# Plasma technology

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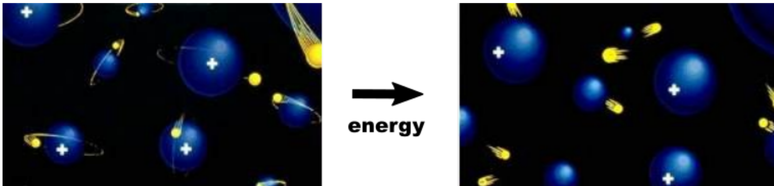
# 1.1 Plasma - 4th State of Matter

Plasma is created from gas by adding sufficient energy (**4th state of matter**). Added energy leads to **ionization of neutral gas**, i. e. generation of electron-ion pairs:




**degree of ionization:** $\alpha_\mathrm{i} = n_\mathrm{i}/(n_\mathrm{i} + n_\mathrm{g})$

For the system of $N$ weakly interacting particles that is closed (does not exchange energy with its surroundings), the average number of particles in the states with energy $E_i$ is given by **Boltzmann factor**

$$\bar{N}_i = C \exp\left(-\frac{E_i}{kT}\right)$$

where $C$ is a constant determined by $N = C \sum_i \exp(-E_i/kT)$

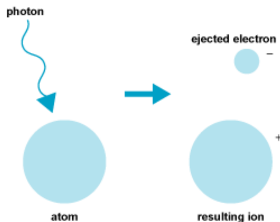
If plasma is created by **adding sufficient thermal energy** $\Rightarrow$ the system is in **thermodynamic equilibrium**, characterized by one $T$ - fusion plasma, Sun's plasma

**Plasma in laboratory:** out of thermodynamic equilibrium by increasing the ionization degree $\alpha_\mathrm{i}$ above the equilibrium value with an **additional ionization source**

# 1.2 Non-equilibrium Plasmas

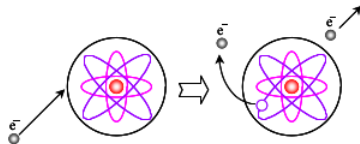
Many plasmas are created out of thermodynamic equilibrium by increasing the **ionization degree** $\alpha$ above the equilibrium value with an **additional ionization source**

**photoionization** - ionization potential of e. g. oxygen atom is 13.6 eV $\Rightarrow$ photon with 91 nm (vacuum UV)

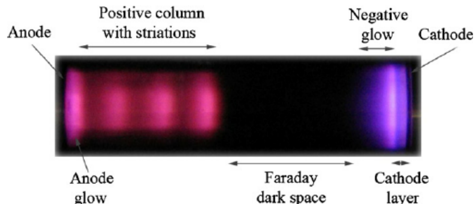



example: Earth ionosphere - natural photoionized plasma

**ionization by electron impact**

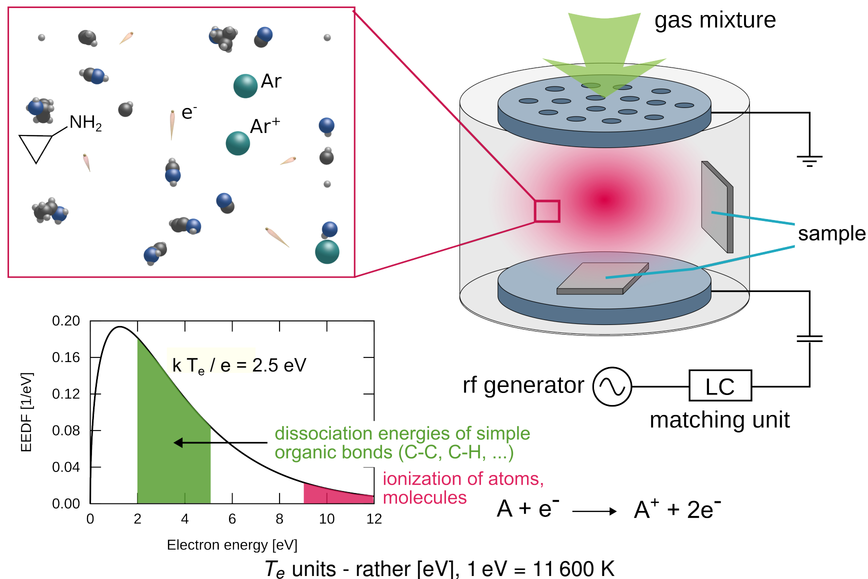



in **gaseous electrical discharges** - el. field accelerates free electrons to ionization energies
example: d.c. glow discharge




Switching off the ionization source leads to plasma extinction due to the recombination.

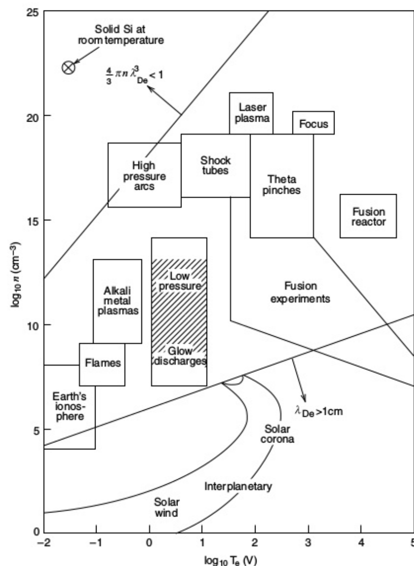
# 1.3 Electron Temperature $T_e$




$$A + e^- \longrightarrow A^+ + 2e^-$$

$T_e$ units - rather [eV], 1 eV = 11 600 K

# 1.4 Fundamental Plasma Parameters $n_e$, $T_e$, $B$




Processing plasmas are not in thermodynamic equilibrium $\Rightarrow$ other $T$ appear ($T_\mathrm{i}$, $T_\mathrm{g}$, $T_\mathrm{rot}$, $T_\mathrm{vib}$)!

Essential quantities are derived from the fundamental plasma parameters
Debye length

$$\lambda_\mathrm{D} = \left(\frac{\varepsilon_0 k T_\mathrm{e}}{n_\mathrm{e} e^2}\right)^{1/2}$$

plasma frequency

$$\omega_\mathrm{pe} = \left(\frac{n_\mathrm{e} e^2}{m_\mathrm{e} \varepsilon_0}\right)^{1/2}$$

cyclotron frequency $\omega_\mathrm{c} = qB/m$

Larmor radius $r_\mathrm{c} = v_\perp/\omega_\mathrm{c}$

thermal velocity $\sqrt{kT_j/m_j}$

*M. A. Lieberman & A. J. Lichtenberg, Principles of Plasma Discharges & Mater. Processing, 1994, Wiley*

# Plasma Conditions & Collective Behaviour

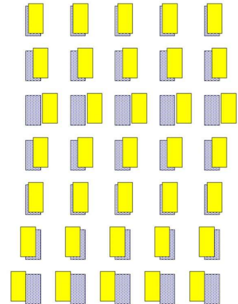
- Plasma contains **many interacting charged particles**. Condition: $n_e \lambda_D^3 \gg 1.$

- Plasma exhibits **collective behavior of electrons** (plasma frequency)

$$\omega_{pe} = \left( \frac{n_e e^2}{m_e \varepsilon_0} \right)^{1/2}$$

that is not much disturbed by electron-neutral collisions:

$$\omega_{pe}/(2\pi) > \nu_{en}$$

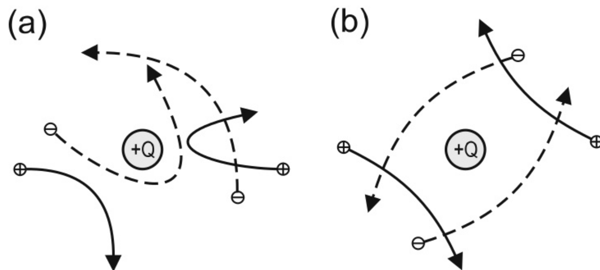


A plasma oscillation: displaced electrons oscillate around fixed ions. The wave does not necessarily propagate.

*podle Chen & Chang 2003*

# Debye Shielding

The most important plasma property - **ability to reduce electric fields very effectively**, thanks to the collective behaviour
An extra charge $+q_{\mathrm{T}}$ is placed at the origin of the coordinate system:




*After A. Piel, Plasma Physics: An Introduction to Laboratory, Space, and Fusion Plasmas, Springer 2010*

Shielding arises from a net attraction of electrons and repulsion of positive ions, leading to trajectory bending: (a) significant for low thermal velocities. (b) For higher energy the trajectories become stiffer and the shielding less efficient.

$$\phi(r) = \frac{q_{\mathrm{T}}}{4\pi\varepsilon_o r}\exp\left(-\frac{r}{\lambda_{\mathrm{D}}}\right)$$

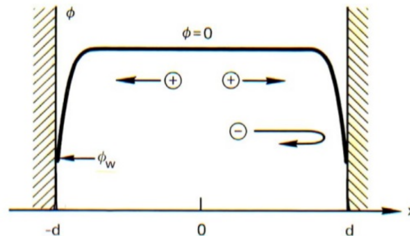
# 1.5 Plasma Sheath

Quasineutrality $n_\mathrm{e} \approx n_\mathrm{i}$ is fulfilled on the scale $L \gg \lambda_\mathrm{D}$, i. e. on the dimensions larger than Debye length

$$\lambda_\mathrm{D} = \left(\frac{\varepsilon_0 k T_\mathrm{e}}{e^2 n_\mathrm{e}}\right)^{1/2}$$

but this is violated in regions adjacent to walls and other solid objects in contact with plasma – **plasma sheath**.

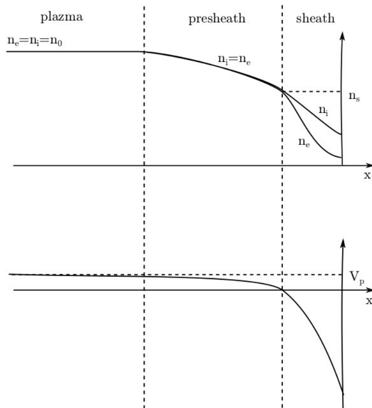
Plasma sheath regions are very important for plasma processing. Plasma potential is always the most positive potential $\Rightarrow$ electrons are repelled by a Coulomb barrier, ions accelerated towards solid surfaces.




*F. F. Chen, J.P. Chang, Lecture notes on principles of plasma processing, 2003, Plenum/Kluwer*

# Plasma Sheath for Low Voltage Drop

Charge densities and potential in bulk plasma, presheath and sheath adjacent to the wall or electrode




*M. A. Lieberman, A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, 1994, Wiley*

Relations valid for

- low sheath voltage (at floating or grounded walls)
- weakly ionized plasmas $T_\mathrm{e} \approx \mathrm{few\,eV}$, $T_\mathrm{i} \approx 0$

Densities of electrons and positive ions are expressed as

$$n_\mathrm{e} = n_\mathrm{s} \mathrm{e}^{\frac{eV}{kT_\mathrm{e}}} \qquad n_\mathrm{i} = n_\mathrm{s} \left(1 - \frac{2eV}{Mv_\mathrm{s}^2}\right)^{-1/2}$$

where $v_\mathrm{s}$ is ion velocity at the sheath edge, approximated by so called Bohm velocity $u_\mathrm{B}$

$$v_\mathrm{s} \geq u_\mathrm{B} = \sqrt{\frac{kT_\mathrm{e}}{M}}$$

Charge density at the sheath edge is

$$n_\mathrm{s} \approx 0.5 n_0 .$$

# Floating and Plasma Potentials

Electron and ion fluxes toward surface

$$\Gamma_\mathrm{e} = \frac{1}{4} n_\mathrm{s} \sqrt{\frac{8kT_\mathrm{e}}{\pi m}} \mathrm{e}^{\frac{eV}{kT_\mathrm{e}}}$$

$$\Gamma_\mathrm{i} = n_\mathrm{s} u_\mathrm{B}$$

have to equal at the **floating** wall (surface dielectrically disconnected from ground or electrode) $\Rightarrow$

$$V_\mathrm{float} - V_\mathrm{plasma} = \frac{kT_\mathrm{e}}{2e} \ln\left(\frac{2\pi m}{M}\right)$$

For a typical low pressure discharge:

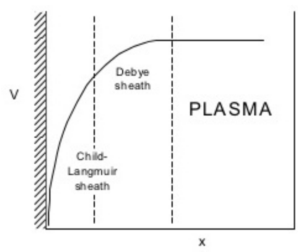
- $T_\mathrm{e} = 2\,\mathrm{eV}$, $n_\mathrm{e} = 10^8\ \mathrm{cm}^{-3}$
- in argon

floating potential is approx. $5T_\mathrm{e} = 10\,\mathrm{V}$
sheath thickness is approx. $5\lambda_\mathrm{D} = 0.37\,\mathrm{mm}$.

# Plasma Sheath for High Voltage Drop (Applied Voltage)

High-voltage sheath (a voltage is applied) can be approximated by a model with **Child-Langmuir sheath**:

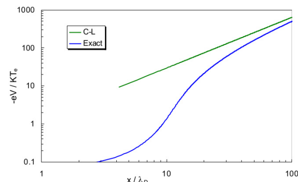
Sheath is artificially divided into **Debye sheath** which contains electrons and high-voltage **Child-Langmuir** sheath which has ions only.




Then, current density $j$, voltage drop $V_0$ and sheath thickness $d$ are related by the Child-Langmuir Law of Space-Charge-Limited Diodes

$$j = \frac{4}{9}\left(\frac{2e}{m_{\mathrm{i}}}\right)^{1/2}\frac{\varepsilon_0 V_0^{3/2}}{d^2} \qquad d = \frac{2}{3}\left(\frac{2V_0}{kT_{\mathrm{eV}}}\right)^{3/4}\lambda_{\mathrm{D}}$$

An exact calculation for a plane sheath shows that C-L scaling is not followed unless the sheath is very thick (notice log-log scale)



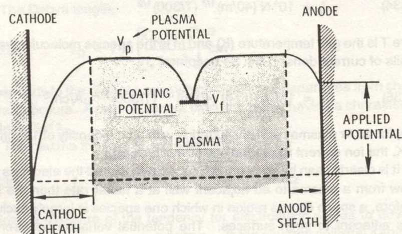

*following previous example*
with assumption $V_0 = 400\,\mathrm{V} \Rightarrow$
$d = 30\lambda_{\mathrm{D}}$, total sheath thickness $35\lambda_{\mathrm{D}}$,
i.e. about 1 cm

*F. F. Chen, J.P. Chang, Lecture notes on principles of plasma processing, 2003, Plenum/Kluwer, p. 33*

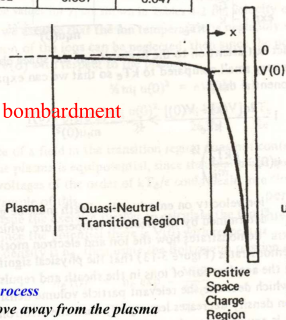
# DC Plasma in Touch with Electrodes/Walls

Table 4-2 Secondary Electron Coeficients $\gamma_i$ for Argon Ion Impact

| | Ion Energy | | |
|---|---|---|---|
| | 10 eV | 100 eV | 1000 eV |
| Mo | 0.122 | 0.115 | 0.118 |
| W | 0.096 | 0.095 | 0.099 |
| Si (100) | 0.024 | 0.027 | 0.039 |
| Ni (111) | 0.034 | 0.036 | 0.07 |
| Ge (111) | 0.032 | 0.037 | 0.047 |




high-energy ion bombardment at the cathode




$$u(0) > \left(\frac{kT_e}{m_i}\right)^{1/2}$$

$$\tfrac{1}{2}\, m_i u(0)^2 = eV(0)$$

*therefore,*

$$V(0) = m_i u(0)^2 / 2e = (m_i/2e)\,(kT_e/m_i) = kT_e/2e$$

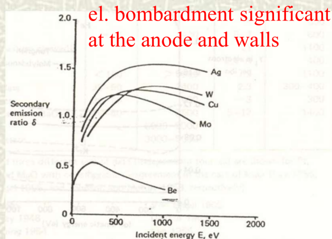
***Self-limiting process***

*: 1) electron move away from the plasma*

*→ 2) the plasma results in more positive*

*→ 3) it hinders the escape of the negative electrons*

el. bombardment significant at the anode and walls




Secondary emission coefficient δ of different metals as a function of the energy of incident electrons (Hemenway et al. 1967)

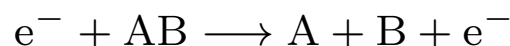
## 2. Plasma in Material Processing

# 2. Plasma in Material Processing

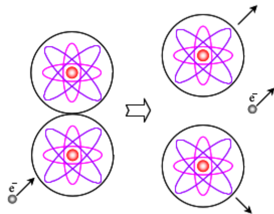
# 2.1 Why Plasma Is Used in Material Processing?

**Low temperature plasma of gaseous discharges** provides unique environment for material processing:

- **hot electrons** ($T_\mathrm{e}$ few eV, $1\mathrm{eV} = 11600$ K)
  $\Rightarrow$ dissociation of molecules into reactive species



$$\mathrm{e}^- + \mathrm{AB} \longrightarrow \mathrm{A} + \mathrm{B} + \mathrm{e}^-$$




- **positive ions** that can be accelerated by ≈ 100 eV near solid surface
  $\Rightarrow$ sputtering of targets, implantation, modification of surfaces and growing films
- **cold neutral gas**
  $\Rightarrow$ highly energetic process can be kept in a vessel, heat sensitive materials can be treated (e. g. polymers)

*figure taken from Chen & Chang, 2003, p. 127*

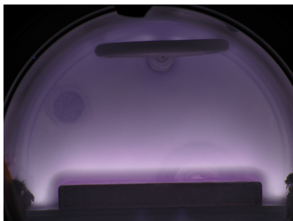
# Unique Features of Plasma Technologies

## Unique Features of Plasma Technologies:

- dry process (gas phase), i.e. with low consumption of chemicals,
- offering replacement of toxic and explosive reactants, i.e. environmentally and user friendly
- preparation of new materials that cannot be obtained by pure chemical methods

## How it can be used?

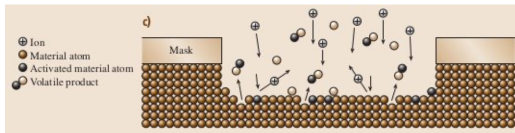
- in vacuum reactor - excellent control over the process
- at atmospheric pressure - easy-to-use method, no need of vessel except because of safety reasons in case of toxic chemicals



# 2.2 Overview of Plasma Processing Methods I

## Plasma etching - irreplaceable etching method

anisotropic dry etching: combination of chemistry and effect of ions (reactive ion etching)




*ed. B. Bushan, Handbook of Nanotechnology, 2010, Springer*

## Plasma treatment

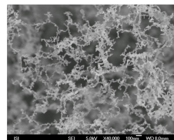
dry modification of the top surface layer (no material added, modification of existing material by oxidation, nitridation etc.) in Ar, $O_2$, $NH_3$ . . . discharges for

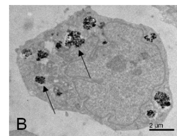
- change of roughness
- change of surface chemistry
- creation of dangling bonds

## Plasma synthesis - high purity

- plasma in liquids
- plasma synthesis of nanoparticles (dry or in liquid)

e. g. iron oxide superparamagnetic NPs - (minimum toxic effects for cells)



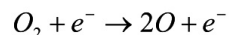



# 2.2 Overview of Plasma Processing Methods II

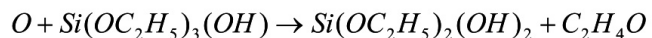
## plasma enhanced chemical vapor deposition (PECVD)

- from gases and vapors
- very easy for organic materials and Si compounds ($SiH_4$, variety of volatile organosilicon compounds)
- for metals - necessary to find sufficiently volatile compounds (organometallic)

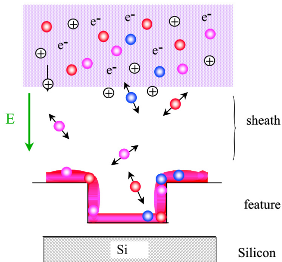
$$Si(OC_2H_5)_4 + e^- \rightarrow Si(OC_2H_5)_3(OH) + C_2H_4 + e^-$$



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



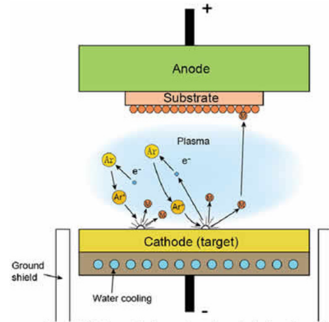
$$O + Si(OC_2H_5)_3(OH) \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_4O$$




*Chen & Chang, 2003*

## plasma sputter-deposition - physical vapor deposition (PVD)

- gasification of solid targets by ion sputtering $\Rightarrow$ deposition
- simple method for metals
- a bit more complex for oxides, nitrides, carbides (reactive sputtering)



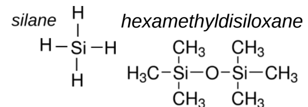

(dc diode sputtering, magnetron sputtering)

# 2.3 Applications of Plasma Treatment and Deposition

Material surface can be **plasma treated** or **plasma coated with a thin film** thickness of the plasma modified layer ranges from **few nm to tens of $\mu$m**.

- hydrophilic surfaces for improved painting, printing, lacquering
- surfaces for improved adhesion of coatings or strength of adhesive bonds
- hydrophobic surfaces for nonadhesive, self-cleaning or antifouling applications
- thin films for optical applications (low and high refractive index oxides)
- thin films for electronic applications (a-Si:H, Si-based dielectric films)
- hard and tribological coatings (metal nitrides, metal carbides, diamond like carbon)

plasma coating for hydrophobic & oleophobic surfaces




Si-based plasmachemistry

- barrier coatings (a-C:H, organosilicon plasma polymers)

- bioapplications such as biosensors, drug immobilization, tissue engineering (surface functionalization, plasma polymers)

# 3. Chemical Reactions and Surface Processes

Plasma treatment in reactive gases, plasma etching, reactive sputter-deposition, plasma enhanced chemical vapor deposition - PECVD, and its subset, plasma polymerization **all use chemical reactions in bulk plasma and at the surfaces**

# 3.1 Chemical Reactions

- **homogeneous** - if reactants are of the same phase (e.g. reactions in gas phase)
- **heterogenous** - if reactants are of two or more different phases (e.g. reaction between gas and solid, reactions on the catalytical surface)

For a homogeneous reaction $aA + bB \longrightarrow qQ + sS$
the **rate of reaction** is (for constant volume) e. g.

$$r = -\frac{1}{a}\frac{\mathrm{d}C_A}{\mathrm{d}t}. \quad (1)$$

where $C_A$ is the molar concentration of A ($\mathrm{kmol/m^3}$).

The **rate of reaction** can be expressed also as

$$r = K_{AB} C_A^{a'} C_B^{b'}. \quad (2)$$

where $K_{AB}$ is the **rate constant**, the powers $a'$, $b'$ are called **partial orders** of the reactions, the sum $a' + b'$ is (global) **order**.

**Arrhenius** concluded from thermodynamics ($T$ is temperature, $R$ and $k_\mathrm{B}$ gas and Boltzmann constants):

$$\ln K = -\frac{\varepsilon_\mathrm{a}}{RT} + \ln A_0 = -\frac{E_\mathrm{a}}{k_\mathrm{B} T} + \ln A_0$$

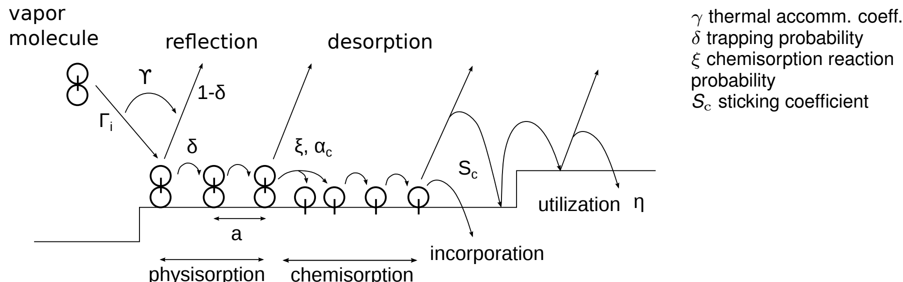
$\varepsilon_\mathrm{a}$ and $E_\mathrm{a}$ **activation energies** in J/mol and J, $A_0$ constant frequency factor.

# 3.2 Surface Reactions

Deposition may be considered as six sequential substeps:

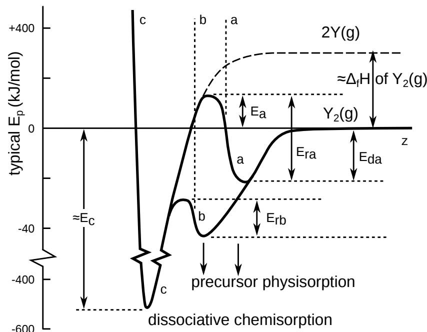
1. **Adsorption** of arriving atoms and molecules on the surface.
2. **Diffusion** before becoming incorporated into the film.
3. **Reaction** of adsorbed species with each other and the surface to form the bonds of the film material.
4. Initial aggregation of the film material - **nucleation**.
5. Development of a structure (**morphology**) as the film grows thicker. It includes topography (roughness) and crystallography.
6. **Diffusional interactions** within the bulk of the film and with the substrate

## Adsorption, Diffusion and Reaction:




*after Donald L. Smith, Thin-Film Deposition, Principles and Practice, 1995, McGraw-Hill*

# Energetics of Precursor Adsorption Model




*after Donald L. Smith, Thin-Film Deposition, Principles and Practice, 1995, McGraw-Hill*

The **curve a** represents **activated chemisorption** - there is an activation energy $E_\mathrm{a}$ to be overcome for $Y_2$(g) to become dissociatively chemisorbed.

For deeper precursor well, **curve b**, chemisorption is not activated though there is still a barrier $E_\mathrm{rb}$.

If **curve c** is followed ($E_\mathrm{p}$ is high enough) direct chemisorption occur.
**Energy-enhanced deposition processes** provide enough energy $E_\mathrm{p} > E_\mathrm{a}$

- sputter deposition - arriving species have kinetic energy $\sim$ 1000 kJ/mol and $E_\mathrm{p} > 0$.
- plasma-enhanced deposition - vapor molecules are dissociated in plasma

# 4. Electrical Discharges

# 4.1 Classification of Discharges

- **according to pressure**
  - low pressure
  - atmospheric pressure

$\Rightarrow$ importance of mean free path

$$\lambda = 1/n_g\sigma$$

$n_g$ is gas density, $\sigma$ is collisional cross section and **its comparison to Debye length $\lambda_D$ and plasma reactor dimensions**

- **according to frequency**
  - d.c.
  - low frequency (50 Hz, audio range, low radio frequency up to 1 MHz)
  - high frequency (typically 13.56 MHz)
  - microwave (typically 2.45 GHz)

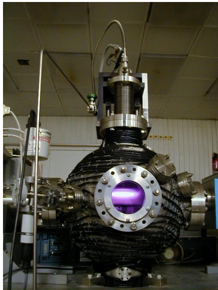
$\Rightarrow$ importance of electron and ion plasma frequencies

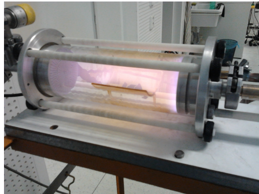
$$\omega_{pe,i} = \sqrt{\frac{e^2 n_e}{\varepsilon_0 m_{e,i}}}$$

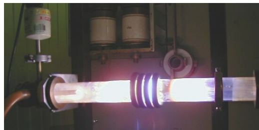
and **their comparison to discharge frequency**

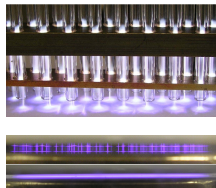
# Examples of Discharges

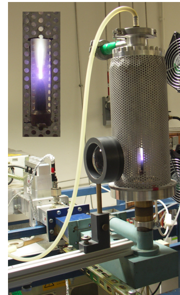
- d.c. - d.c. glow discharge (planar diode), d.c. magnetron, vacuum arc
- low frequency (50 Hz, audio range, low radio frequency up to 1 MHz) - low pressure glow discharge, atmospheric pressure dielectric barrier discharge, glide arc, plasma jet
- high frequency (typically 13.56 MHz) - **radio frequency capacitively or inductively coupled discharges**
- microwave (typically 2.45 GHz) - microwave resonator, surface wave discharge, atmospheric pressure plasma torch



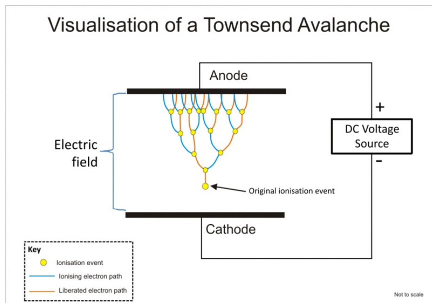


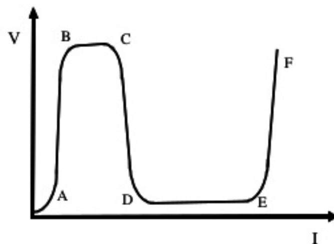






# Electrical Breakdown and Glow Discharge Modes

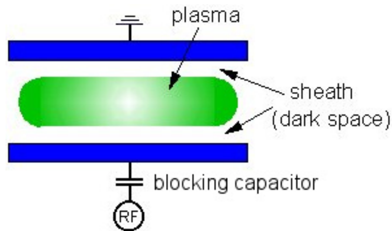


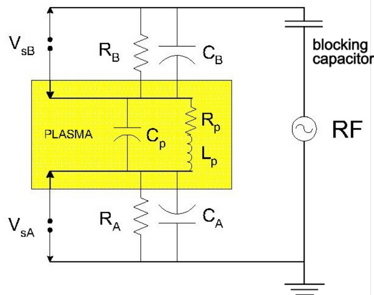




- (A) region of non-self-sustaining discharge
- (BC) Townsend discharge
- (CD) subnormal glow discharge
- (DE) normal glow discharge
- (EF) abnormal glow discharge

# 4.2 Low Pressure Capacitively Coupled Plasma

Radio frequency discharges (typically 13.56 MHz) sustained by r.f. current and voltage coupled via **capacitive plasma sheath** are **capacitively coupled plasma (CCP)**.



CCPs belong to **glow discharges** (discharges with high voltage cathode sheath - electrons originate by secondary emission from the cathode).

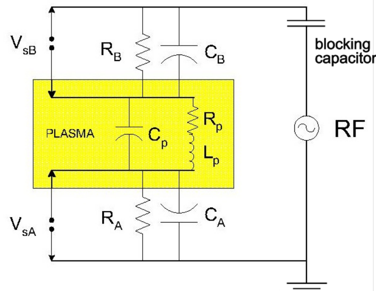
# Capacitively Coupled Plasma - D.C. Self Bias

- External electrical circuit usually contains „blocking“ capacitor, i. e. dc current cannot flow
- Most CCPs are asymmetric $A_{\mathrm{sA}} \neq A_{\mathrm{sB}}$

$\Rightarrow$ plasma acts as a voltage divider due to equal displacement currents through both the plasma sheaths:

$$\frac{V_{\mathrm{sB}}}{V_{\mathrm{sA}}} = \left(\frac{A_{\mathrm{sA}}}{A_{\mathrm{sB}}}\right)^q$$

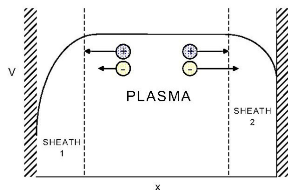
where scaling exponent $q = 1.25$–$4$ depends on the sheath and plasma glow models (Lieberman 1989 J. Appl. Phys. 65 4186)




Easily measurable **d.c. self bias** is set up between RF electrode and the ground

$$U_{\mathrm{bias}} = -(V_{\mathrm{sB}} - V_{\mathrm{sA}})$$

It is negative in the usual case of smaller RF electrode, i. e. $V_{\mathrm{sB}} > V_{\mathrm{sA}}$.




$\Rightarrow$ Ions are accelerated in high-voltage sheath at (smaller) RF electrode. Sheath voltage is proportional to RF voltage, i. e. RF power.

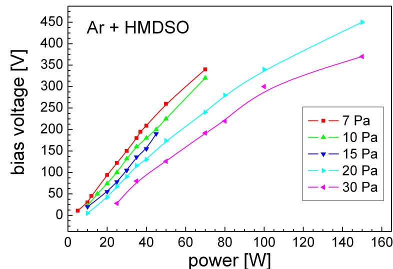
**If ions do not collide in the sheath (at low pressure of few Pa) they hit the surface with high energy of several 100 V.**

# Capacitively Coupled Plasma - Energy of Ions

Example for Ar + hexamethyldisiloxane (HMDSO) CCP at 13.56 MHz:

- Ar + HMDSO 1:1 mixture
- total flow rate 6 sccm
- pressure $p$ 7–30 Pa
- power $W$ 5–150 W

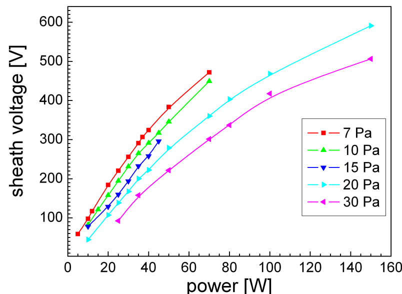
- dc bias-voltage at RF electrode $U_\mathrm{b}$ varied with $W$ and $p$




*E. Kedroňová et al. Plasma Process. Polym. 12 (2015) 1231*

**⇒ Sheath voltage at RF electrode**

$V_\mathrm{sB} = 0.39 V_\mathrm{rf} + 0.73 U_\mathrm{bias}$



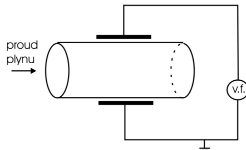

$$U_\mathrm{bias} = 0.83 V_\mathrm{rf} \frac{\xi^q - 1}{\xi^q + 1}$$

where $\xi = A_\mathrm{sA}/A_\mathrm{sB}$. For a highly asymmetric case $A_\mathrm{sA} \ll A_\mathrm{sB}$, the asymmetry term tends to -1.

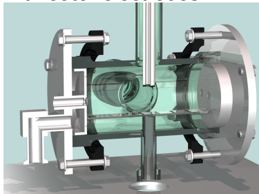
# Construction of CCP Reactors

## horizontal reactor

with inner electrodes



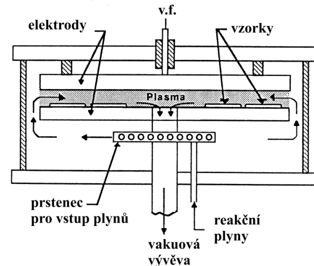

with outer electrodes



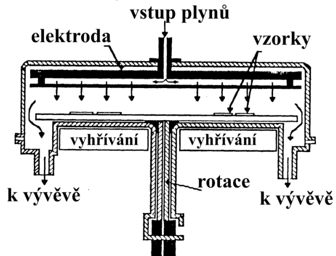
## vertical reactor with inner parallel-plate electrodes

(parallel-plate diode discharge)

radial gas flow




inverse radial gas flow (showerhead electrode)

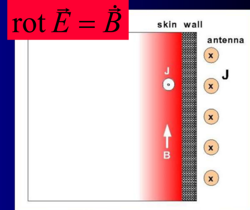


# 4.3 Low Pressure Inductively Coupled Plasma

## Principle of ICP discharges

r.f. antenna in the form of coil attached to dielectric window – electromagnet creating rf mg field – induction of rf el field

$\mathrm{rot}\,\vec{E} = \dot{\vec{B}}$

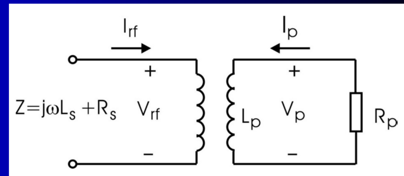



Energy of electrical field is transferred to the electrons in thin „skin“ layer.

- non-collisional processes – electrons „collide“ with induced oscilating el. field
- energy is dissipated by collisional (ohmic) processes

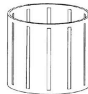
skin depth (collisionless)

$$\delta_s = \delta_c \equiv c/\omega_p$$



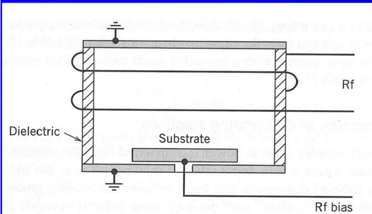

☞ non-capacitive coupling is a key point for low voltages (typically 20-30 V) in sheaths at electrodes and reactor walls

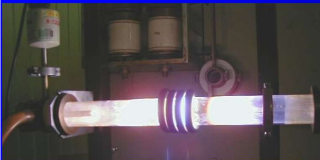
☞ Farraday shielding is used to surpress capacitive coupling (high voltage on the coil)



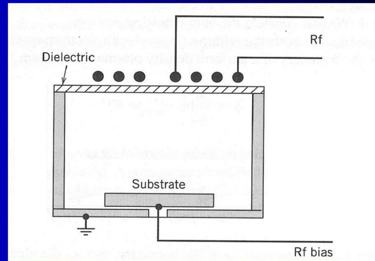
# Construction of ICP reactors

- cylindrical geometry

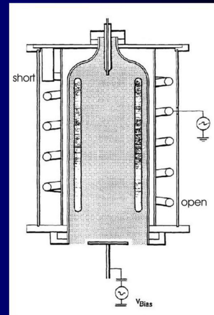


- planar geometry




- helical resonator

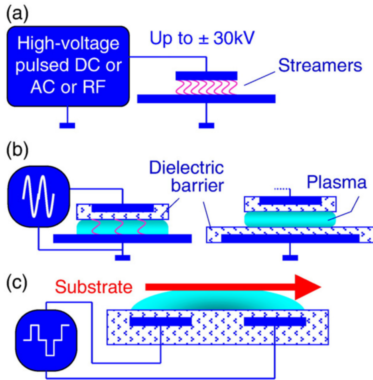


## 4.4 Comparison of Plasma Sources (low $p$, high $f$)

| plasma source | frequency | density [$cm^{-3}$] | el. temper. [eV] | mg. field |
|---|---|---|---|---|
| CCP | r.f. | $10^{9}$-$10^{11}$ | 1-5 | no |
| ICP | r.f. | $10^{11}$-$10^{12}$ ($\leq 10^{13}$) | 2-7 | optional |
| ECR | m.w. | $10^{10}$-$10^{12}$ | 2-7 | 875 G |
| helicon | r.f. | $10^{11}$-$10^{12}$ ($10^{11}$-$10^{14}$) | 2-7 | 20-200 G |

# 4.5 Atmospheric Pressure Dielectric Barier Discharges

## Plate-to-plate configuration




**At low** $p$, the collision frequency is low $\Rightarrow$ electron energies remain high compared to ion neutral energies $\Rightarrow$ non-equilibrium (cold) plasma.

**At high** $p$, the collision frequency is high $\Rightarrow$ plasma tends to equilibrate temperatures $\Rightarrow$ **formation of streamers** (fast-moving ionization fronts in the form of filaments) - **precursors of sparks** (hot plasmas)

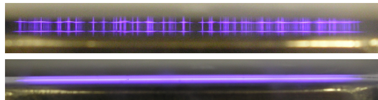
Suppression of sparks using:

- high-frequency AC fields or short-pulsed DC power
- dielectric barriers on AC electrodes
- high gas flow rates
- special electrode shapes with multiple structures
- suitable gas, e. g. He.

# Filamentary versus Homogeneous DBD

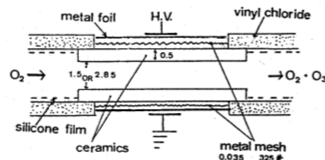
Two forms of dielectric barrier discharges (DBDs) with parallel plate electrodes:

- filamentary
- homogeneous



Stabilization of **homogeneous DBDs requires suppression of filament formation**.

Important role of

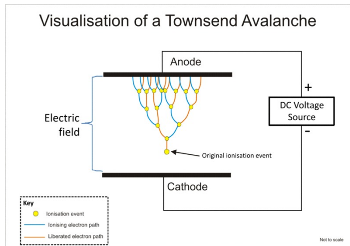


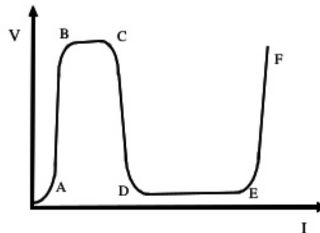

- **structure and material of electrodes**
  e.g. M. Kogoma, S. Okazaki, JPD (1994) 27 1985
- **higher frequencies of power supply**
  T. Nozaki et al., Plasma Process. Polym. (2008) 5 300)
- **gas mixture** (He, Ne, $N_2$, Ar + $NH_3$ etc.):
  - homogeneous DBD in He, Ar/$NH_3$ and $N_2$
    *F. Massines et al. Surf. Coat. Technol. 174–175, 8 (2003); Plasma Phys. Controlled Fusion 47, B577 (2005).*
  - PECVD in HMDSO/$N_2$ and HMDSO/$N_2$/synthetic air mixtures
    *D. Trunec et al. J. Phys. D: Appl. Phys. 37 (2004) 2112; J. Phys. D: Appl. Phys. 43 (2010) 225403*
  - PECVD in Ar/$C_2H_2$
    *M. Eliáš et al. J. Appl. Phys. 117(10) (2015) 103301*

# Homogeneous Dielectric Barrier Discharges

**Two different forms of homogeneous discharges** were classified by Massines et al. Both start with Townsend breakdown initiating a Townsend discharge but

- in He, during the current increase, the discharge transits to a glow discharge ($n_\mathrm{e} \approx 10^{11}$ cm$^{-3}$) having a cathode fall and a positive column if gas gap is > 2 mm - **atmospheric pressure glow discharge (APGD)**
- in $N_2$, the ionization level is too low ($n_\mathrm{e} \approx 10^{8}$ cm$^{-3}$) to allow formation of cathode fall. Localization of the electrical field and the glow regime cannot be achieved - **atm. pressure Townsend discharge (APTD).**

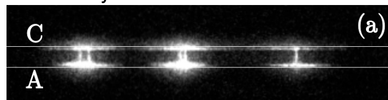


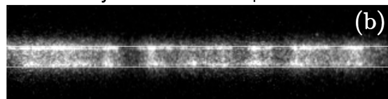

- (A) region of non-self-sustaining discharge
- (BC) Townsend discharge
- (CD) subnormal glow discharge
- (DE) normal glow discharge
- (EF) abnormal glow discharge

# Homogeneous DBD (APGD) in Ar/acetylene

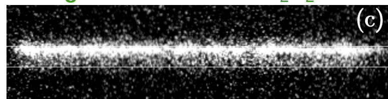
filamentary DBD in Ar




filamentary DBD in Ar/$CH_4$

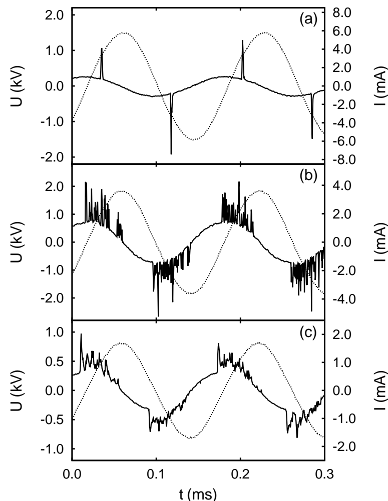



**homogeneous DBD in Ar/$C_2H_2$**




(80 $\mu$s (one half-period) exposure time)

- difference caused by possibility of Penning ionization of $C_2H_2$ in Ar
- Ar $1s^5$ metastable - 11.55 eV,
- $C_2H_2$ ionization potential 11.40 eV but $CH_4$ 12.61 eV



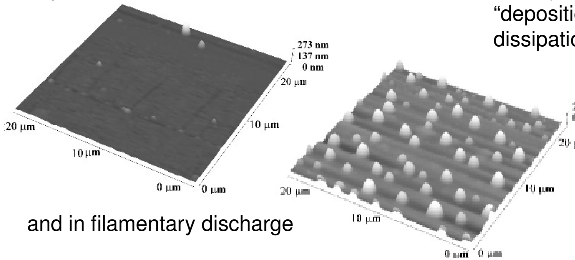

DBD
(a) DBD in pure Ar, (b) DBD in Ar/$CH_4$,
(c) APGD in Ar/$C_2H_2$

*M. Eliáš et al., J. Appl. Phys. 117(10) (2015) 103301*

# Why to Use Homogeneous DBD for Deposition?

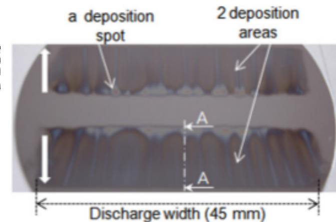
**... to eliminate unwanted surface structures and non-uniformities**

*D. Trunec et al. J. Phys. D 37 (2004) 2112:*
deposition in APTD (HMDSO/$N_2$)

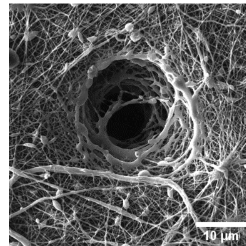



and in filamentary discharge

*H. Caquineau et. al J. Phys. D 42 (2009) 125201*:
Locally increased deposition rate ≡ “deposition spots”, due to non-uniform power dissipation in micro-filaments:




**... to modify temperature sensitive polymer substrates and polymer nanofibers**



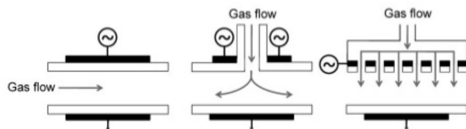
# Problem of Film Uniformity

Amospheric-pressure plasmas are characterized by high collision frequencies of particles (several orders of magnitude higher compared to low pressure)

⇒ Delivery of active species to the substrate is much more advection than diffusion-driven (opposed to low-pressure).

⇒ High electron-neutral collision frequency ⇒ fast monomer conversion

Basic gas delivery set-ups




are **modified for optimization of flow patterns by gas dynamics simulations**

*P. Cools et al., Plasma Process. Polym. 2015, 12, 1153–1163*

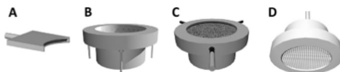
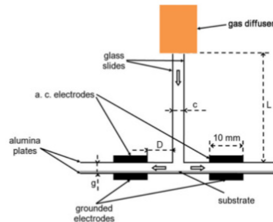


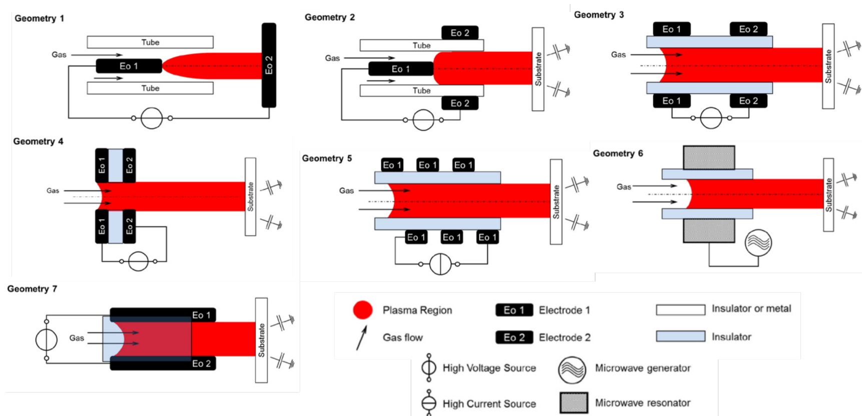

*Figure 2.* Schematic representation of the four different inlet set-ups: a) Sideway inlet, b) ring inlet, c) porous glass inlet, and d) microplasma-electrode.

*H. Caquineau et al. J. Phys. D: Appl. Phys. 42 (2009) 125201*



# 4.6 Atmospheric Pressure Plasma Jets

- operating in local thermal equilibrium (LTE) $T_\mathrm{e} \sim T_\mathrm{n}$, $n_\mathrm{e} \geq 10^{15}$ cm$^{-3}$ - **transferred arc (torch), plasmatron**
- translational plasmas (non-LTE but with a significant heating of the background gas $T_\mathrm{n} \sim$ several thousand Kelvin - **gliding arc, expanding sparks, non-transferred arc**
- non-LTE **"cold" plasma jets** $T_\mathrm{e} \gg T_\mathrm{n}$, $T_\mathrm{n} = 300 - 1000\,\mathrm{K}$, $n_\mathrm{e} < 10^{13}$ cm$^{-3}$




J. Winter at al. Plasma Sources Sci. Technol. 24 (2015) 064001

# Arc-Based Atmospheric Pressure Plasma Jets

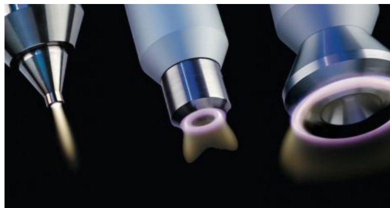
Plasma jets:

- operating in local thermal equilibrium (LTE) $T_{\rm e} \sim T_{\rm n}$, $n_{\rm e} \geq 10^{15}$ cm$^{-3}$ - **transferred arc (torch), plasmatron**
- translational plasmas (non-LTE but with a significant heating of the background gas) $T_{\rm n} \sim$ several thousand Kelvin - **gliding arc, expanding sparks, non-transferred arc**
- non-LTE **"cold" plasma jets** $T_{\rm e} \gg T_{\rm n}$, $T_{\rm n} = 300 - 1000$ K, $n_{\rm e} < 10^{13}$ cm$^{-3}$

*J. Winter at al. Plasma Sources Sci. Technol. 24 (2015) 064001*

Industrial plasma jets based on arc:

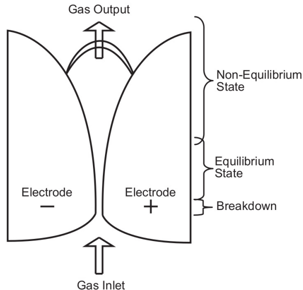
- Sura Instruments, non-transferred arc (patent WO 2015/107059 A1), dc or low $f$, argon flow, precursors for deposition
- PlasmaTreat, non-transferred arc (DE10223865 A1, US2002179575, DE102008058783 A1), 1-100 kHz, air flow, plasma cleaning, activation, deposition



... and some others

# Gliding Arc

A. Fridman, Plasma Chemistry, Cambridge University Press 2008



The glide arc can be operated in the **transitional regime** (combines the benefits of both equilibrium and non-equilibrium discharges):

- the discharge **starts thermal**
- **becomes non-thermal** during the space-time evolution

$f = 50\,\text{Hz}$
max. $P = 500\,\text{W}$,
max. $U = 10\,\text{kV}$

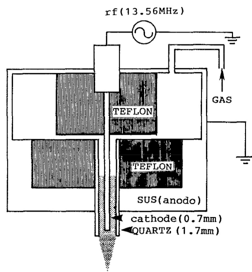
typical operation conditions:
500 W, 10 kV, (dry) air 11.8 slm

# RF Plasma Jets

**"Cold" plasmas** required for surface modification of thermosensitive materials (bonding, painting, printing) or plasma medicine/agriculture

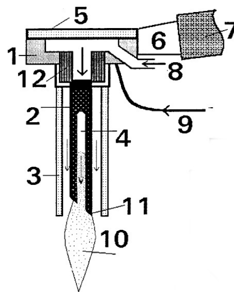
**Non-LTE atmospheric pressure plasma jets** need to prevent the transition to arc ⇒ **pulsed or high *f* discharges, a dielectric barrier at one or both the electrodes**

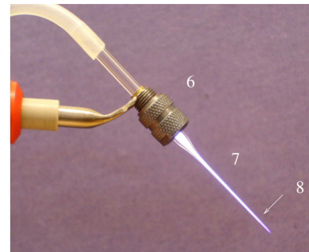
Earliest cold RF plasma jet proposed by Koinuma et al.




APL 60 (1992) 816

Development of cold RF jets in Brno, Masaryk University

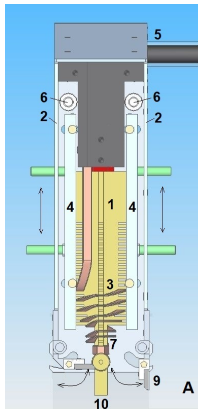


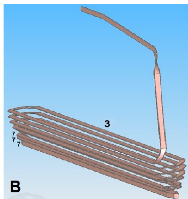




M. Klíma et al. Czech Patent PV147698 (1998), US6,525,481 (2003)
J. Janča et al. Surf. Coat. Technol. 116–119 (1999) 547

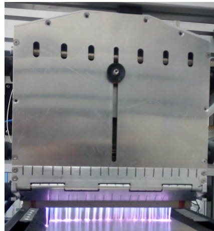
# RF Plasma Slit Jet

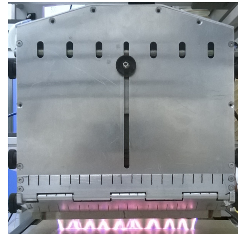
In Brno, we developed a new type of RF plasma jet. Unlike other jets working with capacitive coupling ($E$ component important) it should generate EM with both the components ($E$, $H$) high (according to preliminary EM field calculations $E_{\mathrm{max}} = 10^5$ V/m, $H_{\mathrm{max}} = 800$ A/m).




1 jet body
2 metal shield
3 resonance coil
4 metal plates of matching circuit
5 coaxial cable
6 gas inlet
7 open end of RF coil
9 movable grounded electrodes
10 outlet slit of plasma jet





RF plasma slit jet is successfully constructed with the **width of 15 or 30 cm**.

typical operating conditions:
300-600 W, 50–100 slm of Ar, 0-4 slm of $N_2$

The jet accommodates periodic structures consisting of varying combinations of inductors with specially designed geometry and winding - matching is an integral part.

# 5. Plasma Treatment

# 5. Plasma Treatment

**Plasma treatment of surfaces -** dry modification of the top surface layer (few nanometers) of original material in Ar, $O_2$, $NH_3$ . . . discharges, that can involve:

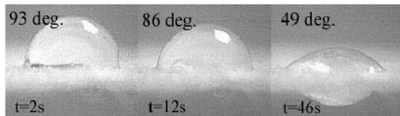
- removal of material
- chemical bond rearrangement - breaking and creation of new bonds
- creation of dangling bonds (unpaired spins)
- incorporation of other elements (O, N, F, . . . )

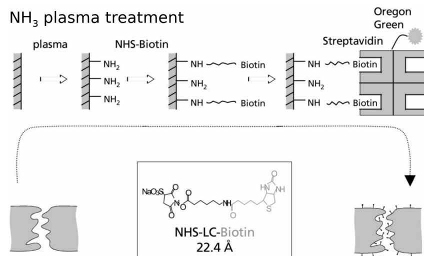
In contrary to depositions the changes are limited to a very thin surface layer (in the order of nm) but please note that the term "surface" is a matter of definition!

It can lead to

- modification of surface chemistry
- change of roughness
- creation of dangling bonds followed up by grafting the functional groups from air or interacting chemical compounds

hydrophobic–hydrophilic crossover

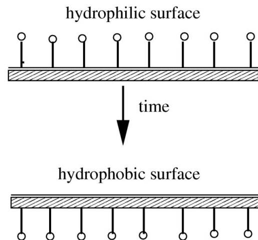


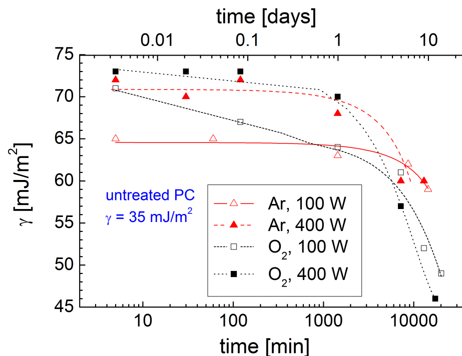

C. Oehr *et al.*, Surf. Coat. Technol. 116–119 (1999) 25–35

# 5.1 Aging of Plasma Treatment Polymer Surfaces

Aging of plasma treated polymer surface - hydrophobic recovery




polycarbonate treatment in Ar or $O_2$ low pressure CCP discharge:




⇒ significantly increased (↑) surface energy $\gamma$ (original PC is hydrophobic, plasma-treated PC hydrophilic) **but the hydrophobicity is partly recovered after aging.**

L. Zajíčková *et al.* unpublished

# 5.2 Plasma Treatment of Polymers in Inert Gas

➢ discharge in argon, helium:

chemical bonds, such as C-H, C-C, C=C, are broken
☞ generation of free radicals at or near the surface
☞ radicals react with each other either directly (if polymer chain is flexible enough) or due to migration along polymer chain („chain-transfer“)
☞ **cross-linking, branching, removal of low molecular weight material or its conversion into high molecular weight one (no new functional groups)**

CASING

(cross-linking by activated species of inert gas)

R. H. Hansen, H. Schonhorn, J. Polym. Sci. B 4 (1966) 203
H. Schonhorn, R. H. Hansen, J. Appl. Polym. Sci. 11 (1967) 1461

increase of surface hardness, improvement of adhesive forces at the interface

Additionally, changes of surface roughness

# 5.3 Plasma Treatment of Polymers in Reactive Gas

- plasma containing oxygen ($O_2$, $H_2O$, $CO_2$ …)
  - etching of surface carbon radicals by atomic oxygen
  - new functional groups, e.g. C-O, C=O, O-C=O, C-O-O, $CO_3$, OH

hydrophilic surface, change of roughness

- plasma containing nitrogen ($N_2$, $NH_3$ …)
  - new functional groups such amine (N-C), imine (N=C), nitrile (N≡C), amide (N-C=O)
  - incorporation of oxygen and its functional groups
  - grafting of amine groups $-NH_2$

hydrophilization, biocompatibility, imobilization of biomolecules

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

  F and $CF_x$ radicals react with surface and two different processes compete:
  - etching
  - grafting and deposition

hydrophobization, change of roughness

# Conclusion

- Plasma chemistry employed in plasma treatment, plasma etching and plasma deposition offers high versatility of material processing.
- Reaction scheme in plasma chemistry and physics of plasma-surface interaction are very complex $\Rightarrow$ variety of “knobs”, i. e. external parameters, with a complex influence on final result.
- The ion energy flux are important internal parameters for low pressure plasma processing.

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