F4280 Technology of Thin Film Deposition & Surface Treatments
8. Electrical Discharges

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Outline

8.1 Classification of Electrical Discharges

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

$\Rightarrow$ importance of mean free path

$$\lambda = 1/n_\mathrm{g}\sigma$$

n_g is gas density, σ is collisional cross section and **its comparison to Debye length λ_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)

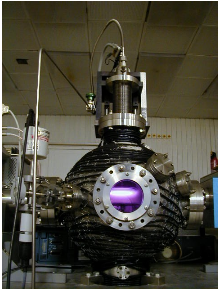
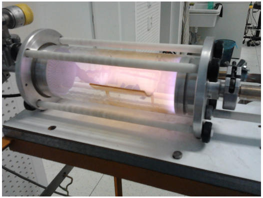
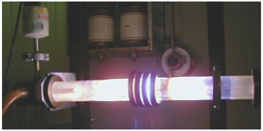
$\Rightarrow$ importance of electron and ion plasma frequencies

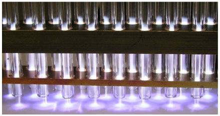
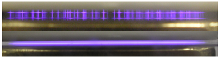
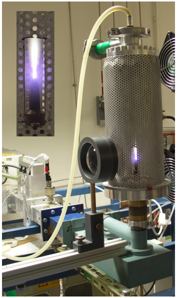
$$\omega_\mathrm{pe,i} = \sqrt{\frac{e^2 n_\mathrm{e}}{\varepsilon_0 m_\mathrm{e,i}}}$$

and **their comparison to discharge frequency**

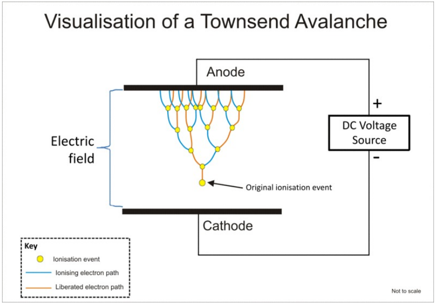
Examples of Discharges

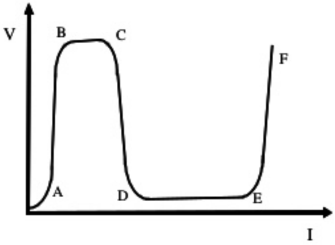
- d.c. - d.c. glow discharge (planar diode), d.c. magnetron, vacuum arc
- low frequency (50 Hz, audio range, low radio frequency up to 1 MHz) - low pressure glow discharge, atmospheric pressure dielectric barrier discharge, glide arc, plasma jet
- high frequency (typically 13.56 MHz) - radio frequency 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



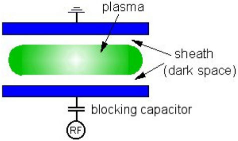


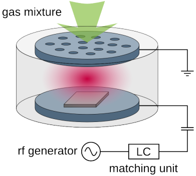
- (A) region of non-self-sustaining discharge
- (BC) Townsend discharge
- (CD) subnormal glow discharge
- (DE) normal glow discharge
- (EF) abnormal glow discharge

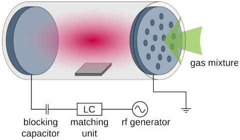
Low Pressure RF Discharges

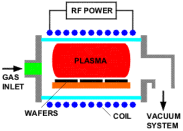
radio frequency (13.56 MHz)

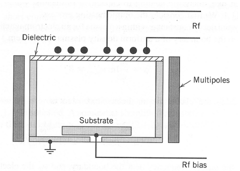
- capacitively coupled (CCP) discharge
- inductively coupled (ICP) discharge







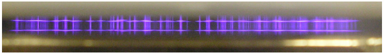
sustained by r.f. current and voltage coupled via **capacitive plasma sheath**

Atmospheric Pressure Discharges

- **planar configurations** - low frequency (≈ few kHz) dielectric barrier discharge (DBD)

Example of DBD - volume DBD (parallel plate electrodes)

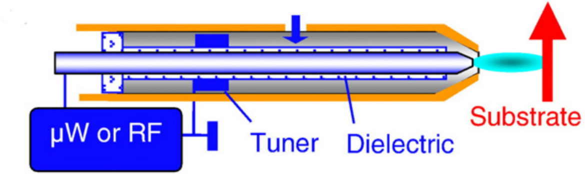
filamentary



homogeneous

- **plasma jets**

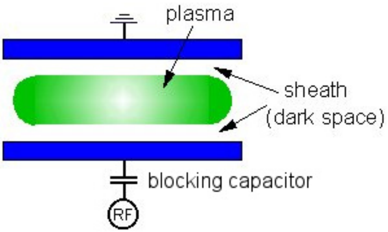
wide variety of frequencies (50 Hz gliding arc jet – 13.56 MHz plasma jet), configurations, working gases ⇒ variations of gas temperature, active species, area

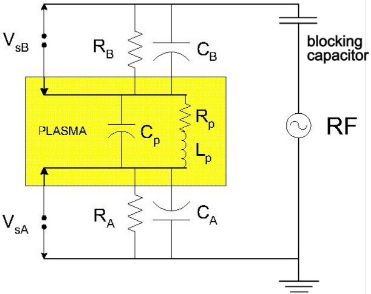


L. Bárdos, H. Baránková, Thin Solid Films

8.2 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).

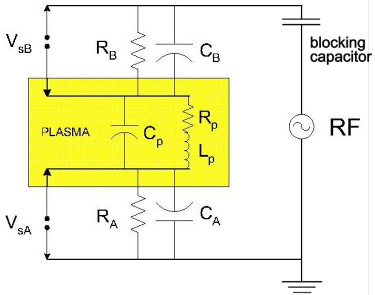
Capacitively Coupled Plasma - D.C. Self Bias

- 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:

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

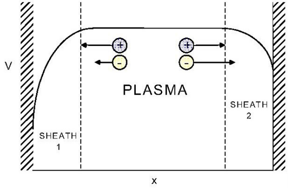
where scaling exponent $q = 1.25$–4 depends on the sheath and plasma glow models (Lieberman 1989 J. Appl. Phys. 65 4186)



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.

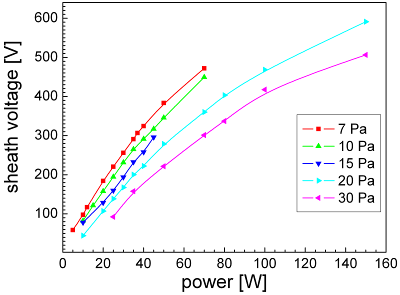
Capacitively Coupled Plasma - Energy of Ions

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

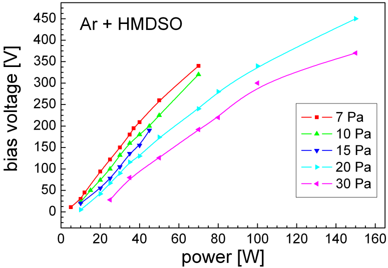
- Ar + HMDSO 1:1 mixture
- total flow rate 6 sccm
- pressure p 7–30 Pa
- power W 5–150 W

⇒ Sheath voltage at RF electrode

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



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



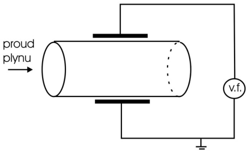
E. Kedroňová et al. Plasma Process. Polym. 12 (2015) 1231

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

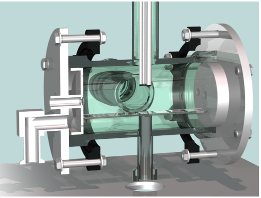
where $\xi = A_{\mathrm{sA}}/A_{\mathrm{sB}}$. For a highly asymmetric case $A_{\mathrm{sA}} \ll A_{\mathrm{sB}}$, the asymmetry term tends to -1.

Construction of CCP Reactors

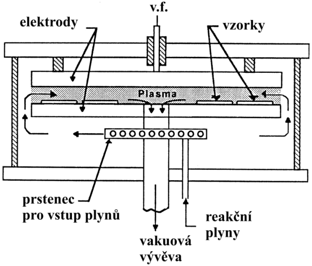
horizontal reactor
with inner electrodes



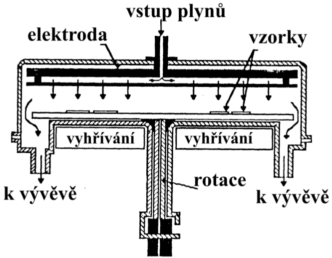
with outer electrodes



vertical reactor with inner parallel-plate electrodes
(parallel-plate diode discharge)
radial gas flow



inverse radial gas flow (showerhead electrode)

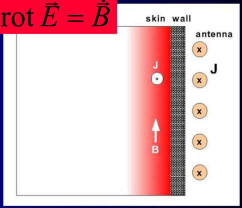


8.3 Low Pressure Inductively Coupled Plasma

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

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

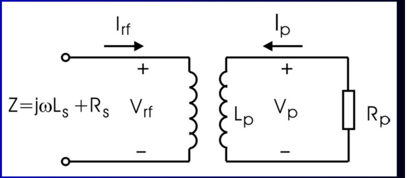


Energy of electrical field is transferred to the electrons in thin „skin“ layer.

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

skin depth (collisionless)

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

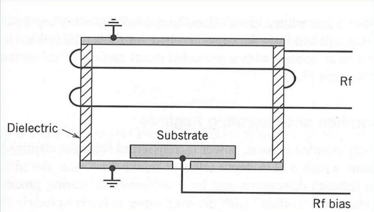


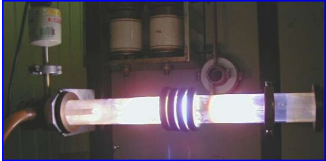
☞ non-capacitive coupling is a key point for low voltages (typically 20-30 V) in sheaths at electrodes and reactor walls

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

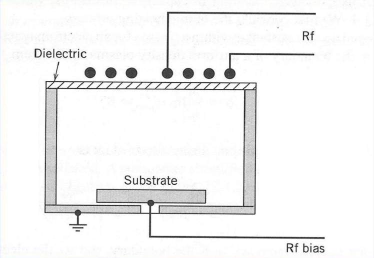
Construction of ICP reactors

- cylindrical geometry

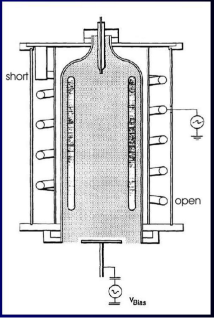




- planar geometry



- helical resonator

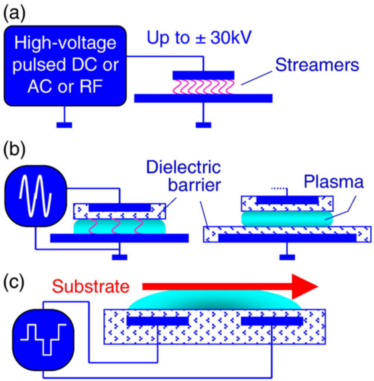


8.4 Comparison of Plasma Sources (low p, high f)

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

8.5 Atmospheric Pressure DBDs (AP-DBDs)

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)

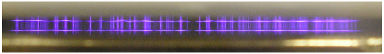
Suppression of sparks using:

- 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:

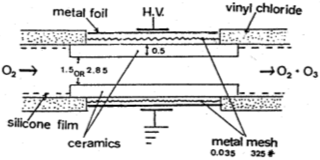
- filamentary



- homogeneous

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

Important role of

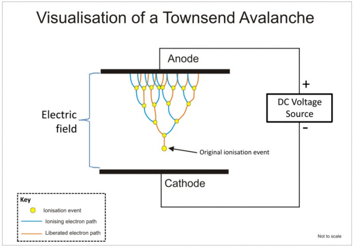


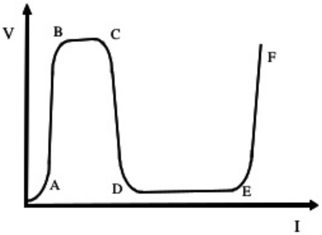
- **structure and material of electrodes**
  e.g. M. Kogoma, S. Okazaki, JPD (1994) 27 1985
- **higher frequencies of power supply**
  T. Nozaki et al., Plasma Process. Polym. (2008) 5 300)
- **gas mixture** (He, Ne, N_2, Ar + NH_3 etc.):
  - homogeneous DBD in He, Ar/NH_3 and N_2
    F. Massines et 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).**

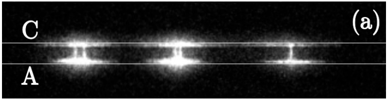




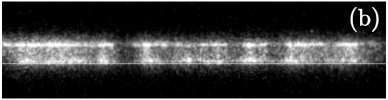
- (A) region of non-self-sustaining discharge
- (BC) Townsend discharge
- (CD) subnormal glow discharge
- (DE) normal glow discharge
- (EF) abnormal glow discharge

Homogeneous DBD (APGD) in Ar/acetylene

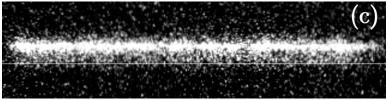
filamentary DBD in Ar



filamentary DBD in Ar/CH_4



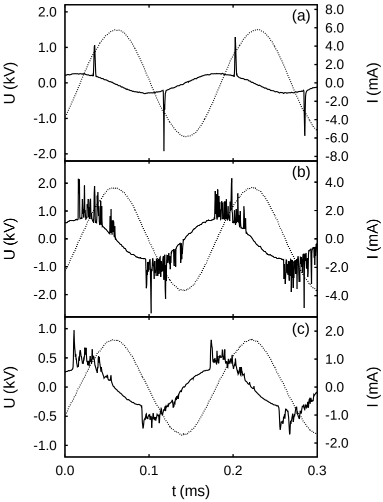
homogeneous DBD in Ar/C_2H_2



(80 μs (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

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



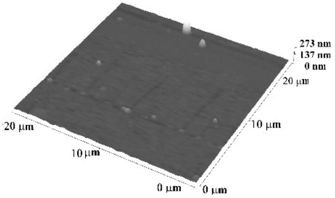
DBD
(a) DBD in pure Ar, (b) DBD in Ar/CH_4, (c) APGD in Ar/C_2H_2

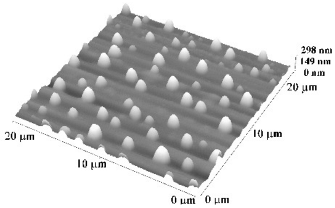
Why to Use Homogeneous DBD for Deposition?

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

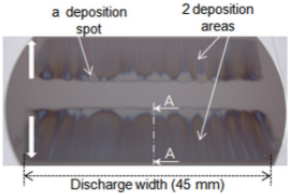
D. Trunec, Z. Navrátil, P. Sťahel et al. J. Phys. D: Appl. Phys. 37 (2004) 2112:

deposition in APTD (HMDSO/N_2) and in filamentary discharge





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



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

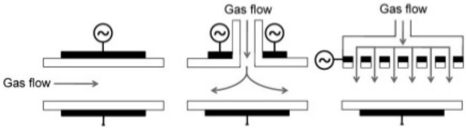
Problem of Film Uniformity

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

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

$\Rightarrow$ High electron-neutral collision frequency $\Rightarrow$ 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

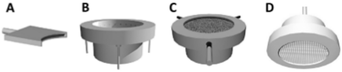
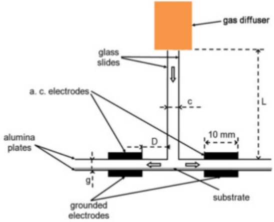


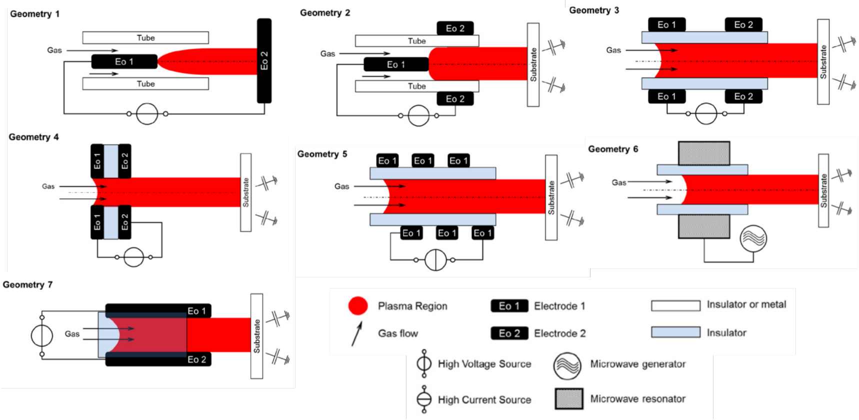
Figure 2. Schematic representation of the four different inlet set-ups: a) Sideway inlet, b) ring inlet, c) porous glass inlet, and d) microplasma–electrode.

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



8.6 Atmospheric Pressure Plasma Jets

- operating in local thermal equilibrium (LTE) $T_\mathrm{e} \sim T_\mathrm{n}$, $n_\mathrm{e} \geq 10^{15}\ \mathrm{cm}^{-3}$ - **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** $T_\mathrm{e} \gg T_\mathrm{n}$, $T_\mathrm{n} = 300 - 1000\,\mathrm{K}$, $n_\mathrm{e} < 10^{13}\ \mathrm{cm}^{-3}$



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

Arc-Based Atmospheric Pressure Plasma Jets

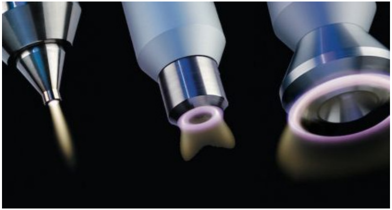
Plasma jets:

- operating in local thermal equilibrium (LTE) $T_\mathrm{e} \sim T_\mathrm{n}$, $n_\mathrm{e} \geq 10^{15}$ 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

Industrial plasma jets based on arc:

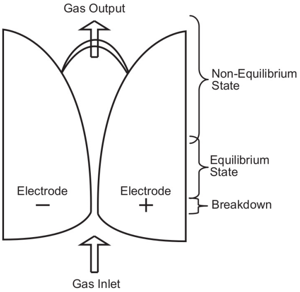
- Sura Instruments, non-transferred arc (patent WO 2015/107059 A1), dc or low f, argon flow, precursors for deposition
- PlasmaTreat, non-transferred arc (DE10223865 A1, US2002179575, DE102008058783 A1), 1-100 kHz, air flow, plasma cleaning, activation, deposition

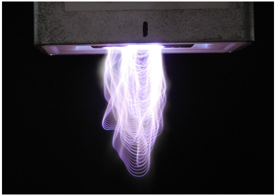


. . . and some others

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

SurfaceTreat

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

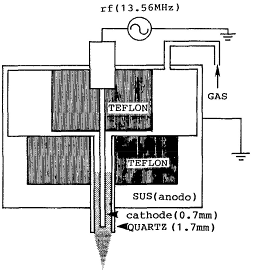
typical operation conditions:
500 W, 10 kV, (dry) air 11.8 slm

RF Plasma Jets

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

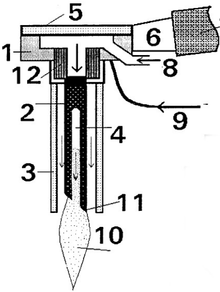
Non-LTE atmospheric pressure plasma jets need to prevent the transition to arc ⇒ **pulsed or high *f* discharges, a dielectric barrier at one or both the electrodes**

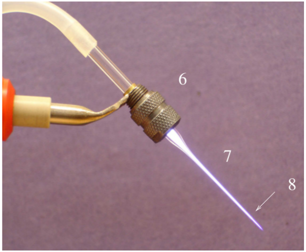
Earliest cold RF plasma jet proposed by Koinuma et al.



APL 60 (1992) 816

Development of cold RF jets in Brno, Masaryk University

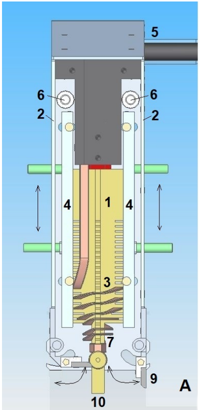


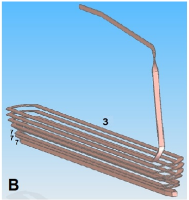


M. Klíma et al. Czech Patent PV147698 (1998), US6,525,481 (2003)
J. Janča et al. Surf. Coat. Technol. 116–119 (1999) 547

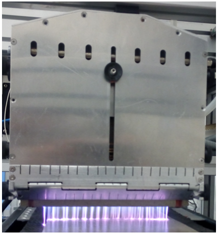
RF Plasma Slit Jet

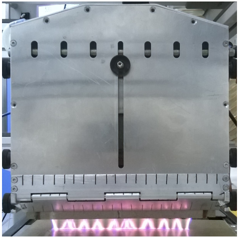
In Brno, we developed a new type of RF plasma jet. Unlike other jets working with capacitive coupling (E component important) it should generate EM with both the components (E, H) high (according to preliminary EM field calculations $E_{\mathrm{max}} = 10^5$ V/m, $H_{\mathrm{max}} = 800$ A/m).





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.