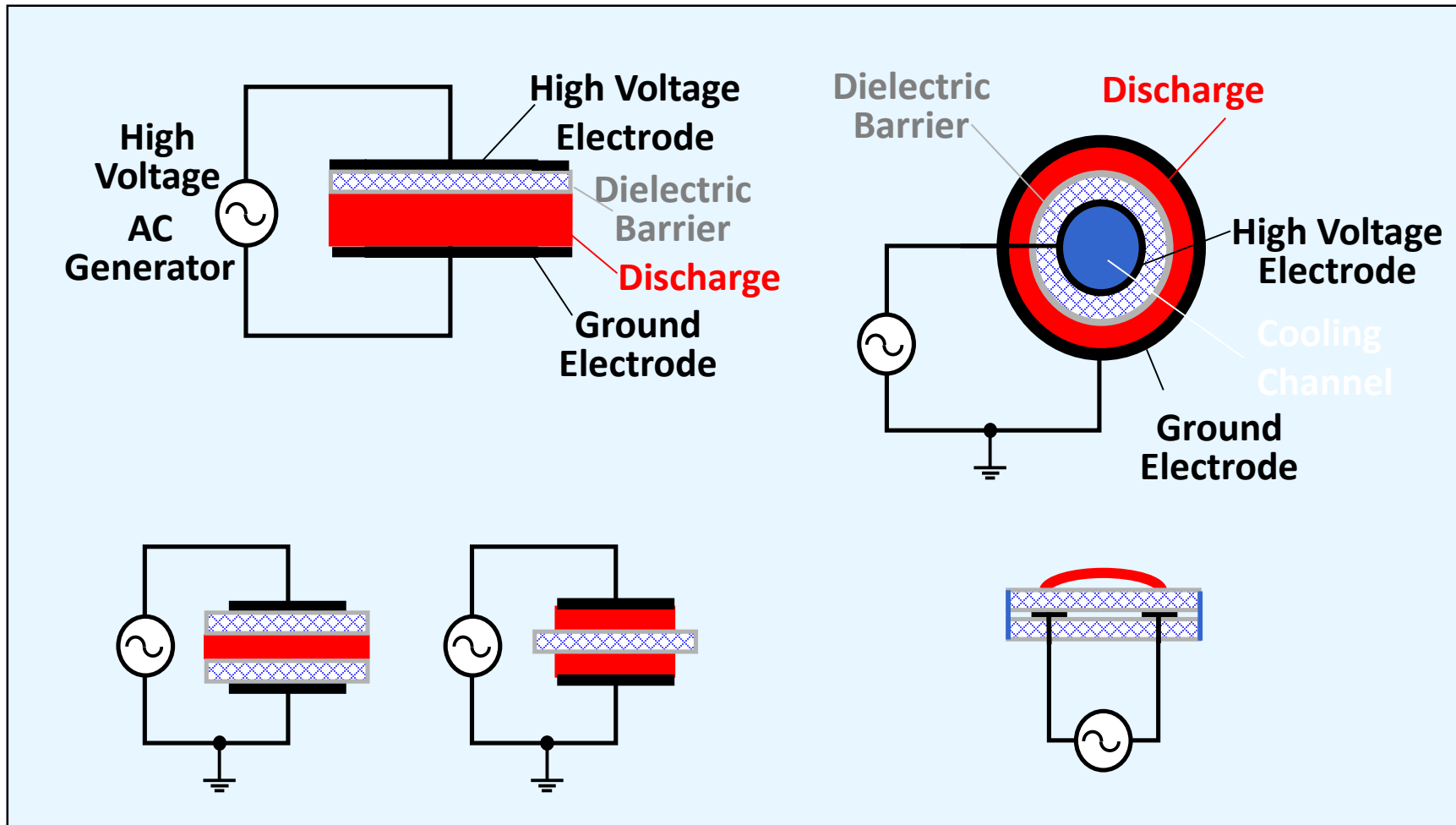
# Modifica superficiale di materiali

Trattamento di web polimerici per incrementarne bagnabilità e proprietà adesive



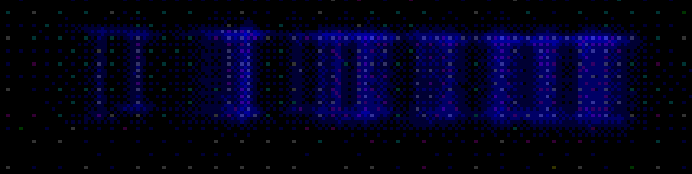
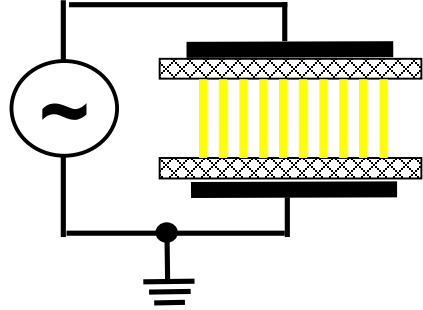


# Dielectric Barrier Discharge (DBD) Configurations

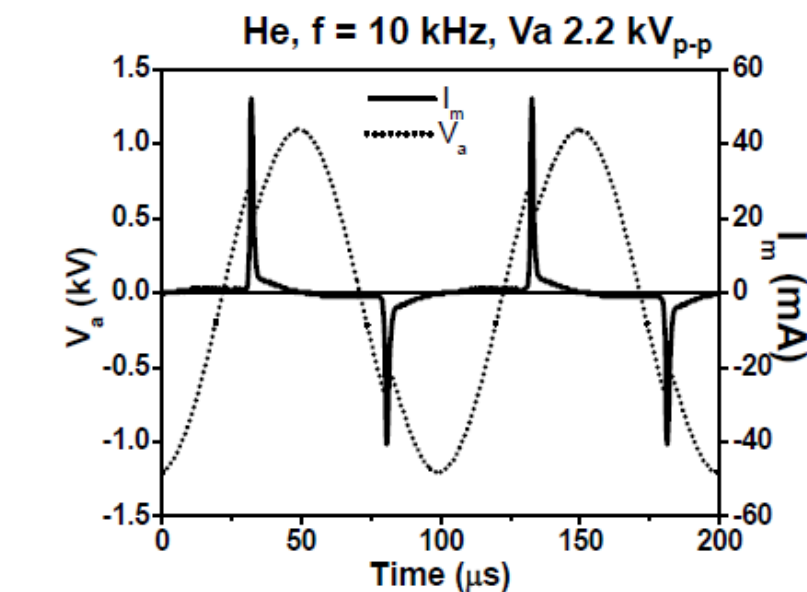
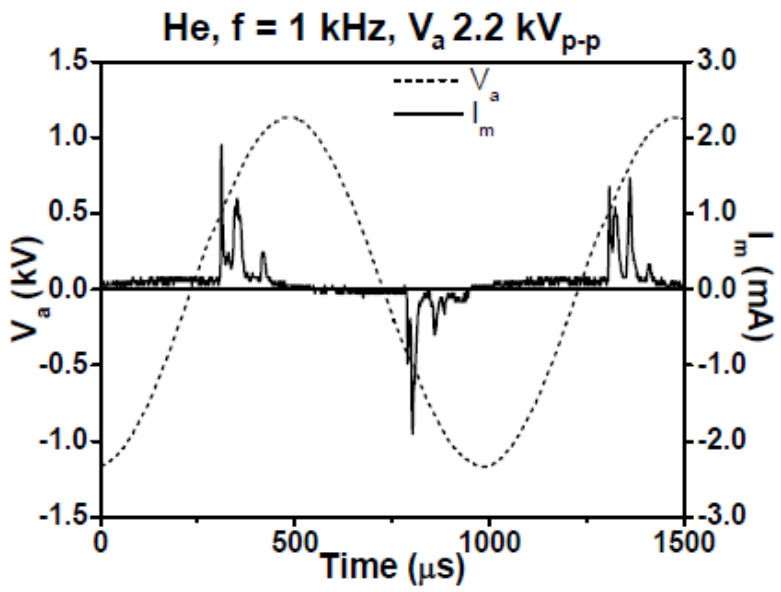
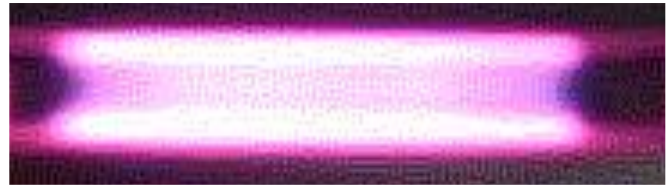
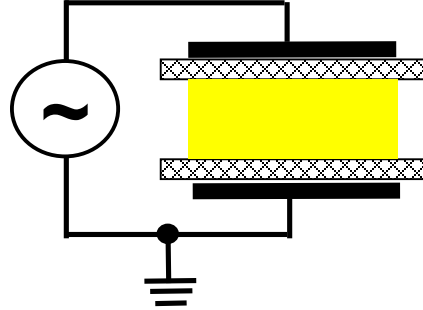


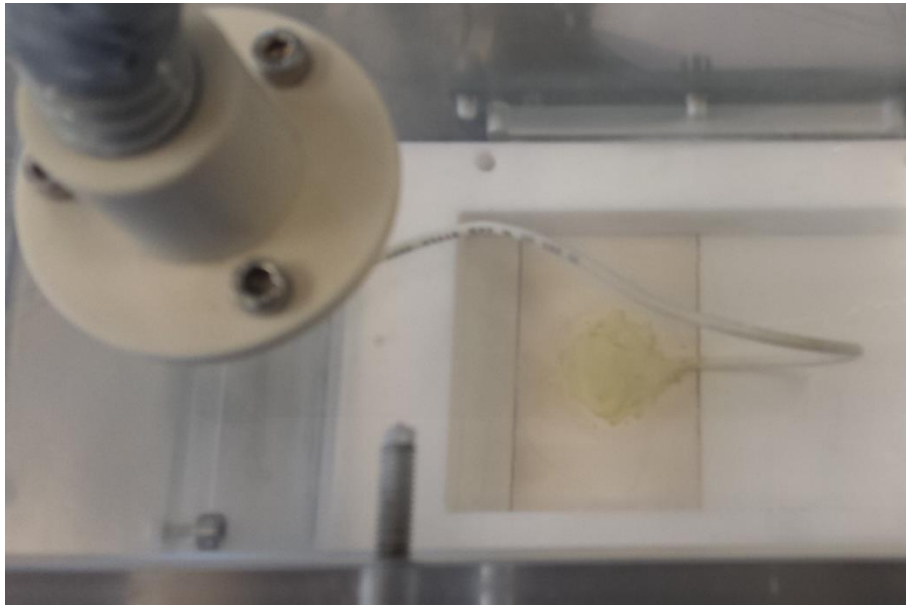
# REGIMI DI SCARICA

Filamentary discharge FDBD

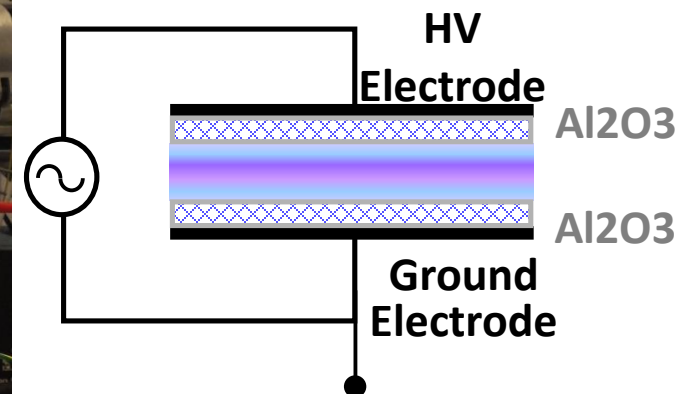
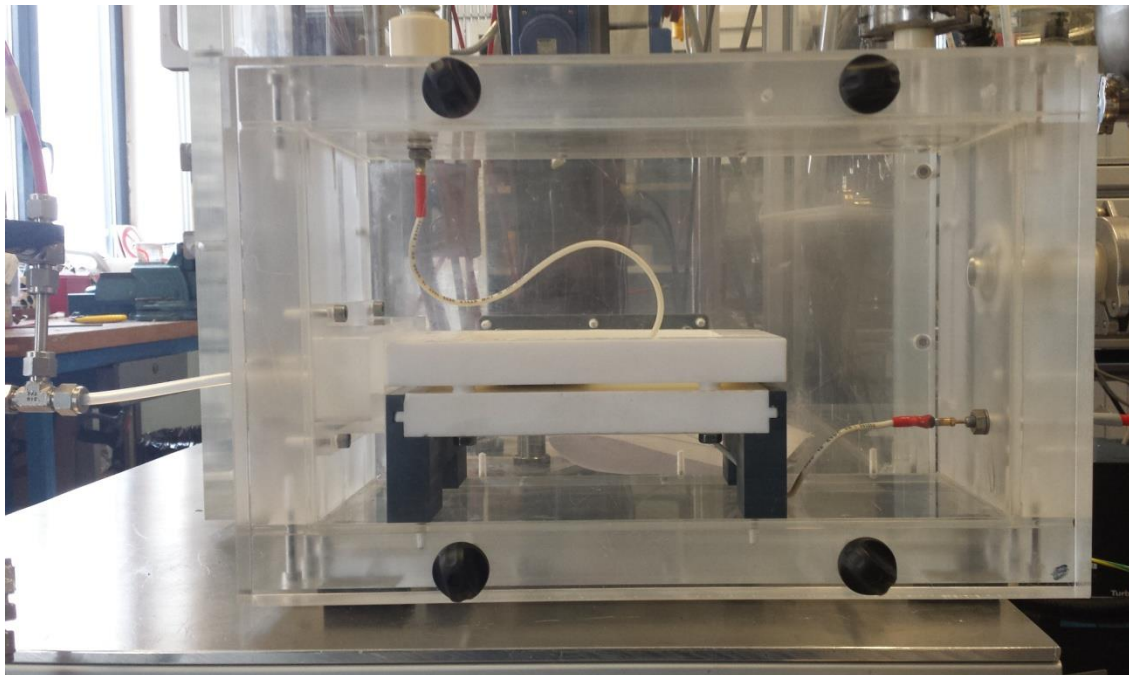
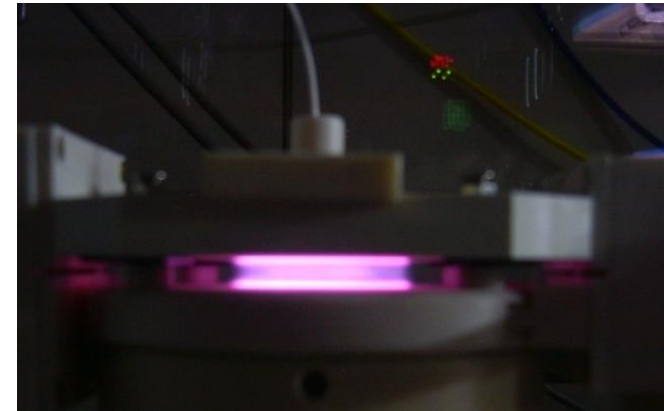


Glow discharge GDBD

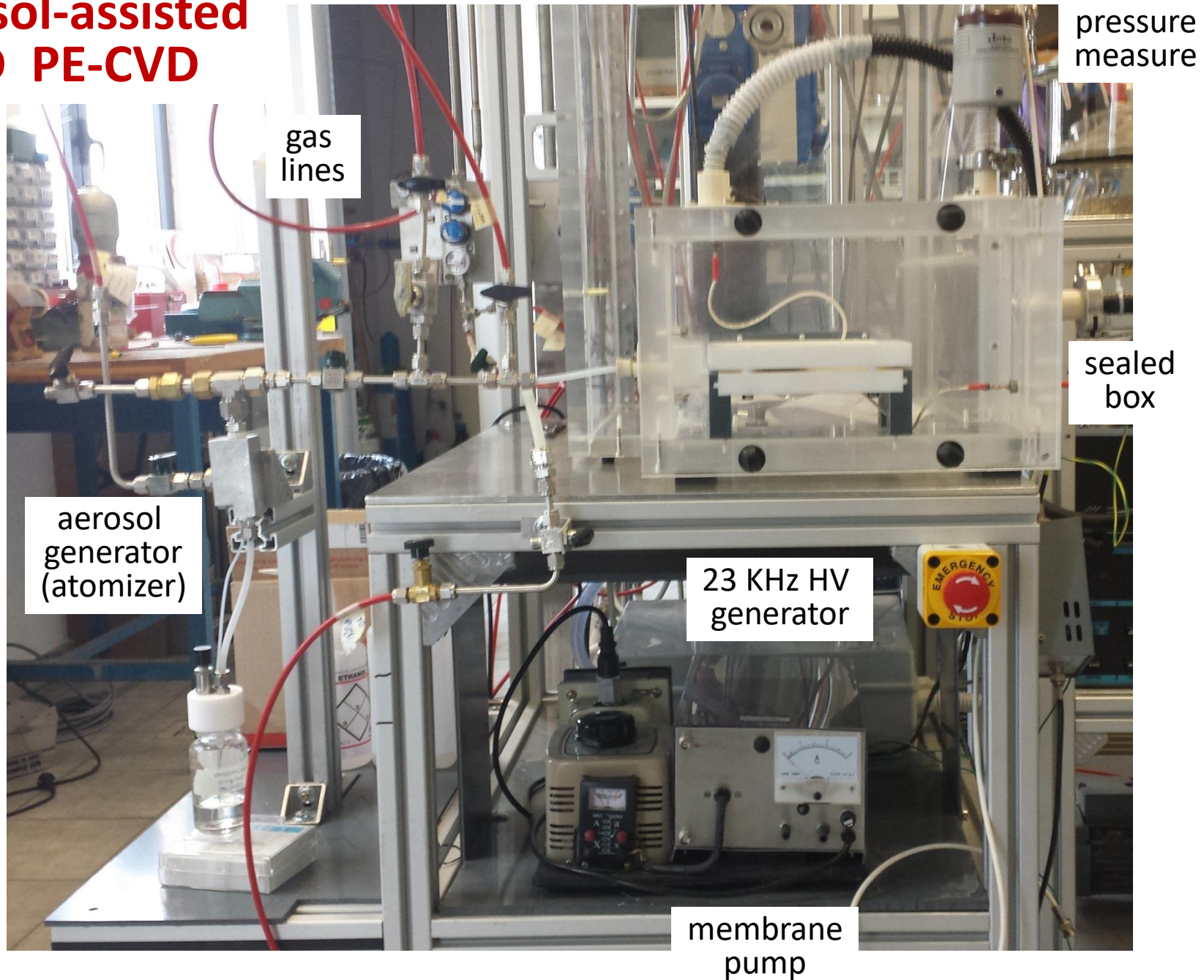


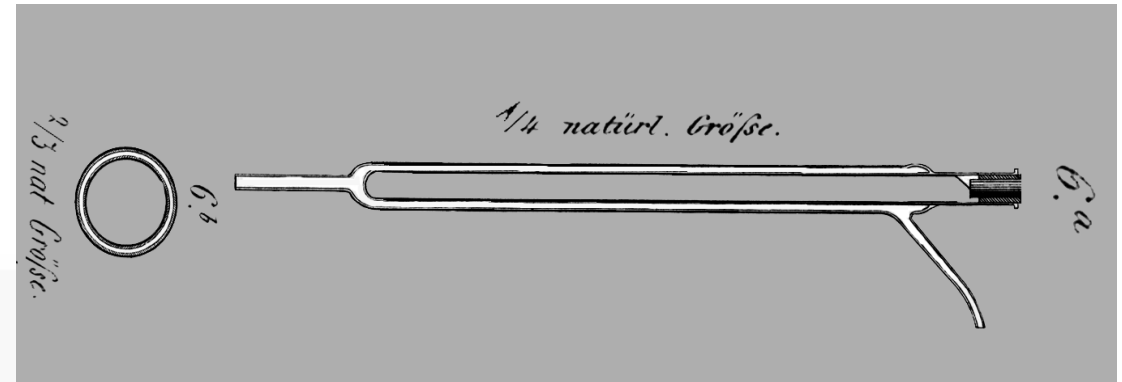
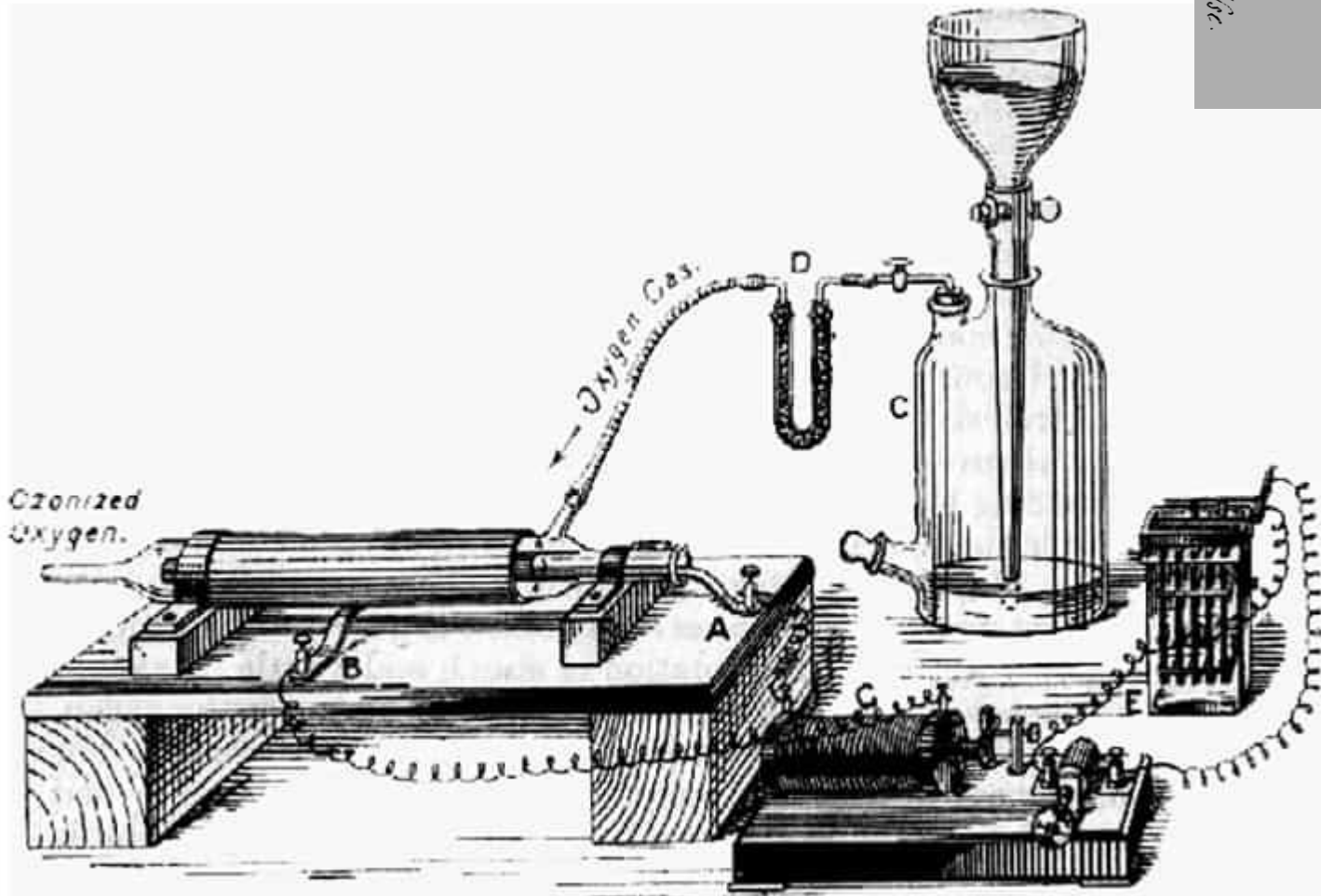


**High Voltage  
Electrode**



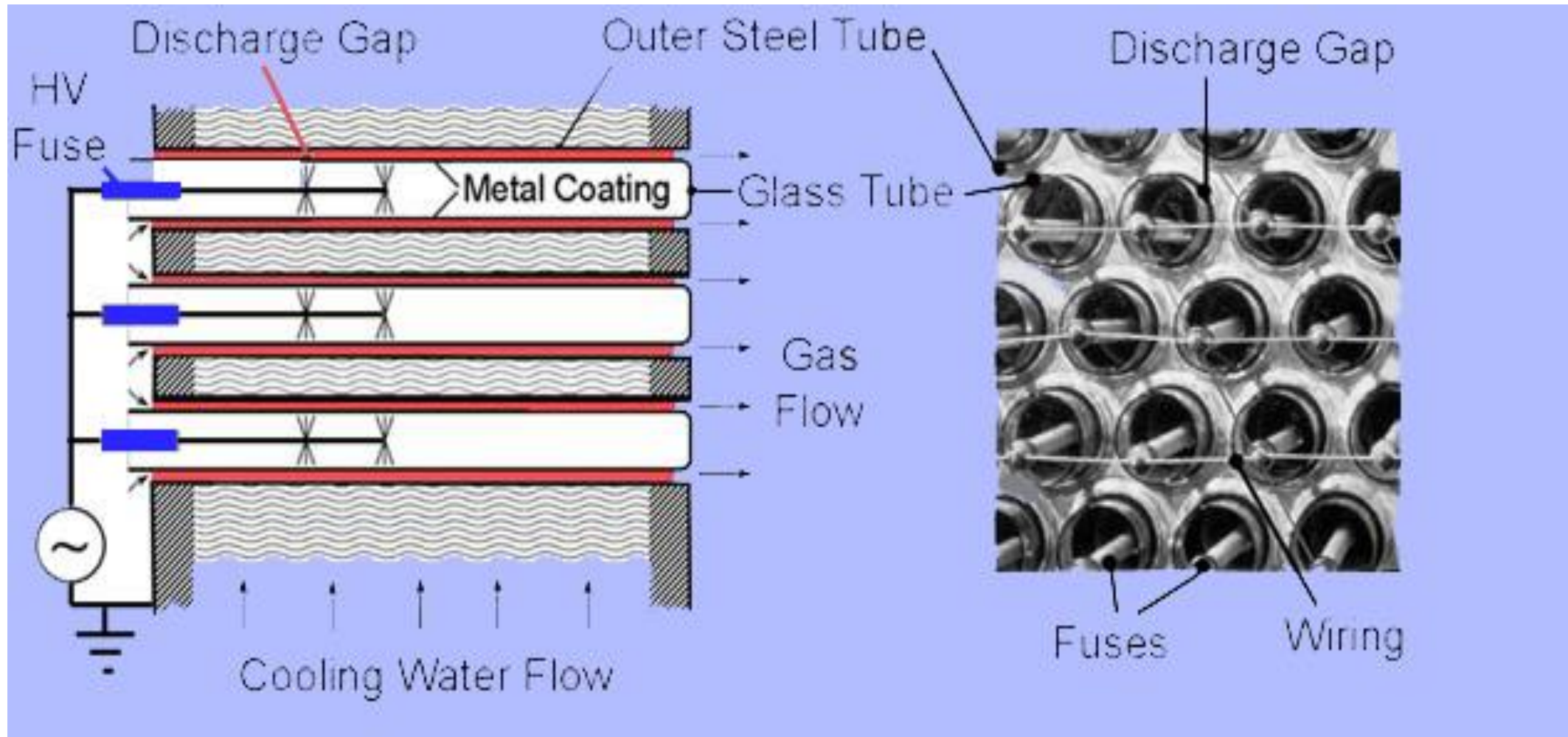
# aerosol-assisted DBD PE-CVD



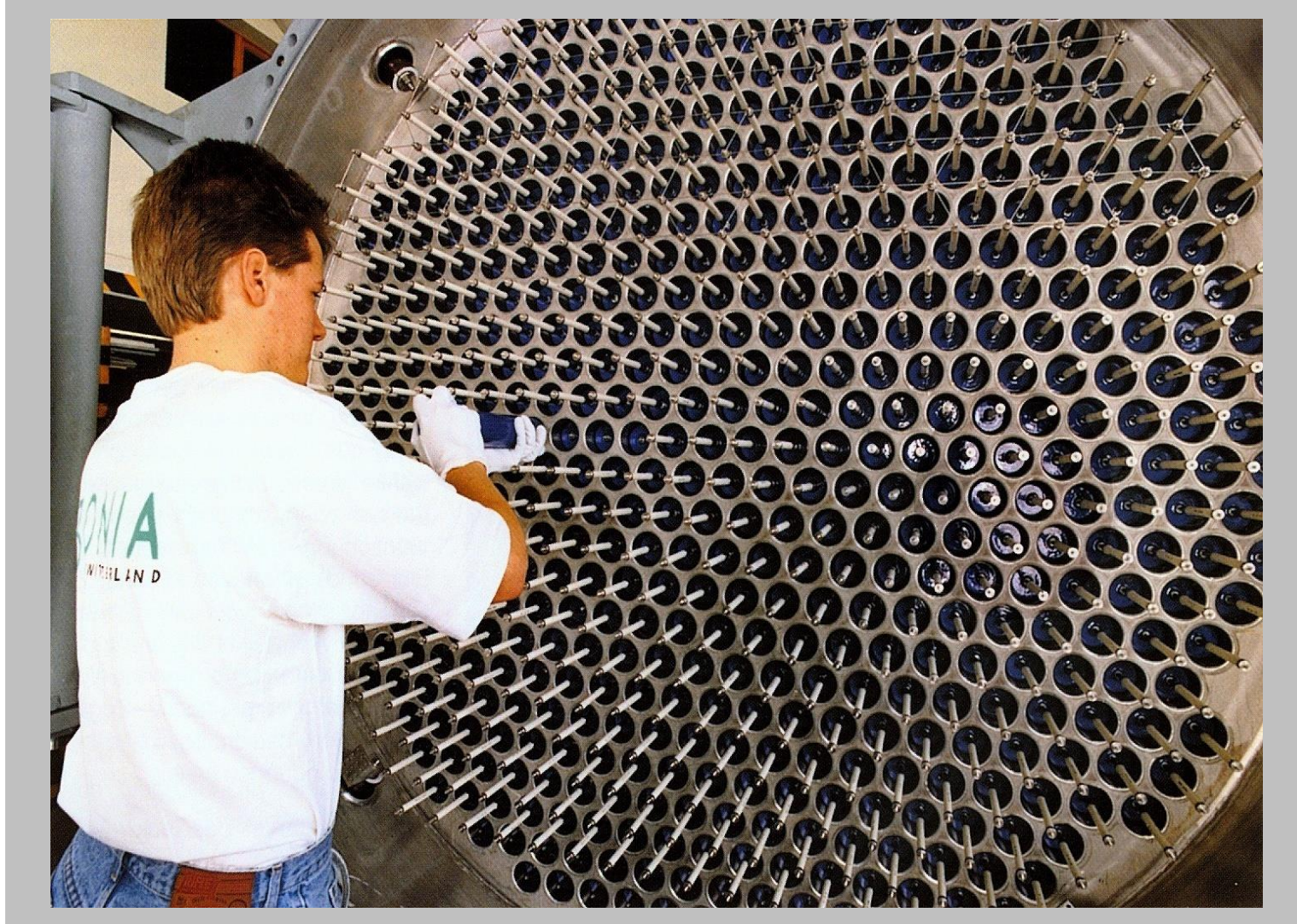


Historical Ozone Tube  
of W. Siemens 1857

## Discharge Tubes in Ozone Generators



# Ozonia AT Ozone Generator



*Courtesy of Dr. Uli Kogelschatz*

# Plasma Jet

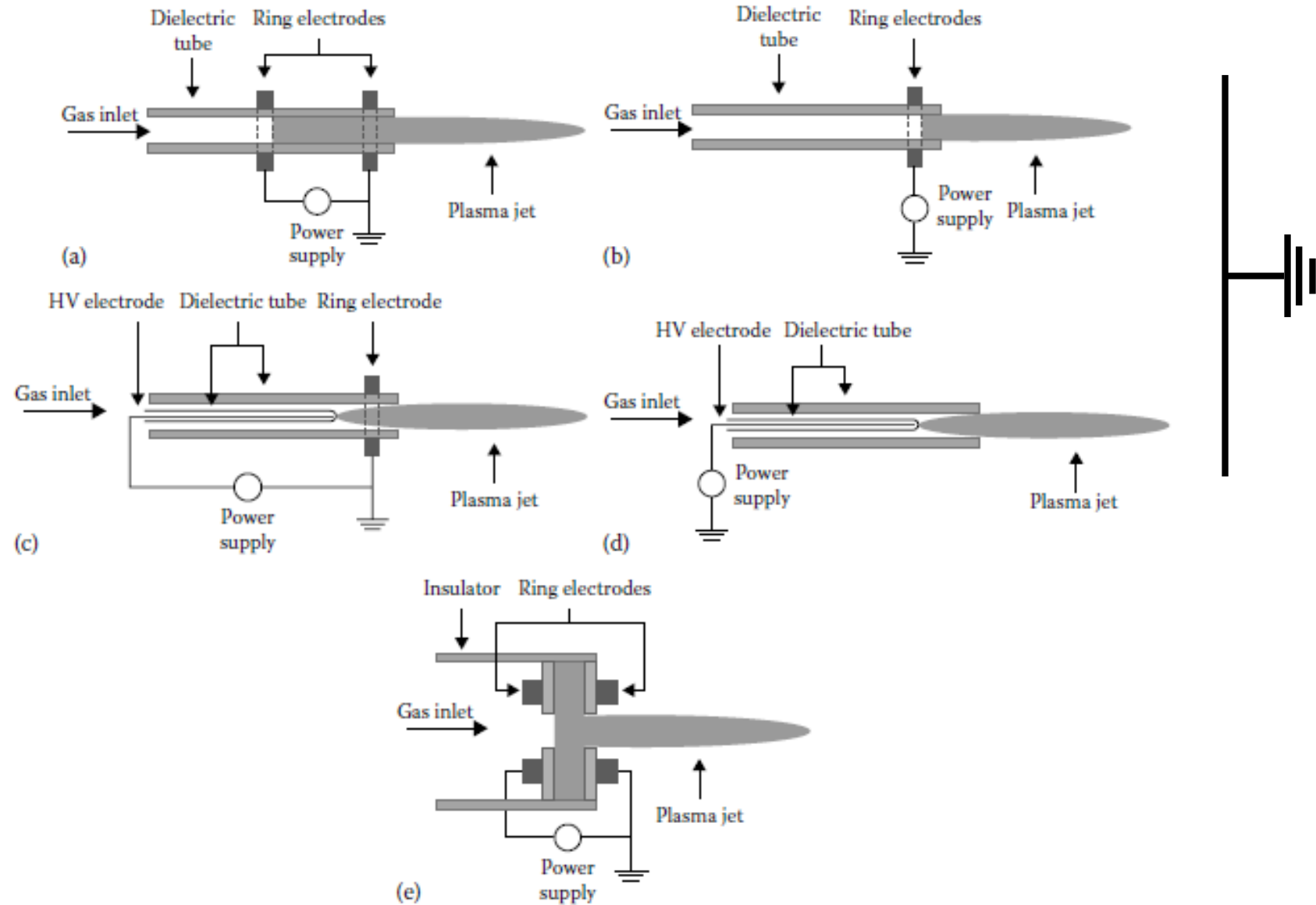


FIGURE 7.2 Schematic of a DBD plasma jet. (a) two ring electrodes DBD jet; (b) single electrode DBD jet; (c) electric field-enhanced two electrode DBD jet; (d) electric field-enhanced single electrode DBD jet; (e) plasma pencil.