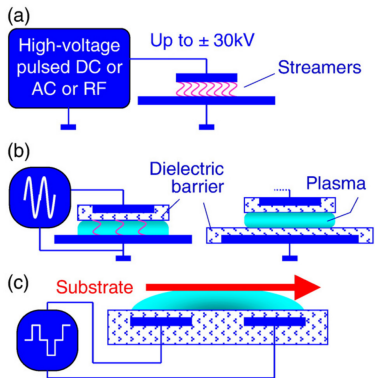


7.3.2 Cold Atmospheric Pressure Discharges

Plate-to-plate configuration



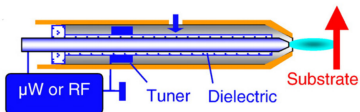
At low p , the collision frequency is low \Rightarrow electron energies remain high compared to ion neutral energies \Rightarrow non-equilibrium (cold) plasma.

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.

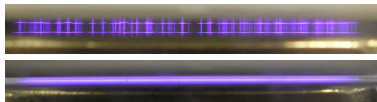
Plasma jet configuration



Atmospheric Pressure DBD (AP-DBD)

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

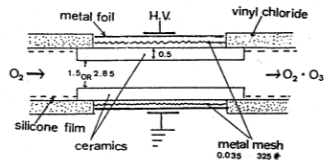
- ▶ filamentary
- ▶ homogeneous



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

Important role of

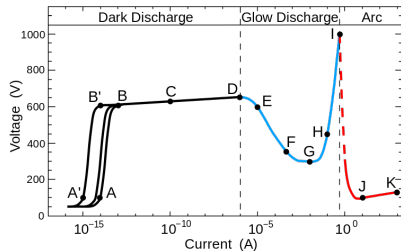
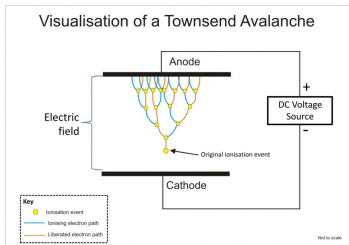
- ▶ **structure and material of electrodes**
e.g. M. Kogoma, S. Okazaki, JPD (1994) 27 1985
- ▶ **higher frequencies of power supply**
T. Nozaki et al., Plasma Process. Polym. (2008) 5 300
- ▶ **gas mixture** (He, Ne, N₂, Ar + NH₃ etc.):
 - ▶ homogeneous DBD in He, Ar/NH₃ and N₂
F. Massines et al. Surf. Coat. Technol. 174–175, 8 (2003); Plasma Phys. Controlled Fusion 47, B577 (2005).
 - ▶ PECVD in HMDSO/N₂ and HMDSO/N₂/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/C₂H₂
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 ($n_e \approx 10^{11}$) 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 ($n_e \approx 10^8$) to allow formation of cathode fall and the glow regime cannot be achieved - **atm. pressure Townsend discharge (APTd)**.



▶ C: avalanche Townsend discharge

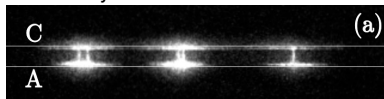
▶ D: self-sustained Townsend discharges

▶ F: sub-normal glow discharge

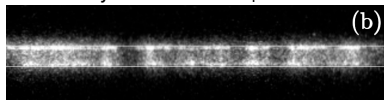
▶ G: normal glow discharge

Homogeneous DBD (APGD) in Ar/acetylene

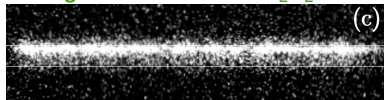
filamentary DBD in Ar



filamentary DBD in Ar/CH₄

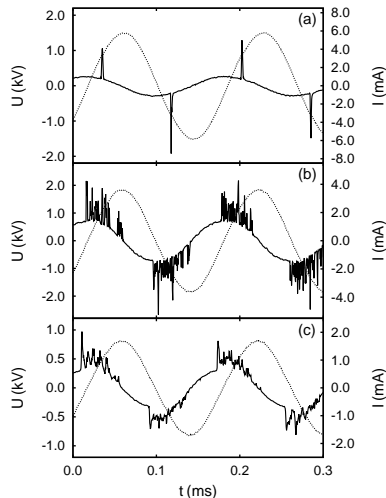


homogeneous DBD in Ar/C₂H₂



(80 μ s (one half-period) exposure time)

- ▶ difference caused by possibility of Penning ionization of C₂H₂ in Ar
- ▶ Ar 1s⁵ metastable - 11.55 eV,
- ▶ C₂H₂ ionization potential 11.40 eV but CH₄ 12.61 eV



(a) DBD in pure Ar, (b) DBD in Ar/CH₄,
(c) APGD in Ar/C₂H₂

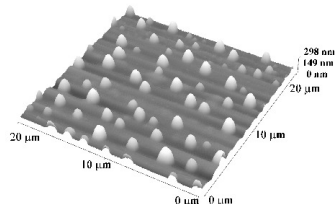
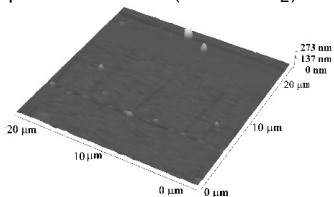
Why to Use Homogeneous DBD for Deposition?

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

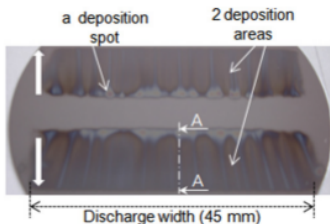
D. Trunec, Z. Navrátil, P. St'ahel et al. J. Phys. D: Appl. Phys. 37 (2004) 2112:

deposition in APTD (HMDSO/N₂)

and in filamentary discharge



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



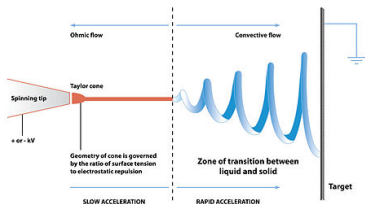
Local increased of the deposition rate, "deposition spots", due to non-uniform power dissipation in micro-filaments.

Why to Use Homogeneous DBD for Deposition?

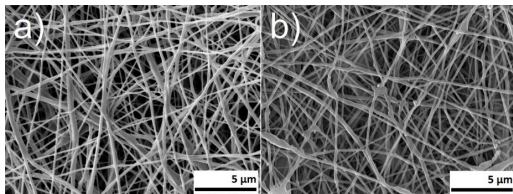
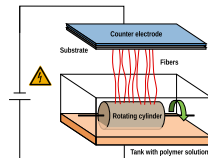
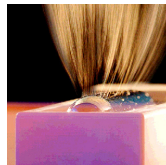
... modification of temperature sensitive and porous polymer nanofibers

Interesting novel material, polymer nanofibers, can be prepared by electrospinning but it requires further modification of surface properties (as usually with polymers)

Classical nozzle electrospinning:



Nozzle-less electrospinning by Nanospider™ from ELMARCO:



a) polycaprolactone electrospun nanofibers b) coated by plasma polymerization in homogeneous DBD

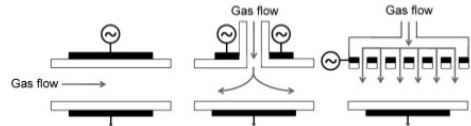
Problem of Film Uniformity

Atmospheric-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

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

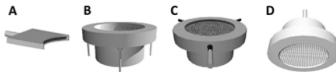
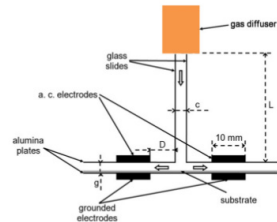
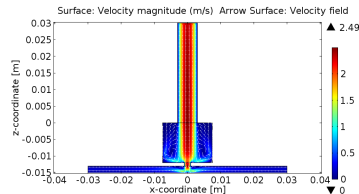
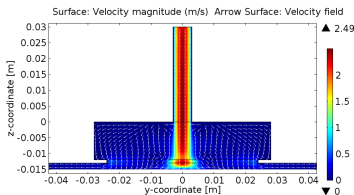
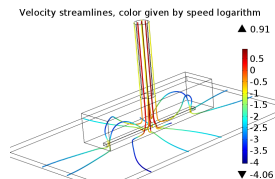
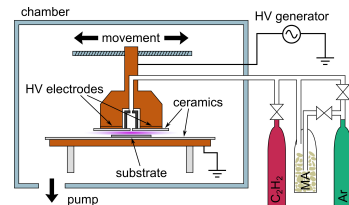


Figure 2. Schematic representation of the four different inlet set-ups: a) Sideway inlet, b) ring inlet, c) porous glass inlet, and d) microplasma-electrode.



Gas Dynamics Simulations in Our Set-up

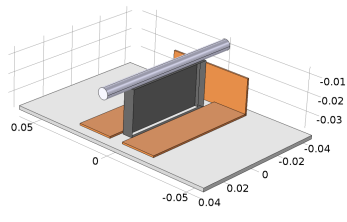
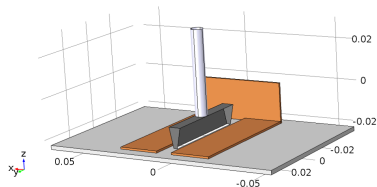
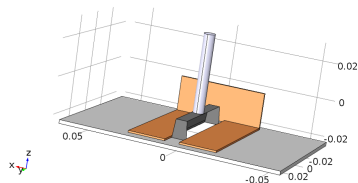
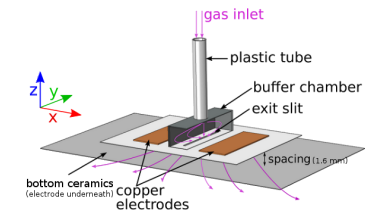
Solving the Navier-Stokes equations (laminar flow) in full 3D geometry for pure Ar (results are shown for 1550 sccm):



⇒ Complex flow patterns inside the buffer chamber make **the flow through the slit relatively even but better designs of the buffer chamber can be found!**

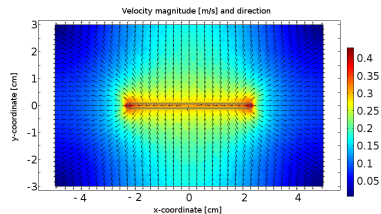
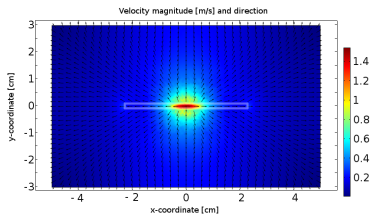
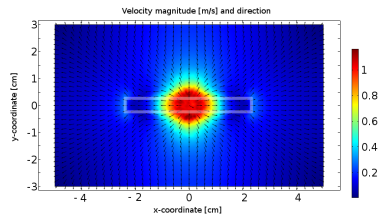
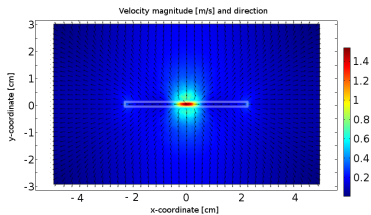
Gas Supply Optimization Using CFD Model

Variations of four different geometries tested



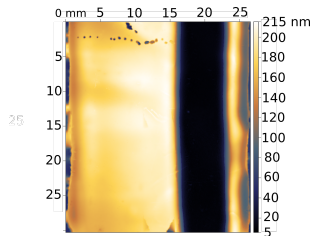
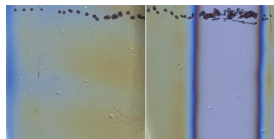
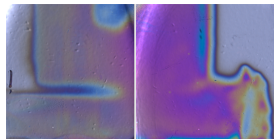
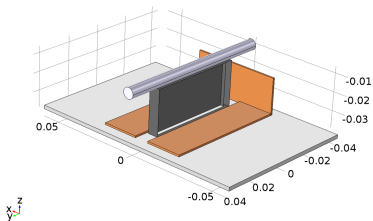
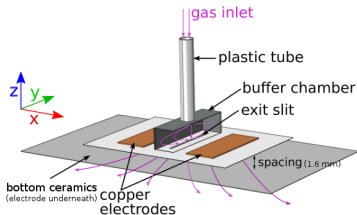
Gas Supply Optimization Using CFD Model

Variations of four different geometries tested



Does It Work in Real Life?

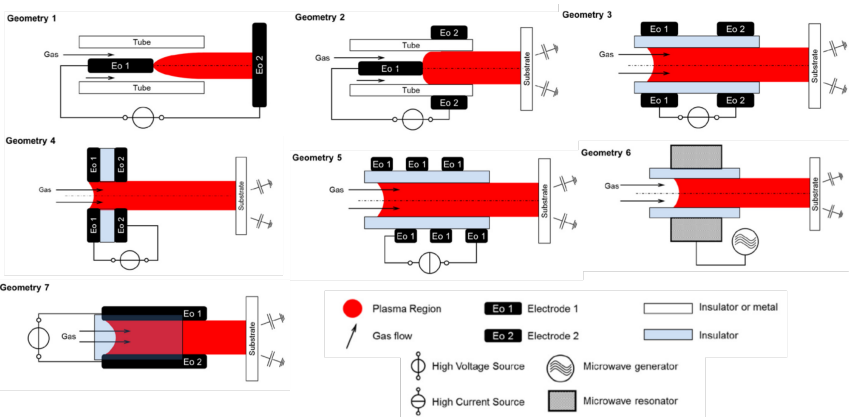
(case study for DBD co-polymerization of MA and C₂H₂ in Ar, no electrode movement)



Interference colours are measured by imaging spectroscopy refractometry \Rightarrow fitting of optical data provides spatially resolved film thickness

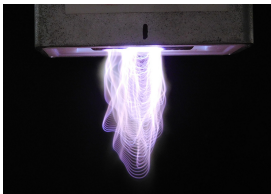
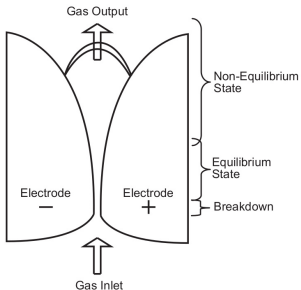
Atmospheric Pressure Plasma Jets

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



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**

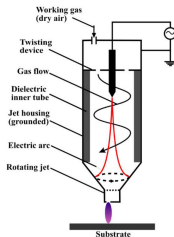
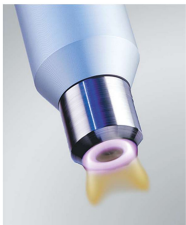
$f = 50 \text{ Hz}$
 max. $P = 500 \text{ W}$,
 max. $U = 10 \text{ kV}$



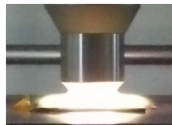
typical operation conditions:
 500 W, 10 kV, (dry) air 11.8 slm

PlasmaTreat Jet

Jet	Principle	Working gas	Working gas flow rate [slm]	Additive	Power [W]	Frequency	Treated area \varnothing [mm]
Plasmatreat rotating plasma jet (PT)	Electrical arc	Dry air	30	–	1000	21 kHz	33
AFS Plasmajet® (AFS)	Electrical arc	Dry air	5–10	–	200–500	16–31 kHz	8
SurfaceTreat gliding arc (GA)	Electrical arc	Dry air	11.8	Ar	550	50 Hz	27–36
RF plasma slit jet (RF)	CCP/ICP	Ar	50–100	N ₂	300–600	13.56 MHz	150–300



 **plasmatreat**



PlasmaTreat Jets in general: non-transferred arc (DE10223865 A1, US2002179575, DE102008058783 A1), 1-100 kHz, air flow, plasma cleaning, activation, deposition

AFS Jet

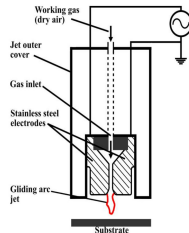
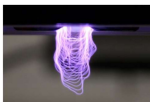
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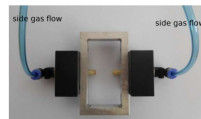
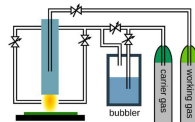
Turned to be not suitable for modification of polypropylene (too hot).

SurfaceTreat Jet

Jet	Principle	Working gas	Working gas flow rate [slm]	Additive	Power [W]	Frequency	Treated area \varnothing [mm]
Plasmatreat rotating plasma jet (PT)	Electrical arc	Dry air	30	–	1000	21 kHz	33
AFS Plasmajet® (AFS)	Electrical arc	Dry air	5–10	–	200–500	16–31 kHz	8
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RF plasma slit jet (RF)	CCP/ICP	Ar	50–100	N ₂	300–600	13.56 MHz	150–300



 **SurfaceTreat**

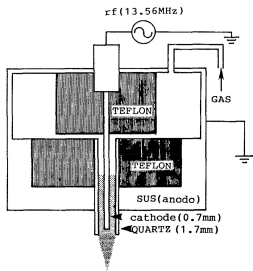


RF Plasma Jets

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

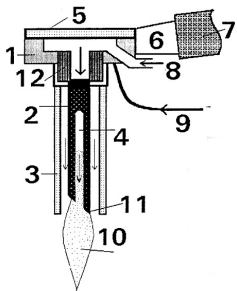
Non-LTE atmospheric pressure plasma jets need to prevent the transition to arc \Rightarrow **pulsed or high f discharges, a dielectric barrier at one or both the electrodes**

Earliest cold RF plasma jet proposed by Koinuma et al.

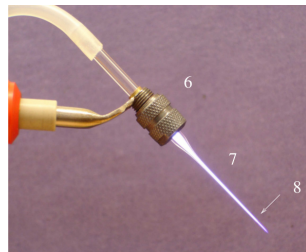


APL 60 (1992) 816

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



“Academic” RF Plasma Slit Jet

Jet	Principle	Working gas	Working gas flow rate [slm]	Additive	Power [W]	Frequency	Treated area \varnothing [mm]
Plasmatreat rotating plasma jet (PT)	Electrical arc	Dry air	30	–	1000	21 kHz	33
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