European Summer School on Plasma Applications in Material Science (PAMS-2011):

Atmospheric Pressure Plasmas

Hans-Erich Wagner and Ronny Brandenburg

Atmospheric pressure plasmas - Topics

Part I (R. Brandenburg): Introduction, overview and selected applications

- Incidences and historical remarks
- Electrical breakdown
- Types and classification of atmospheric pressure plasmas
- Selected applications

Part II (H.-E. Wagner): Diagnostics of selected non-thermal atmospheric pressure plasmas (Barrier discharges, coronas, plasma jets)

- Electrical characterization
- Optical emission spectroscopy
- Cross-correlation spectroscopy, streak photos and ICCD
- Laser-induced fluorescence
- Surface charge measurements
- Mass spectrometry at elevated pressure

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Atmospheric pressure plasmas – Structure part I

Part I: Introduction, overview and selected applications

1. Introduction
   - Incidences and relevances
   - Historical remarks
2. Basics
   - Electrical breakdown
   - Thermal and non-thermal plasmas
   - Scaling laws and miniaturisation
3. Arc discharges and plasma torches
4. Barrier discharges
5. Corona discharges
6. Plasma jets
7. Microplasma arrays
8. Classification and Summary

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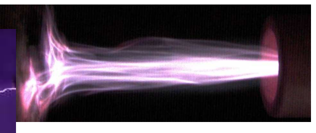
Atmospheric plasmas

1. Introduction: From lightnings to microplasmas



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Pressure range

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log$_{10}$ pressure

High Pressure

1.013 10^5 Pa — 1013.25 mbar → Atmospheric Pres. (AP) "Atmospheric Plasmas"

Low Vacuum

3 10^3 Pa — 30 mbar

Medium Vacuum

10^{-1} Pa — 10^{-3} mbar

High Vacuum

10^{-7} Pa — 10^{-9} mbar

Extremely High Vacuum

10^{-10} Pa — 10^{-12} mbar

→ Plasmas in standard air
→ Plasmas in open atmosphere
→ Plasmas at elevated press.

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Incidences of atmospheric plasmas

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Nature
- **St' Elmos Fire**
- **Aurora**
- **Ligthnings**
- **Transient luminous events**

Engineering and Technology
- **Partial discharges (electrical engineering)**
- **Switching**
- **Welding**
- **Melting and incineration**
- **Surface activation**
- **Chemical conversion**
- **Ligth emission**
- **Environmental protection**

Research and Development
- **Plasma medicine**
- **Film deposition**
- **...**

High economic impact!

→ Detection/Protection
→ Process optimization
→ Novel Applications

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Lightnings

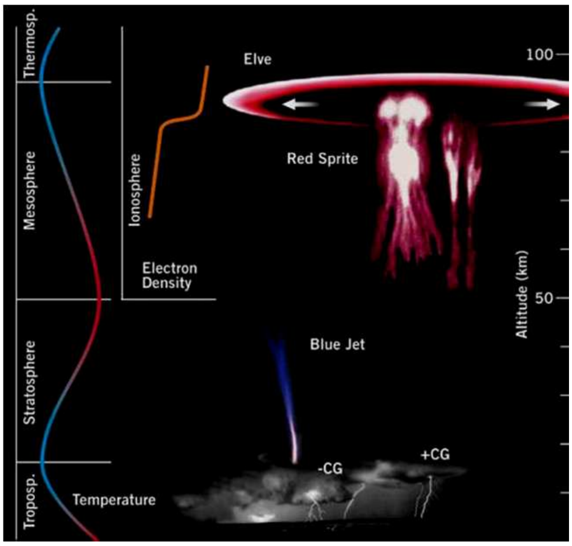
- speed up to of 60,000 m/s
- temperature up to 30,000 ℃
- current 5 – 20 kA (up to 200 kA)
- electric field: 3-4 kV/cm
- total power: sev. hundred MW

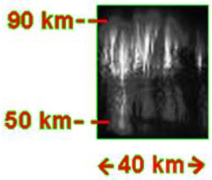
1) cloud-to-ground lightning CG
2) intracloud lightning CC
3) cloud-to-air lightning CA

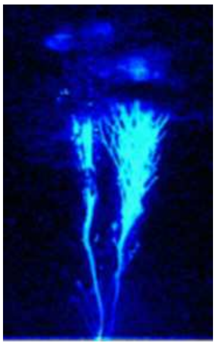
M.A. Uman "All about lightning" Dover Publications, New York

„Megalightnings" (upper atmosphere)

- transient luminous events (TLE)





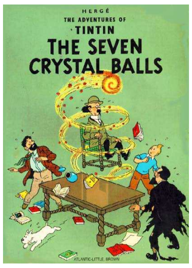


T. Neubert, Science, Vol 300, 2 (2003)

http://www.eurosprite.net; www.spritesandjets.com

Ball lightnings

- since 1638 described by thousands of eyewitnesses
- rarely recorded by meteorologists

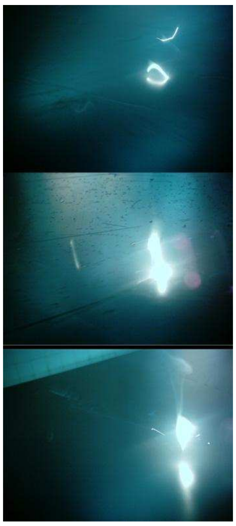
Hypotheses:

- Nikola Tesla 1904
- vaporized silicon clouds burning through oxidation
- nano or submicrometre particles as batteries
- passage of microscopic primordial black holes
- and many more ...

Nagano, 1987

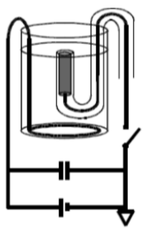
„Ball lightnings“ in laboratory

Numerous studies on plasmoids in mircowave cavaties
e.g. J. Ehlbeck et al.; Surface Coating Technol. 147 (2003)



Oxidation of silicon containing nanoparticle networks, e.g by using dc arc discharge on a silicon wafer to produce small glowing objects
J. Abrahamson and J Dinniss; Nature 403 (2000)
G. S. Paiva et al.; Phys. Rev. Lett. 98 (2007)

Ball-like plasmoids by discharging a high-voltage capacitor in a tank of water (e.g. Shabanov et al. 2001)

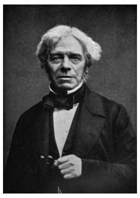
Y. Sakawa et al.; Plasma and Fusion Research 1 (2006)
A Versteegh et al.; Plasma Sources Sci. Technol. 17 (2008)

Historical remarks (Milestones)

1750: Investigations on electricity (**B. Franklin**)
- famous kite experiment → “lightning is electricity”
- conservation of charge; charge labels “+” and “-

1802 Discovery of electric arc effect (V.V. Petrov)

1808 carbon-arc lamp; 1815 arc melting (H. Davy)



1831 – 1853: Electric discharges in gases **(M. Faraday)**
- detailed and structured researches
- law of induction, Faraday effect ...
- terminology (“anode, cathode, electrode, ion, glow discharge”)

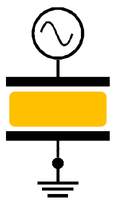
1860: Initiation of chemical reactions (synthesis) by arcs (Berthelot)

1857: Ozoniser/Barrier discharges (**W. Siemens**)

1887: Electric arc furnace for steel making (W. Siemens)
1910: Arc welding
1940: Acetylene and ethylene syntesis (Hüls process)

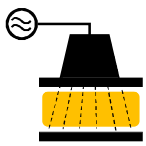
Plasma generation

Electrical gas discharge
→ high voltage power supply
→ DC, AC, pulsed; frequency: Hz ... MHz
→ electrical breakdown according to Paschen law
(breakdown voltage dependent on pressure x distance)



Electromagnetic radiation
→ microwave excited plasmas (915 MHz, 2.54 GHz)
→ ignition structure needed
→ usually hot plasmas (plasma torches for incineration)

Electron beam
→ electron accelerating tubes
(beam gun, keV ... MeV)
→ extensive installations and therefore only suited for large gas flows



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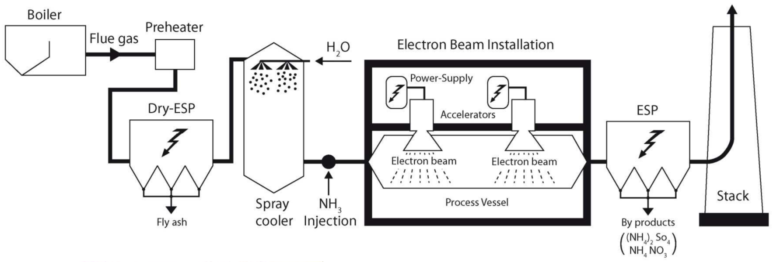
Electron beam flue gas treatment

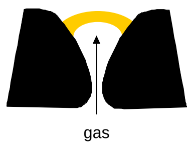


A.G. Chmielewski et al.; INCT Warzaw

Discharge generated plasmas @ 1 atm

Gliding "arc"

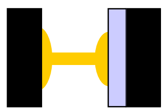
→ Expansion and cooling of plasma in increasing electrode gap by gas flow



Barrier discharge

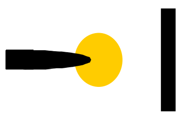
→ Isolator in discharge gap limits discharge duration, energy dissipation and thus spark formation

→ many sub-types (surface discharge, coplanar, packed bed



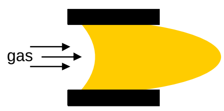
Corona

→ Inhomogeneous electric field enables discharge ignition at lower voltage and limits discharge duration and energy dissipation



Plasmajet (APPJ)

→ Plasma expanded outside electrode configuration by gas flow



Special features / relevance

- **High density of neutral background gas = high collision rates**
  → rapid breakdown
  → high and rapid mass/energy transfer (heating, chemistry, …)
  → high space charges (causing e.g. instabilities)
  → higher breakdown fields

- **Avoidance of vacuum devices (pumps, chambers, ...)**
  → less cost and maintenance intensive
  → linear throughput processing

- **Several applications require ambient/open conditions**
  → biomedical applications ("Plasma medicine")
  → decontamination of exhaust and flue gases
  → material processing
  → plasma chemistry (3-body collisions)

... but be aware of:
gas consumption; by-products; high voltage, heating, etc. ...

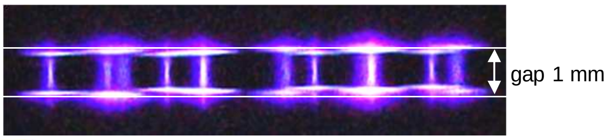
Microdischarges and microplasmas

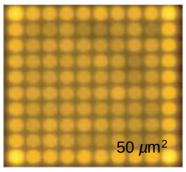
= Discharges with dimensions of µm ... mm

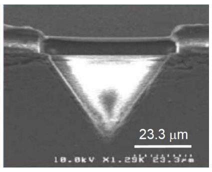
- Generated in small structures or narrow cavities (e.g. as arrays or in tubes)
- Formation of fine plasma channels, so-called filamentary discharges

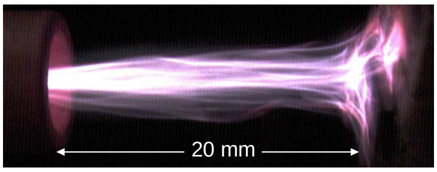
...µP often (usually) operate at atmospheric pressure, but AP are not solely µP!

- characteristics differ from traditional plasmas at lower pressures
- portability and non-equilibrium („cold") plasma character offer variety of new applications



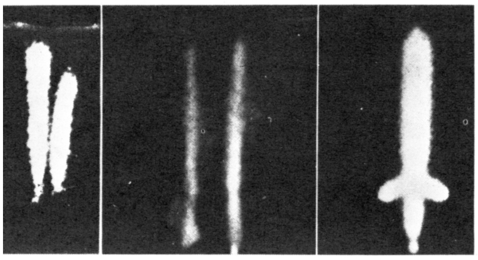






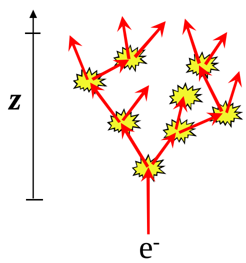
J. G. Eden et al., University of Illinois

2. Physics of plasmas at atmospheric pressure



Electron avalanches

Ionisation cascade



ionisation

electron drift

Townsend-avalanches
John S. Townsend
(1868-1957)

$$N_e = 1 e^{\alpha z}$$

$$\nu_i = \alpha v_{D,e}$$

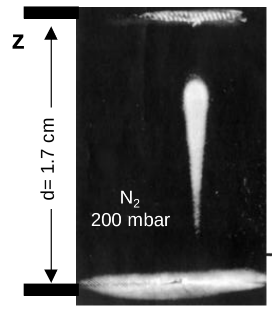
α 1. Townsend coefficient

ν_i ionisation frequency

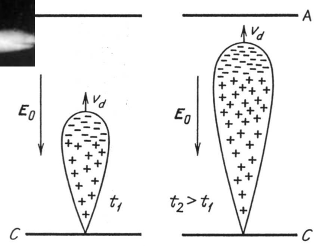
$v_{D,e}$ drift velocity of electrons

H. Raether „Electron avalanches and breakdown in gases“ (1964)
Yu.P. Raizer „Gas Discharge Physics, Springer-Verlag, Berlin Heidelberg (1991)

Shape/charge distribution of el. avalanches



Cloud chamber track of a single avalanche by H. A. Raether (1909-1986), 1939

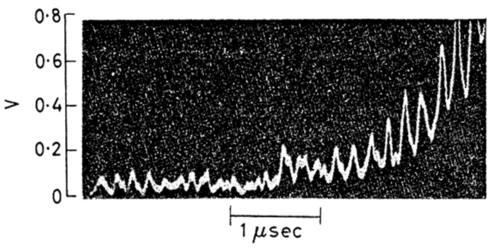


$\mu_e >> \mu_i$

electron/ion mobility

H. Raether „Electron avalanches and breakdown in gases“ (1964)
Yu.P. Raizer „Gas Discharge Physics, Springer-Verlag, Berlin Heidelberg (1991)

Avalanche breakdown



Series of avalanches lead to breakdown

Figure 5.22. Series of avalanches in room air at $U_{stat.}$ which lead to breakdown; $E/p = 37{\cdot}7$, $p_{20} = 760$ Torr, $d = 2{\cdot}5$ cm. The growth of the current in generations can be observed up to current amplitudes ten times higher than the mean amplitude reproduced here[43]

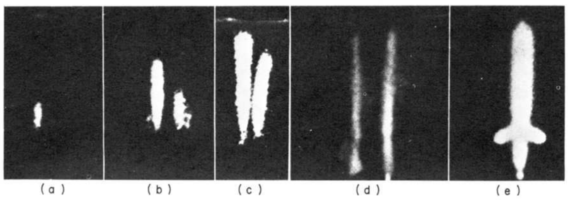


Figure 3.51. Cloud-chamber photographs of electron avalanches and avalanche-streamer transition in a gap of 3·6 cm in air at 260 torr. The field is ~11800 V cm^{-1} in (a) and slightly higher for each successive photograph reaching ~12200 V cm^{-1} in (e) (Raether, 1939. Reproduced by permission of Springer-Verlag)

Avalance-to-streamer transition @ high electric fields and long gaps

H. Raether „Electron avalanches and breakdown in gases“ (1964)

Townsend breakdown

- Direct ionisation

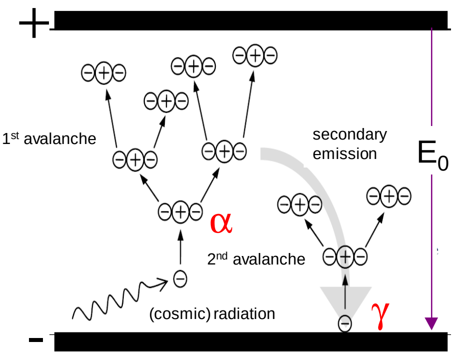
$$N_e = N_{e,0}\, e^{\alpha z}$$

$$\nu_i = \alpha\, v_{D,e}$$

- Secondary electron emission by ion impact

- **Townsend-Criterion:** self-sustained discharge

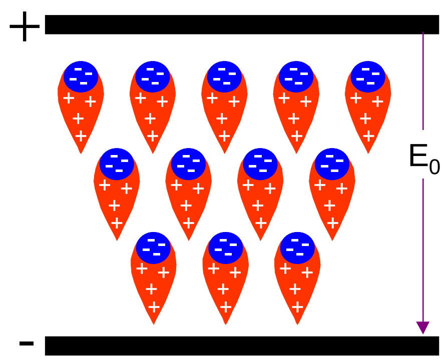
$$\gamma \cdot \left(e^{\alpha d} - 1\right) = 1$$



α	1. Townsend coefficient
ν_i	ionisation frequency
$v_{D,e}$	drift velocity of electrons
γ	3. Townsend coefficient

Townsend breakdown (2)

- many generations of avalanches
- negligible radial distortion by space-charges
- uniform breakdown



$$pd < 1\, bar \cdot cm$$

Streamer breakdown

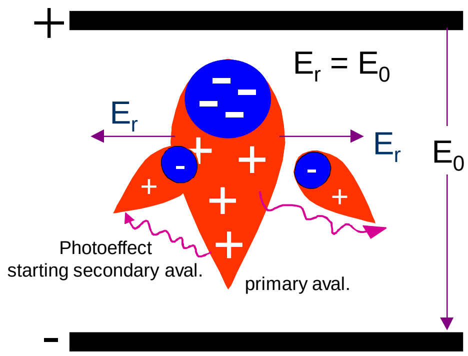
- concept developed by L.B. Loeb; H. Raether; J.M. Meek
- significant field distortion due to space-charge build-up in a single avalanche

$$\mu_e >> \mu_i$$

- formation of thin ionised channel(s)
- Raether-Meek-Criterion

$$e^{\alpha d} \approx 10^8$$

$$\int_0^d \alpha x \, dx = K \approx 18$$



μ_e, μ_i Electron and ion mobility

$$pd > 10 \; bar \cdot cm$$

Cathode- and anode-directed streamers

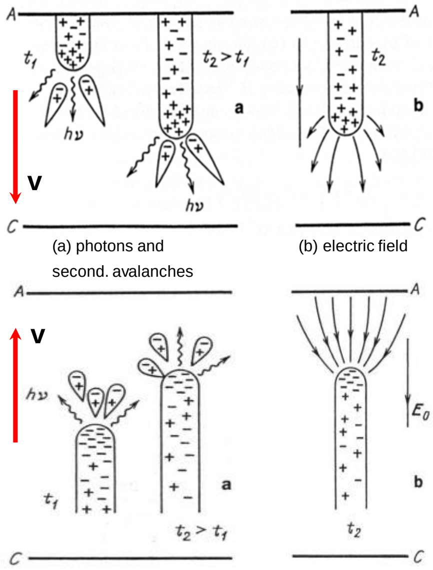
Positive or <u>cathode- directed</u> streamer
(most common)

→ propagating distortion of electric field due to space-charge accumulation

→ secondary avalanches in front of positive streamer end

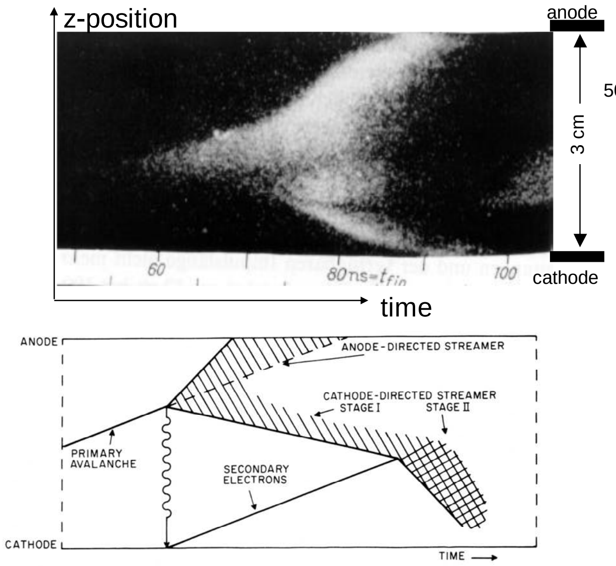
Negative or <u>anode-directed</u> streamer
@ large gaps & overvoltages

→ secondary avalanches in front of negative streamer head



Yu.P. Raizer „Gas Discharge Physics, Springer-Verlag, Berlin Heidelberg (1991)

Streak photo at pre-spark stadium



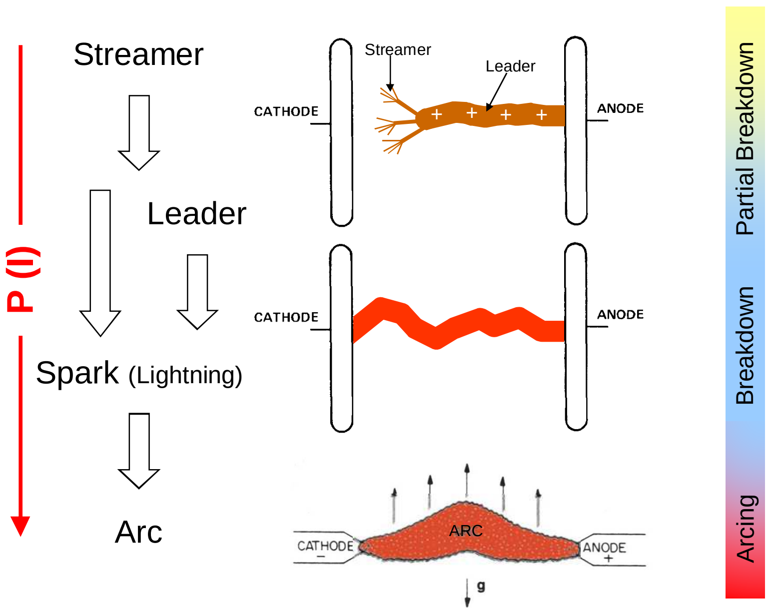
N_2
500 mbar

streamer velocities up to 10^6 m/s

(= 10 times $v_{D,e}$)

K.H. Wagner; Zeitschrift fur Physik 204 (1967) 177 / Loeb & Craggs; Wiley 1978

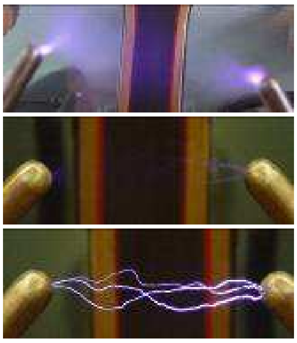
Partial breadkown - leader, spark, arc



Partial breadkown and spark

Influenzmaschine; Uni Greifswald

Streamers



Spark

Cloud-to-ground lightning

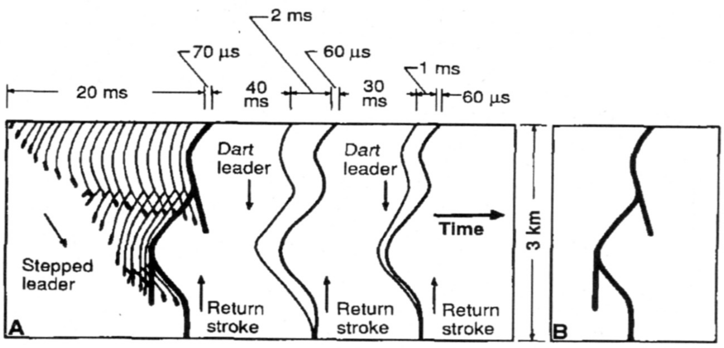


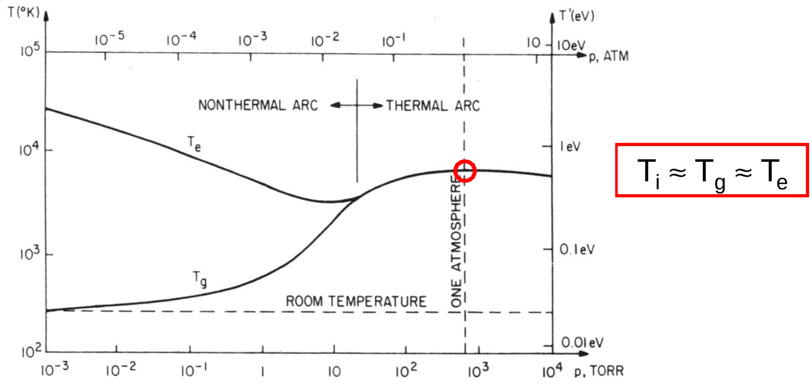
Fig. 6. (A) Luminous features of a lightning flash below cloud base as would be recorded by a streak camera. Increasing time is to the right. For clarity the time scale has been distorted. **(B)** The same lightning flash as would be recorded by a camera with stationary film. [Adapted from (21) with permission, © 1987 Academic Press]

M.A. Uman and E.P. Krider; Science, 246 (1989) pp. 457-464

APP tend to LTE-plasma regime!

Local Thermal Equilibrium ("thermal")

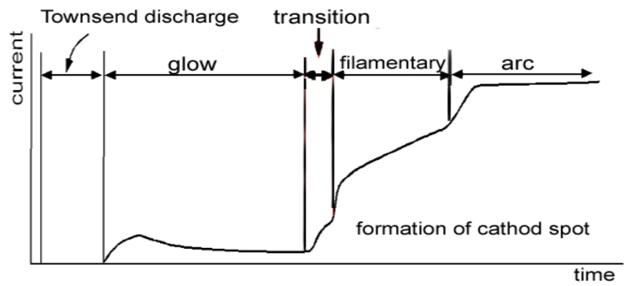
- microreversibility of elementary processes and equipartition of energy between all species of particles
- "local": long-range effects like radiation not in in thermodynamic equilibrium (Planck's law not valid)



J.R. Roth „Industrial Plasma Engineering", Vol. 1: Principles, IOP Publishing Ltd 1995

Non-LTE-plasmas at atmospheric pressure

APP are not solely LTE plasmas



Kekez et al. 1970

Mechanismn of glow-to-art transition:

Increase of current density j → increase of local electric field → constriction of ionization channel (filamentation) = increase of j→ cathode spot formation and thermal ionization → thermalization

Limitation of discharge duration (transient)
- Certain number of collisions necessary to establish equil.

Limitation of current / power density
- reduction local dissipated energy density/ electric field

Non-thermal plasma:
$T_e > T_i > T_g$

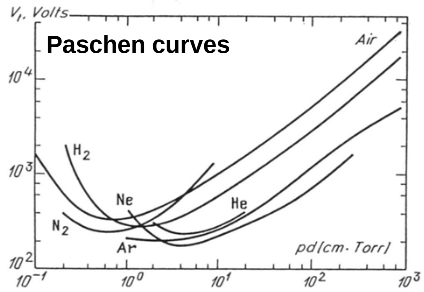
Invariants / similarity parameters

$$U_{Breakdown} = f(p \cdot d)$$

$$j/p^2 = const.$$

$$\alpha/N = const.$$

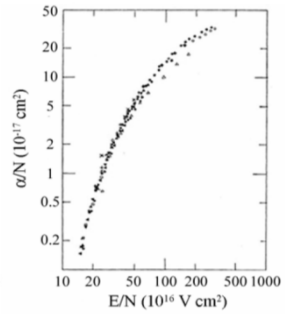
$$E/N$$



p incr. → d decr.	Miniaturisation
p incr. → j incr. → r decr.	Constriction

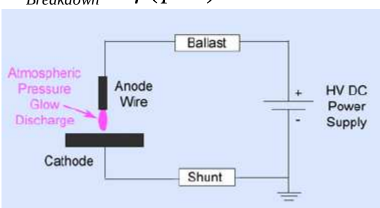
But:

- Discharge susceptible to instabilities (glow to arc transition)
- Wall effects (surface charges, secondary emission, ...)
- Quenching & 3-body collissions

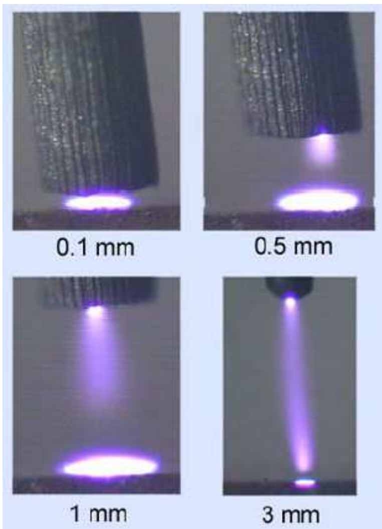


pd-scaling (Paschen law)

$$U_{Breakdown} = f(p \cdot d)$$



- Stable glow discharges in N_2 with small inter-electrode gap spacing down to 20 μm
- thickness of cathode fall: 10 μm



D. Staack et al.; Plasma Sources Sci. Technol. 14, (2005)

3. Arc discharges, arc jets, and plasma torches

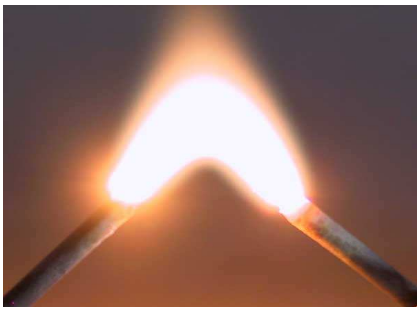
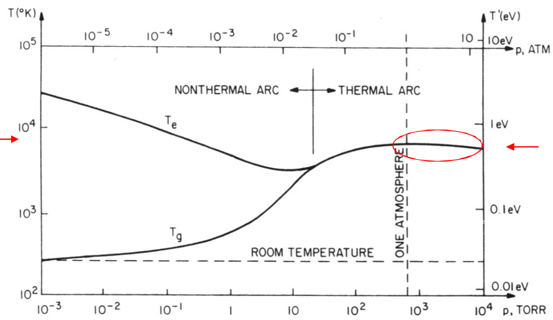


Photo: Achim Grochowski

Arcs at atmospheric pressure: LTE-plasmas

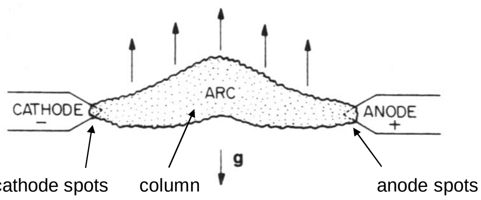


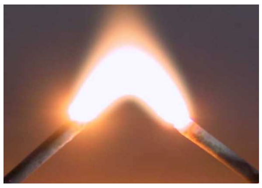
„Thermalization“ due to high density and thus high collision rates

- **LTE: 0.5 eV < $T_e \cong T_g$ < 5 eV** (1eV ≅ 10^4 K); **non-thermal outside the core**
- Arc current: **50 < I < 10^4 A**; Voltage: some **10 V;** Electric field: **500 < E < 5000 V/m**
- Energy density: **10^7 ... 10^9 J/m³**; Current density: **10^7 < j < 10^9 A/m²**
- Typical cathode emission: **field emission** and thermionic emission
- Electron density: **10^{22} < n_e < 10^{25} m^{-3}**
- Ionization degree: SAHA equation

Free-burning arcs / „arc family“

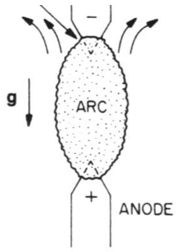
Convective heat transport → „ ARC“





- arcs with hot thermionic cathode
- arcs with external cathode heating
- arcs with cold cathode and cathode spots
- vacuum arc
- high and /or very high -pressure arc
- low pressure arcs
- special modes

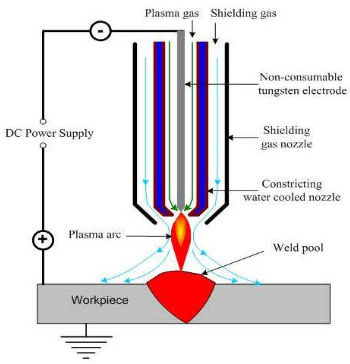
etc. ...



Transferred and non-transferred arc

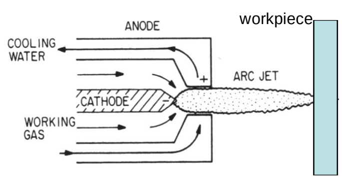
Transferred Arc

- work piece used as electrode
- mainly used for welding (gas tungsten arc welding GTAW; tungsten inert gas TIG; plasma arc welding PAW)
- with shielding gases for special applications



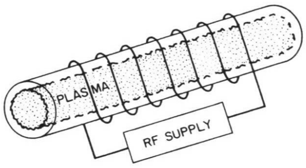
Non-Transferred Arc (Plasma Torch)

- work piece subjected to high-enthalpy plasma flow
- used for spraying and chemistry

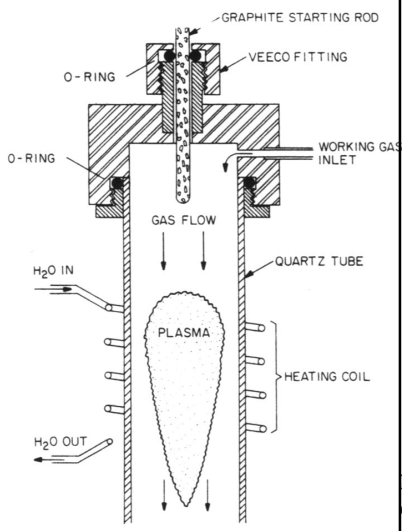


Dmitri Kopeliovich; www.unilim.fr/.../2006limo0029/html/TH.2.html

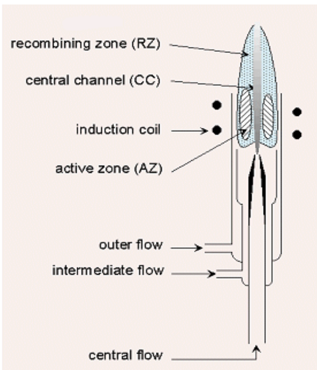
(RF-driven) ICP-Torch

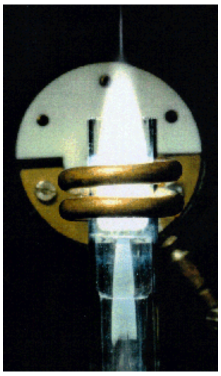


- RF current by transformer action
- 1 bar upper limit
- frequency 10 kHz ... 30 MHz
- power 1 kW ... 1 MW
- T = 10^3 ... 2 10^4 K



ICP-Torch vs. arc jet / applications





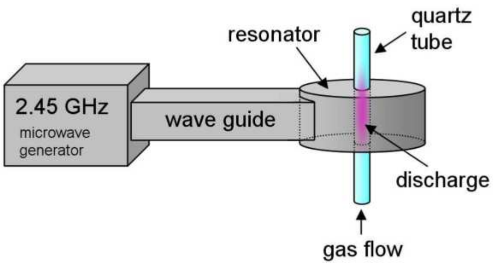
Compare with arc jet:

- Larger beam cross section
- Treating *larger surfaces* with *lower* gas velocities
- No tend to erode electrodes
- Form of exciting coil variable

Applications:

- Surface coating
- Chemical processing
- Purity materials production (e.g. silica, ultrafine powder, ...)
- Heat treatment of surfaces (oxidation, sintering)

Microwave Induced Plasmas (MIP)

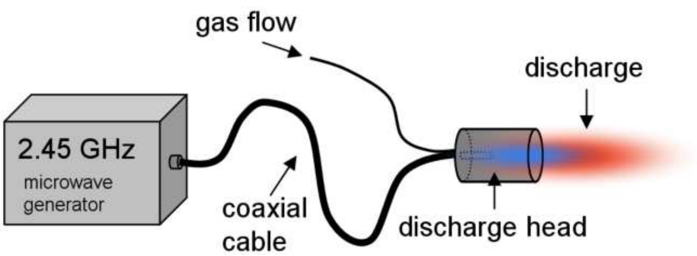


MW Zander

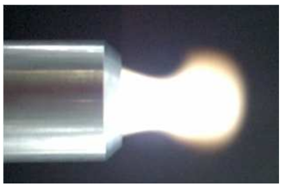
- Resonant cavity plasmas using different kinds of resonators (e.g. round or cylindrical) to induce peaking of field intensity in the center of the resonator

Ehlbeck, Pollack, Winter, et al,. J Phys D 2011

Microwave Induced Plasmas (MIP)

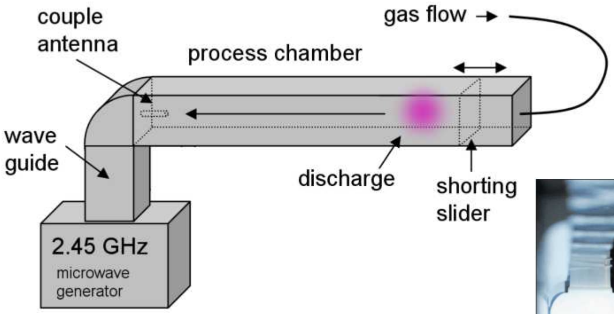


- Free expanding microwave plasma torches with a particular discharge head



Ehlbeck, Pollack, Winter, et al,. J Phys D 2011

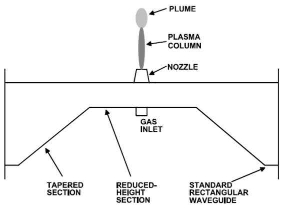
Microwave Induced Plasmas (MIP)

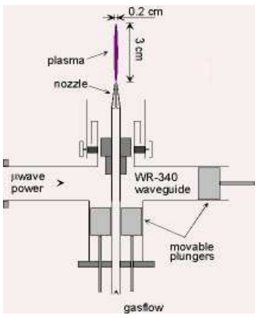


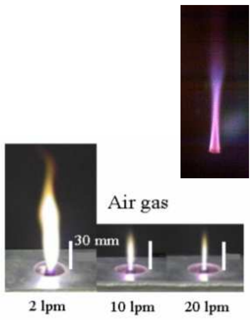
Ehlbeck, Pollack, Winter, et al,. J Phys D 2011

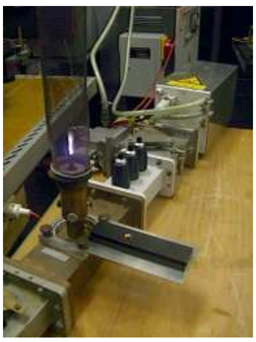
J. Ehlbeck et al. GMS Krankenhaushyg. Interdiszip 3 (2008)

Miniaturized MIP-torches: TIA and TIAGO







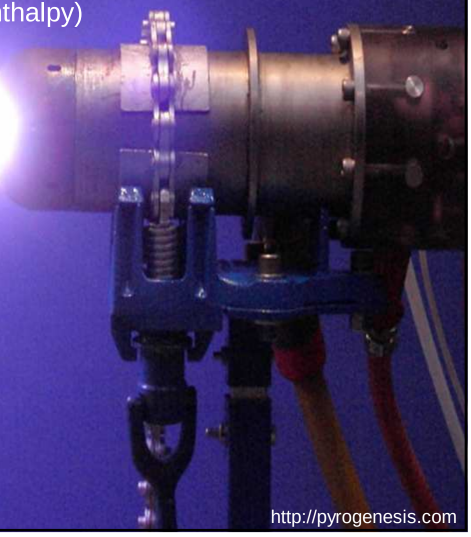


- TIA(GO): torch a injection axial (sur guide donde)
- Surfatron-based coaxial microwave plasma
- Mainly used for spectrochemical analysis applications (atomic emission spectrometry)

M. Moisan et al., Plasma Sources, Sci. and Technol. 3, (1994) and Plasma Sources Sci. Technol. 10 (2001); photos: TU Eindhoven and Y.S.Bae et al. J. Korean Phys. Soc. 48, 1 (2006)

Arc and torch applications

Arcs: Thermal plasmas
Arc-jets & Torches: Thermal or translational plasma („Hot non-thermal“)
→ Most widely used for gas heating (Enthalpy)

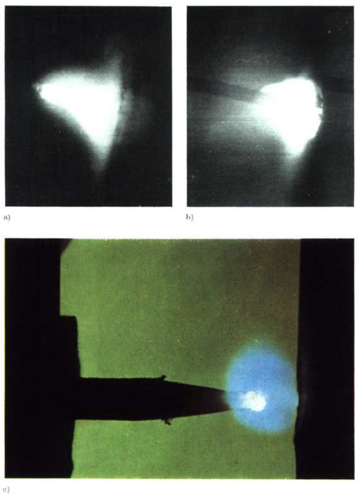


- chemistry:
  pyrolysis, synthesis
- material processing:
  melting, welding, cutting, spraying, ...
- incineration (waste)
- production of powders
- spectrochemical analysis
- switching arcs in circuit breakers

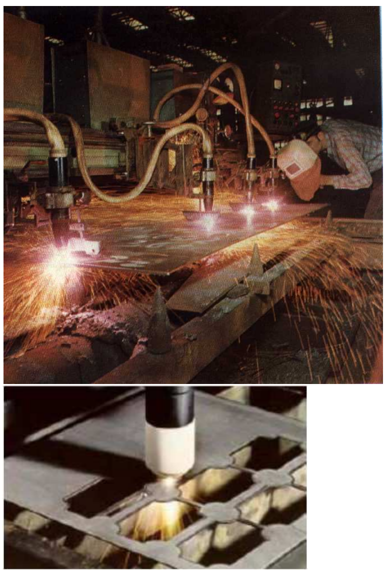
http://pyrogenesis.com

Arc welding and cutting

INP Greifswald



a) I = 90A
b) c) Ar, W cathode, I = 12A

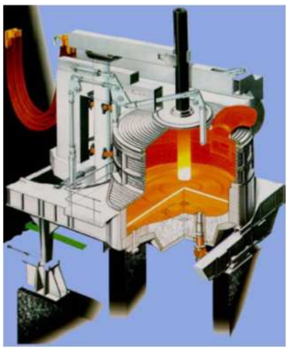


Mierdel “Was ist Plasma”; Hypertherm Inc.

INP Greifswald

Arc melting / steel making / metallurgy

Electric Arc Furnace (EAF)

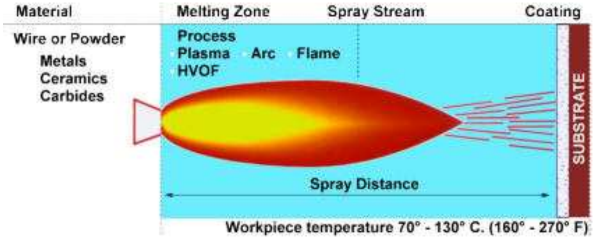


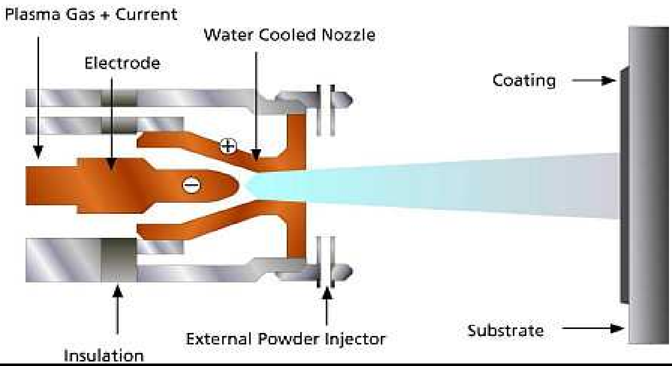
- up to 100 MW active power
- 600 … 320 kWh/t
- graphite electrodes (60 … 80 cm diameter)
- 140 kA (dc); 75 kA (ac)

D. Neuschitz, RWTH Aachen

Plasma spraying

Principle

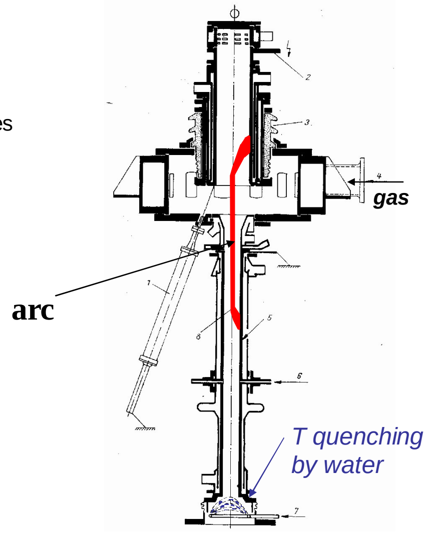




Plasma chemistry

- Industrial production of NO from air (Birkeland-Eyde process 1905)
  → max. 15 kWh / kg NO)
- C_2H_2 synthesis from methane (Hüls process 1940)
  → problem: quenching, frozen states
  → e.g.: 1h operation:
  8 MW (T= 18000K)
  850 kg C_2H_2
- Reduction of metal oxides in metallurgy

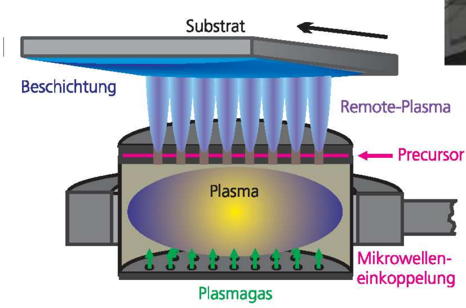
HÜLS reactor (Gladisch 1962)



Surface processing by MIP-remote

Atmospheric pressure chemical vapour deposition (AP-PECVD)

Cyrannus Plasma Source (iplas)
(5 … 10 kW; 50 … 200 slm Ar)

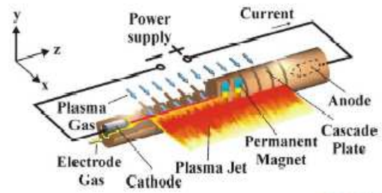


- c-Si Photovoltaik
- etching, texturing
- SiN_x:H

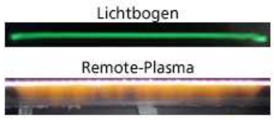
V. Hopfe, I. Dani et al. Fh-IWS Dresden / iplas / Universität der Bundeswehr

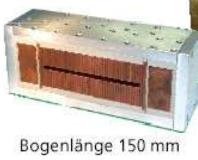
Surface processing by liniar arc remote plasma

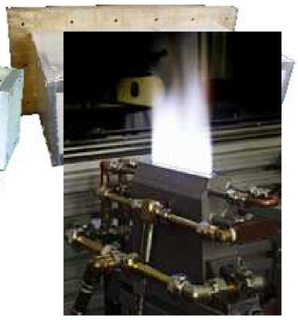
Atmospheric pressure chemical vapour deposition (AP-PECVD)



Linear DC Arc
for remote deposition and etching

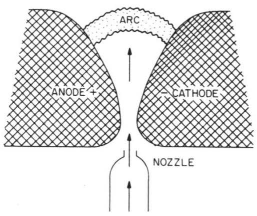


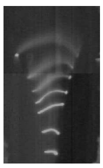


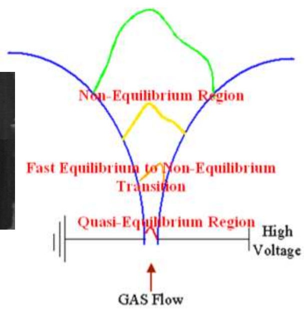


V. Hopfe, I. Dani et al. Fh-IWS Dresden

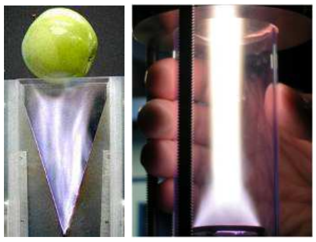
Gliding arc principle („Jacobs ladder“)







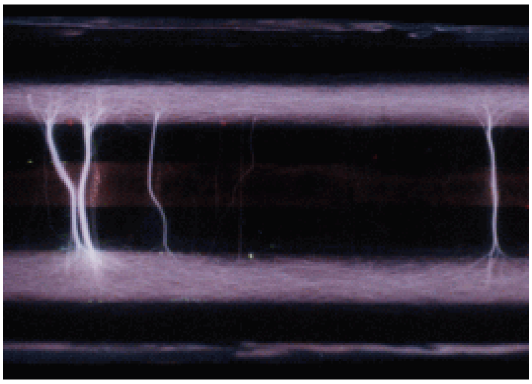
- arc (or spark) discharge in non-perpendicular discharge gap
- expansion cooling → non-thermal
- investigations on surface processing and volume chemistry (e.g. CH_4 conversion)

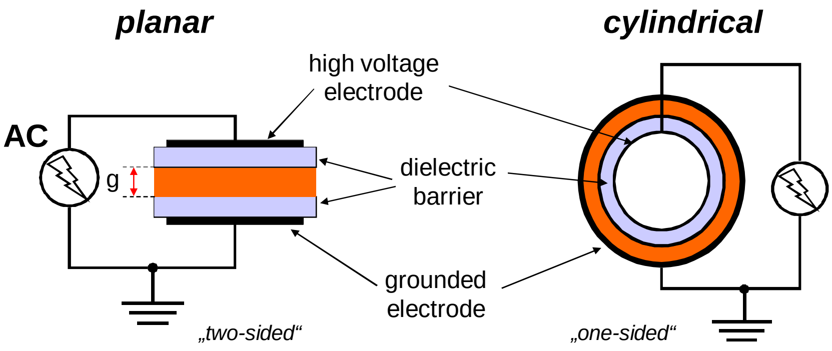


A. Gutsol et al.; Drexel University

4. Barrier Discharges

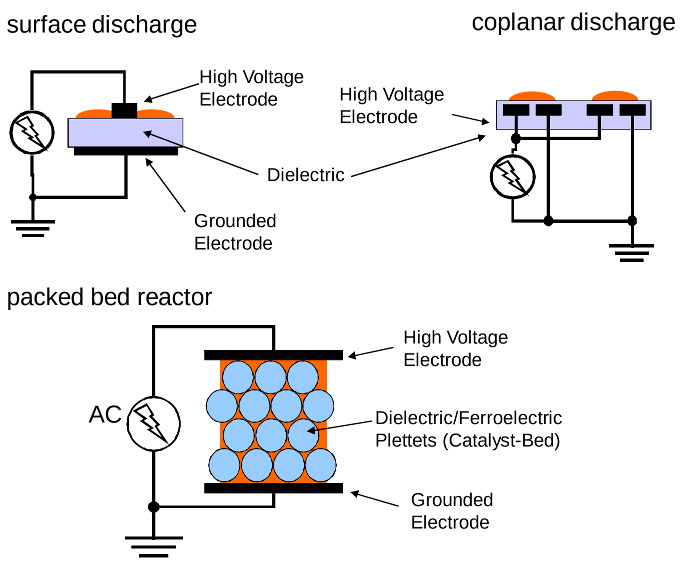
(Silent Discharges; Dielectric Barrier Discharge)



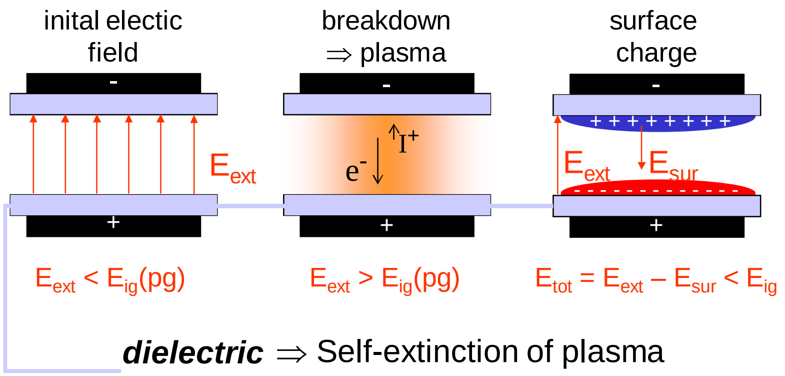


p = 0.5 ... 3 bar
V_{pp} = 3 ... 20 kV; f = 50 Hz ... 100 kHz
g = 0.2 ... 5 mm; ε_r = 5 ... 10 ... 10^4 (dielectric ... ferroelectric)

Surface discharges and packed-bed



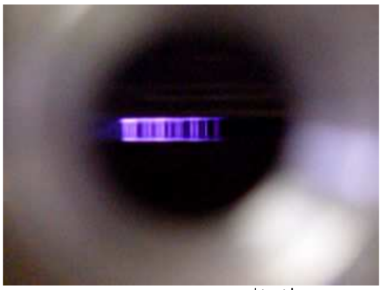
Role of the dielectric

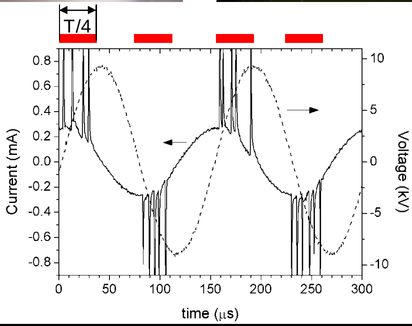


dielectric barrier ⇒ Self-extinction of plasma
⇒ Limitation of dissipated energy

Prevention of sparking / arcing
⇒ non-thermal plasma!

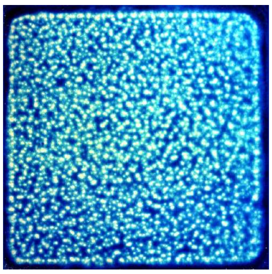
Filamentary plasmas

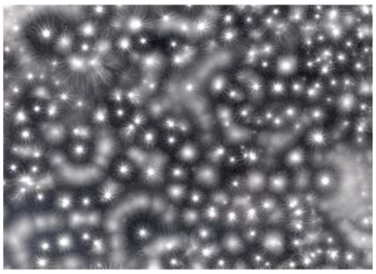




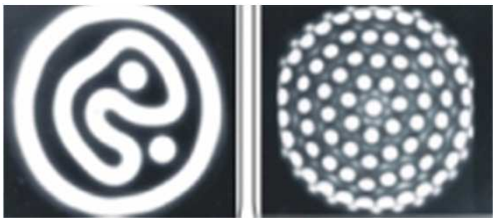
Filamentary structures / Lichtenberg figures

MD footprints (Lichtenberg figures)



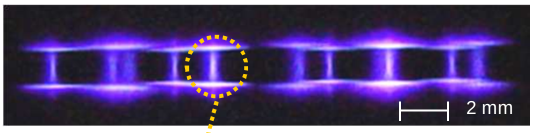


Regular MD-pattern

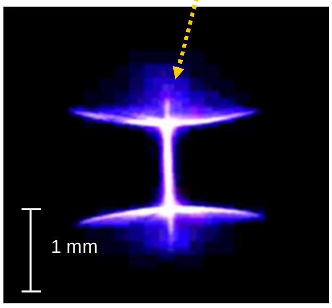


U. Kogelschatz ABB Switzerland; Purwins et al., Uni Münster

Filaments and microdischarges (MDs)



Filamentary plasma



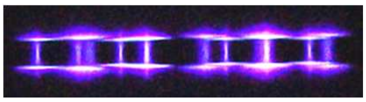
Single Filament=
10^2 ... 10^3 **Microdischarges**

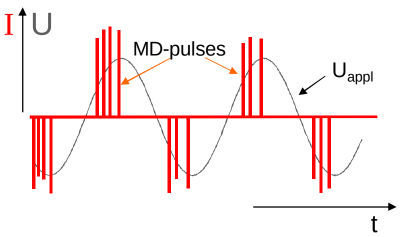
- non-stationary, transient, non-homogeneous plasmas
- small dimension (0.1 ... 1 mm)
- short duration (10 ns ... 1 µs)
- statistical occurrence

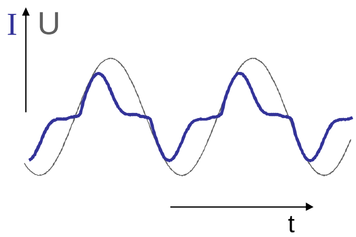
INP Greifswald

Diffuse vs. filamentary BDs

Filamentary	Diffuse







statistical MDs, ns-range	periodical (appl. frequency) µs-range

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Measures to prevent filamentation

- minimum initial electron density
  → pre-ionisation by x-rays or second discharge
- minimum ionization rate before breakdown
  → minimum dU/dt
  → minimum $\delta(\alpha/N)/\delta(E/N)$
- indirect ionisation processes (e.g. Penning-ionisation)
- residual density of ions and excited species (e.g. metastable states)
- surface properties: γ, ε, σ, humidity, ...
- intelligent power-control (ns-pulses, matching, ...)

U. Kogelschatz IEEE Trans. Plasma Sci. (2002)

Pulsed plasma generation

- time for microdischarge development (air: 10 ns for 1 mm gap)
  = time of build-up of possible local non-uniformities t_{MD}
- If voltage rise time << t_M and high overvoltage conditions:
  high electric field in front of ionisation fronts
  → suppression of instabilities by saturation of ionization coefficient
  → expansion and overlapping of ionisation front channels
  → further gas ionisation ahead ionisation fronts
  (photoionization, run-away electrons, …)

$$(U/n)/h \gg (E/n)_{\mathrm{crit}}$$

$$\tau_{\mathrm{rise}} \ll h/v_{\mathrm{d}}$$

U ... maximal pulse voltage,
n … gas density,
h … discharge gap length
τ_{rise} … pulse rise time
v_d … electron's drift velocity at $(E/n)_{crit}$

H. Ayan et al. J. Phys. D: Appl. Phys. 42 (2009) 125202 (5pp)

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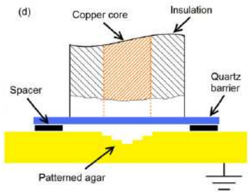
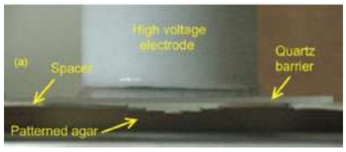
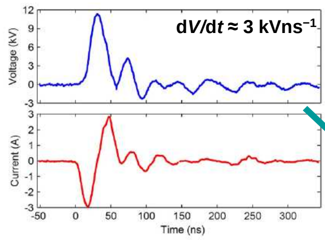
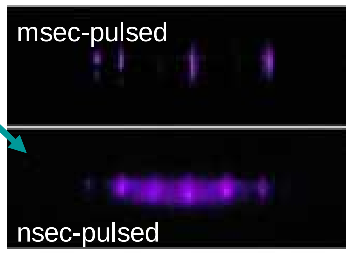
Nanosecond pulsed DBD









$(U/n)/h = 4 \times 10^{-15}$ Vcm$^2 \approx 3(E/n)$crit
$v_d \sim 10^7$ cm s^{-1} $t_{rise} \sim 10$ ns

→ critical voltage increase rate $dV/dt \approx 1$ kVns^{-1}

H. Ayan et al. J. Phys. D: Appl. Phys. 42 (2009) 125202 (5pp)

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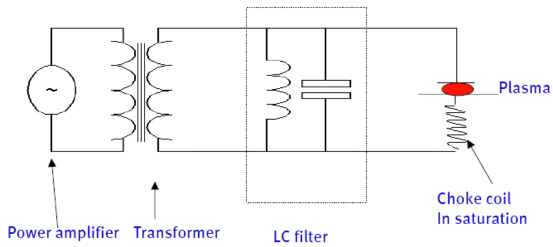
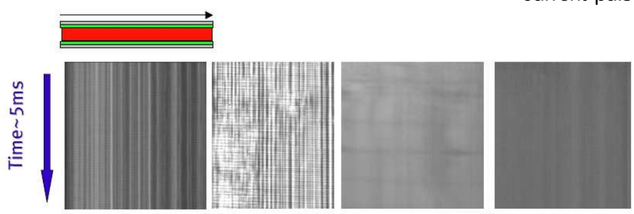
Voltage waveform modulation



choke coil for saturation near plasma breakdown
→ displacement current pulse



Ar no stabilization | Ar+1% O_2 no stabilization | Ar+1% O_2 electronically stabilized | Ar+25% O_2 electronically stabilized

E. Aldea et al., Surf. Coat. Technol. 2005, 200, 46–50

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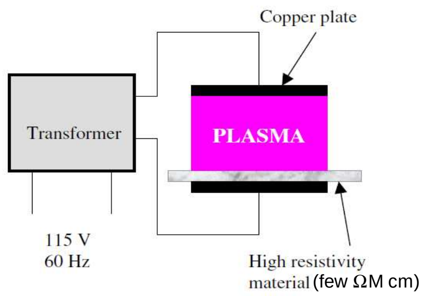
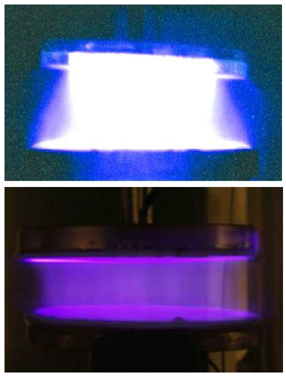
Ressistive Barrier Discharge (M. Laroussi et al. /ODU)

INP Greifswald





- high-resistivity material as barrier acts as a distributed ballast (limitation of discharge current)

INP Greifswald

M. Laroussi et al., New Journal of Physics 5 (2003) 41.1–41.10

General principle and major applications

INP Greifswald

Electric Field

Breakdown

Electrons & Ions

Excited Species

Chemical Reactions

Plasma-CHEMISTRY

Discharge-PHYSICS

Time

10^{-12} s ...

BOLTZMANN-equation

cross-sections of elementary processes

10^{-9} s ...

POISSON-equation; equation of continuity

kinetic coefficients

10^{-6} s ... 10^{-3} s

diffusion; heat transport

local densities, temperatures, ...

ozone generation

surface treatment
modification
coating
erosion

pollution control
hydrogenation of CO_2
NO_x reforming

radiation sources
excimer lamps
AC plasma displays
SD CO_2-laser

INP Greifswald

Ozone synthesis (1)

O_3: important oxidant
- water cleaning (advanced oxidation)
- paper bleaching

- ozone can't be stored → "on-site" production
- high pressure but low temperature required

1. Dissociation of O_2

$e + O_2 \rightarrow O^- + O$
$\rightarrow O + O + e$
$\rightarrow O + O^* + e$
$e + N_2 \rightarrow N_2^* + e$
$N_2^* + O_2 \rightarrow N_2 + 2O$

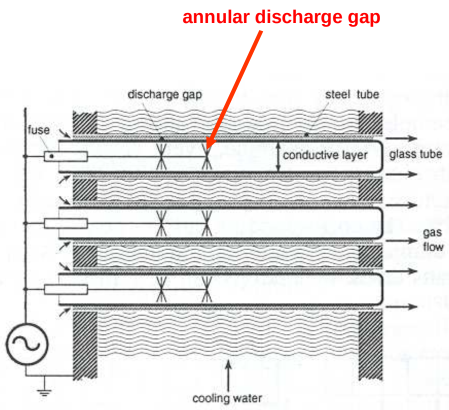
2. Formation of O_3

$O + O_2 + M \rightarrow O_3 + M$
($M = N_2, O_2$)

Ozone yield (g/kWh)	Oxygen	Air
Sinusoidal voltage	150 ... 180	80 ... 95
Impulse voltage (kV/ns)	240 ... 290	130 ... 140
Theoretical limit	430 ... 450	200 ... 220

Largest facility in Brazil: 500 kg/h

Ozone synthesis (2)



U. Kogelschatz et. al; Journal de Physique **7** (1997) C4-47

Surface „Corona“ treatment (1)

Activation to change surface energy / wettability or Coating

- printing
- glueing

on polymers, textiles, ...

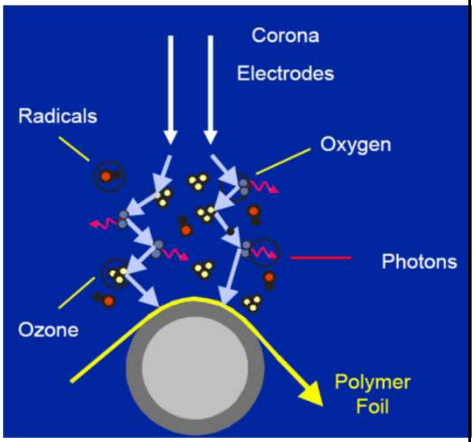
no wetting ⟶ wetting

Activation:

- electrons cause chain breakage
- incorporation of polar groups and other functional groups

Coating (Aldyne):

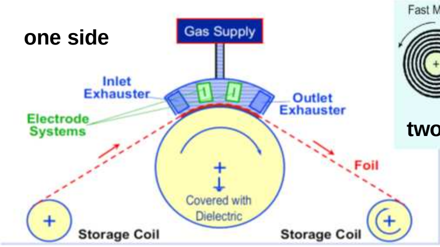
- admixture of precursors (ppm of silane)

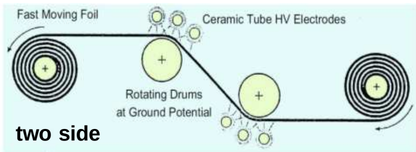


figures: tigres GmbH; softal GmbH

Surface „Corona“ treatment (2)

one side





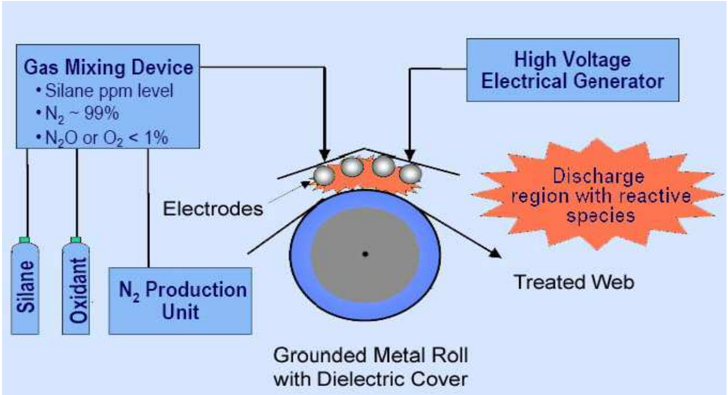
- web speed: 10 – 200 m/min
- residence time: a few seconds
- energy deposition: 0.1 – 1.0 J/cm^2

Tantec

Softal

U. Kogelschatz, J. Salge in „Low Temperature Plasma Physics“ Wiley-VCH Berlin (2001)

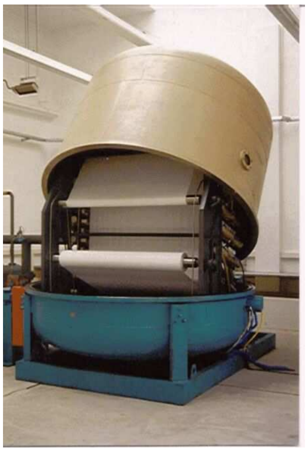
Aldyne process

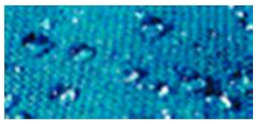


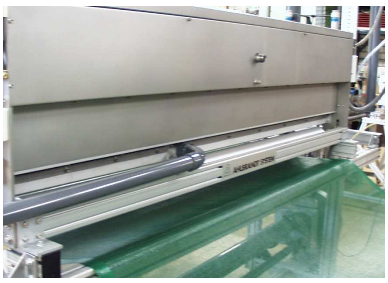
- Silane-Precursor: reactive molecular layer which form stable chemical bonds with commercial inks (varnishes water-based, solvent-based or UV-curable)
- Applications: Labels; Flexible packaging (food and non food); Tapes markets, Graphic arts (Primer free UV Offset Printing and gluing of CPP packaging); Flooring / Coverings

L'Air Liquide/Softal

Treatment of textiles

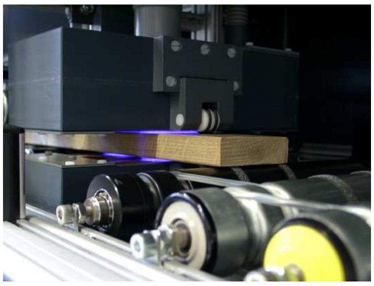


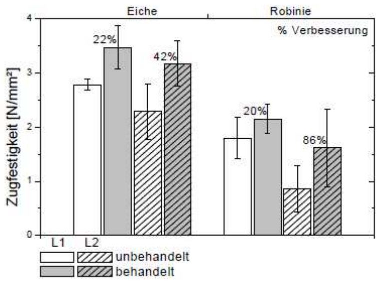




FZM GmbH Flöha; ITV Denkendorf

Wood treatment

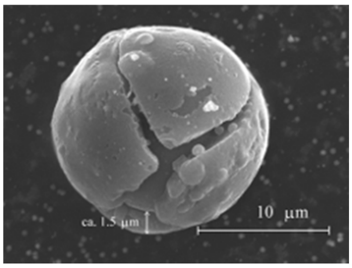


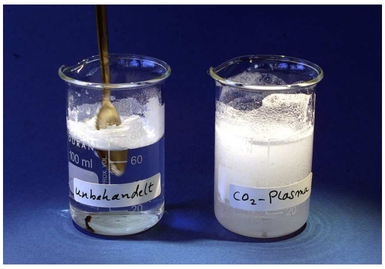


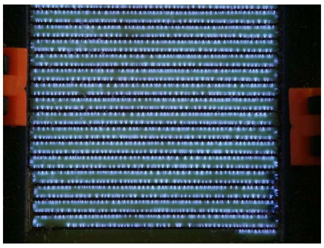
- Surface activation
- Enhanced adsoption and depth of penetration of paints, varnishes and liquid glues
- Imporoved tensile strenght
- Reduction of paint, varnish or glue

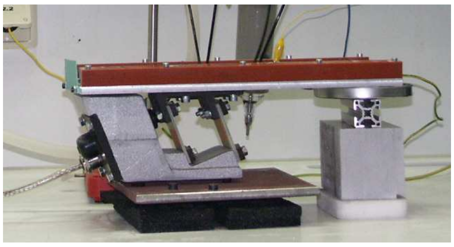
Tigres Dr. Gerstenberg GmbH

Treatment of powders



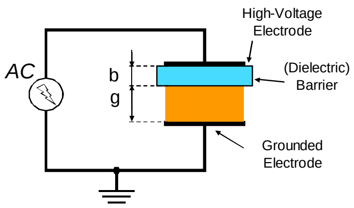


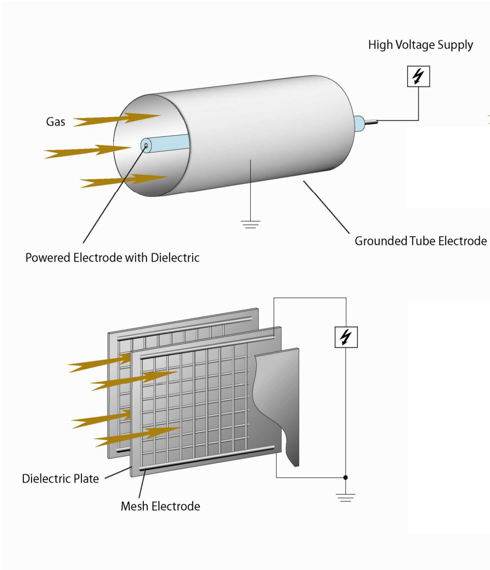




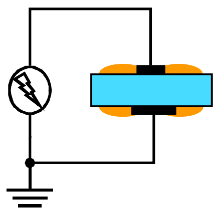
Gas depollution

Volume DBD



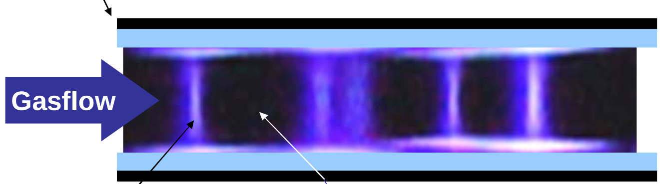


Surface DBD



Gas treatment by barrier discharge

Barrier discharge arrangement



1. Active Zones:
Microdischarges/Filaments

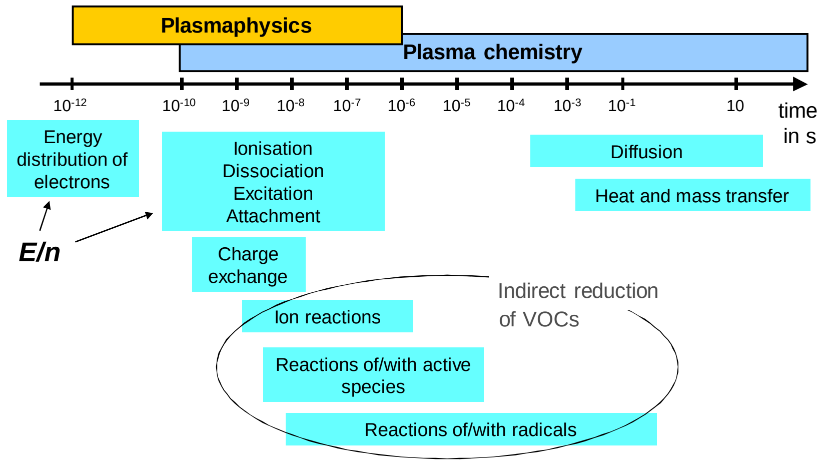
Breakdown
→ Ionisation
→ Free electrons → Radicals (O, OH, HO_2) → Reactions with radicals
Ion-molecule reactions → Formation of O_3

2. Passive Zones:

3. Aerosol formation

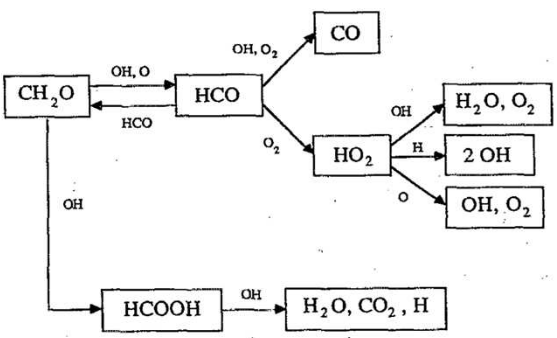
Plasma chemistry

- plasma chemistry based on non-thermal activation of particles via collisions
- no direct dissociation of pollutant molecules
  (low density of contaminants, short duration of electron current)
- reduction via reactions with radicals and other active species



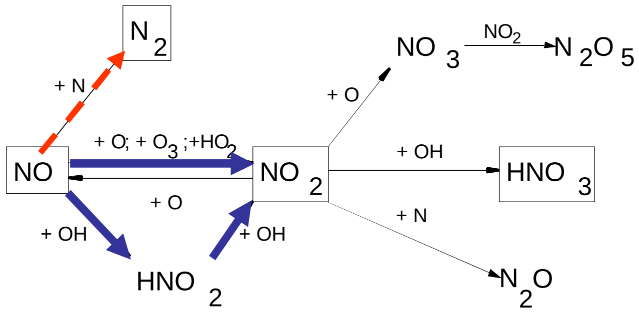
Example: Formaldehyde (CH_2O)

- destruction of CH_20 results dominantly from chemical attack by OH and O radicals
- primary end products: CO, H_2O
- destruction rates typically 2-8 ppm/(1 J/l)



Storch and Kushner, J. Appl. Phys. 1993

NO_x-conversion



- **Oxidative pathways dominate (espacially in case of humid conditions)**
- **Reduction at (to) high energy input**

Problems of plasma depollution

- Formation of aerosols (“dist, mist”)
- Polymerization → film deposition on electrodes
- Energy efficiency (G-value, Energy yield/cost)

$$G\text{-value} = \frac{\Delta[\mathrm{C}]}{\mathrm{J/L}} \times 0.4 \ (\mathrm{molecules/100\ eV})$$

- Low selectivity / formation of by-products

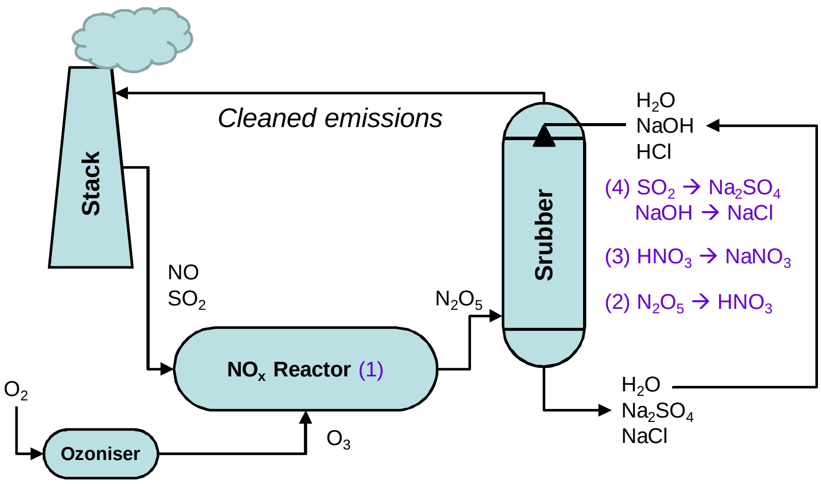
$$S_{CO_2}(\%) = \frac{[CO_2]}{[CO_2]+[CO]} \times 100$$

- Domination of oxidation processes
  e.g. NO → NO_2, N_2O_5 … ~~(N_2, O_2)~~

Challenges of plasma depollution

- Applicable at low pollutant concentration and low gas flows
  → e.g. VOC: $C_{org} < 1\ g/Nm^3$
- Indirect processes (so-called Low-Thermal Oxidation)
  → Oxidation of non-soluble NO to soluble NO_2
  → Pilot-scale installation in USA (flue gas treatment)
- Combination with catalyst or adsorbing agents
  → Activation of catalyst
  → Conditioning of off-gas
  → Cycled processes (regeneration of adsobents)
- Heterogeneous reactions
  → Reactions on liquid particles
  → Plasma-induced conversion of non-soluble in soluble VOCs with following scrubbing

LOTOX (Low Thermal Oxidation)



(1) O_3 injection and NO-conversion to N_2O_5 (via NO_2)
(2) N_2O_5 conversion to nitric acid
(3) Nitric acid conversion to nitrate
(4) Nitrate and SO_2 removal with scrubber purge

Belco/Dupont

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Cycled process

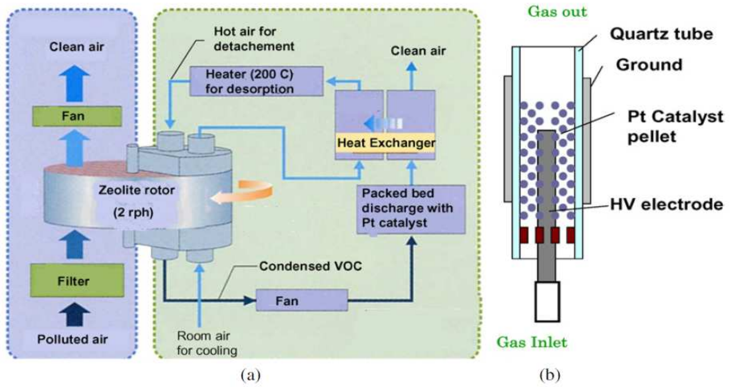

Figure 8. VOC removal apparatus. (*a*) Gas flow system and (*b*) packed bed plasma reactor.

Mizuno, Toyohashi University

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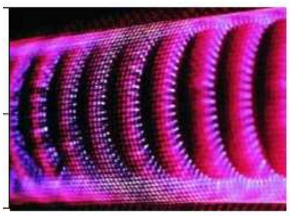
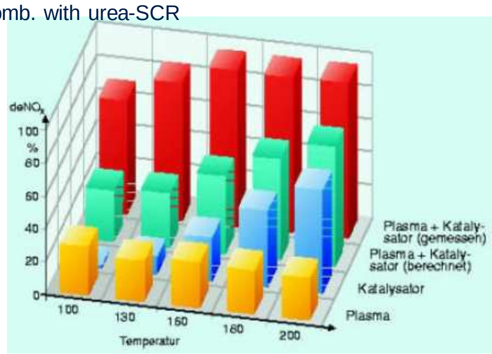
Plasma-enhanced SCR (selective catalytic reduction)

Volume Barrier Discharge comb. with urea-SCR





- up to 85% NO*x* reduction under cold start and urban driving conditions
- less than 300 W of plasma power applied
- model studies: fuel penalty introduced estimated to be below 2%.

T. Hammer; Plasma Sources Sci. Technol. 2002

90

Bypass operated plasma plants

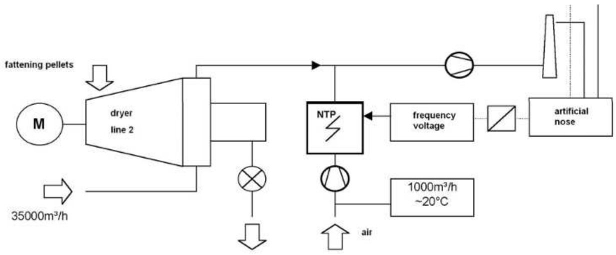


Figure 14: Diagram of a NTP plant for odour reduction in factories for producing fatting food and fish meal (very humid emissions)

- **Indirect plasma treatment of polluted gas by plasma treated gas**

R. Rafflenbeul, Envisolve.com; Germany

Economical benefit

Investment- and running costs

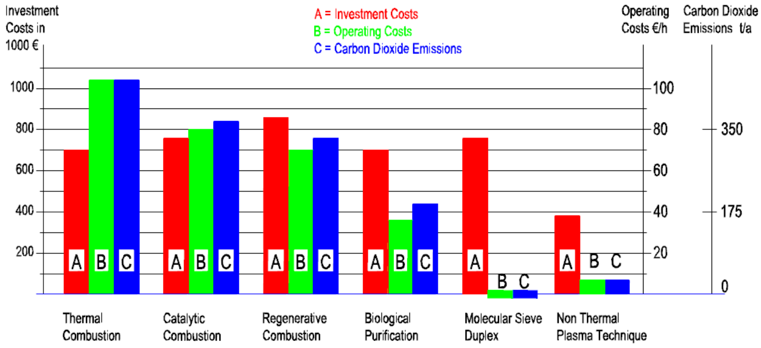
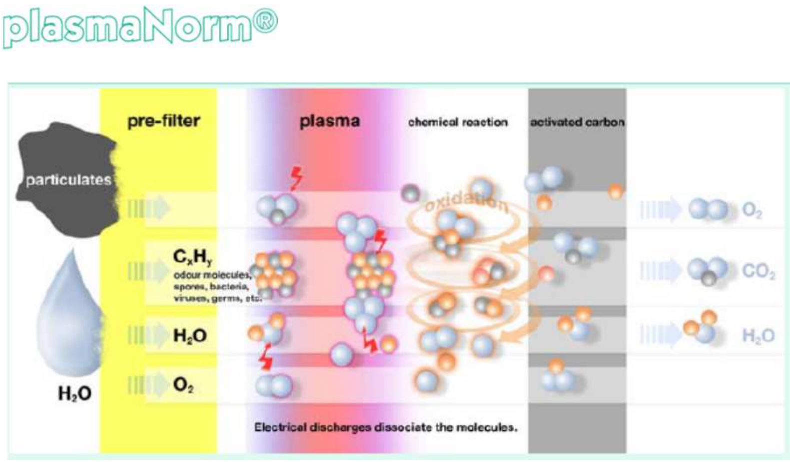


Figure 15: Investment- and running cost comparison of waste air purification processes (50,000 m³N/h) for <100 mg VOC/m³ in the flavour processing industry

R. Rafflenbeul, Envisolve.com; Germany

PlasmaNorm-Technology



M. Langner; Airtec competence GmbH

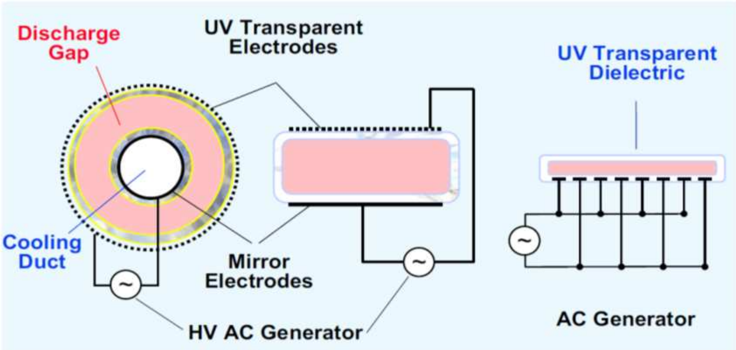
PlasmaNorm-Technology

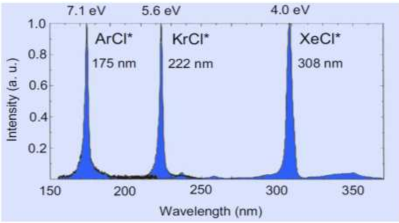
Deodorization of exhaust from ovens for convenience products made of meat (1.5 MW ovens; exhaust stream of 8,000 Nm³/h)

Cooker hoods for large-scale kitchens, gastronomy and private housholds

M. Langner; Airtec competence GmbH

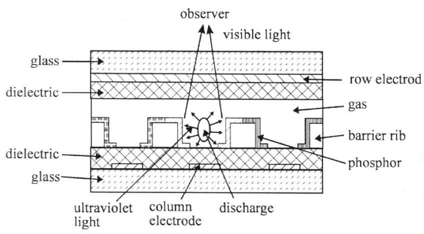
Excimer lamps

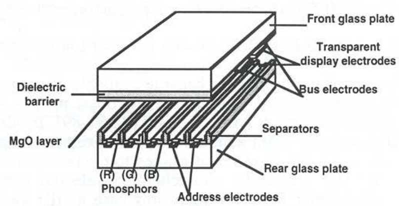




- UV curing in web and sheet offset press
- UV printing
- Photolytic structured metal deposition
- Room temperature oxidation of silicon

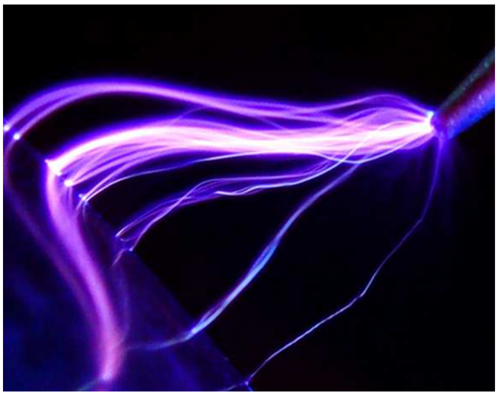
Plasma displays





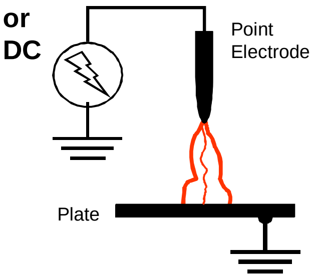
Panasonic (2008): Largest Plasmadisplay 3.81 m (150 Zoll) diagonal/ 8.84 Megapixel

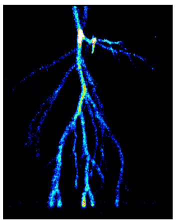
5. Corona Discharges



http://www.dpchallenge.com/

Principle / geometry

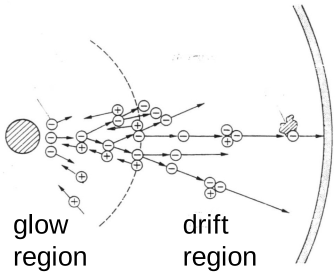




Point-to-plane or wire

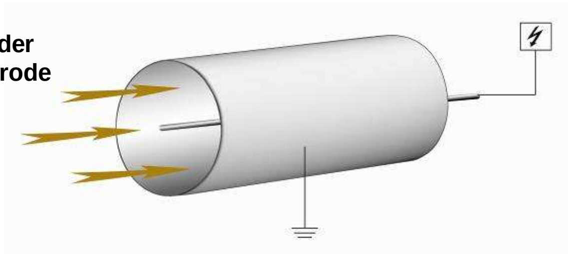
-

non-uniform electric field

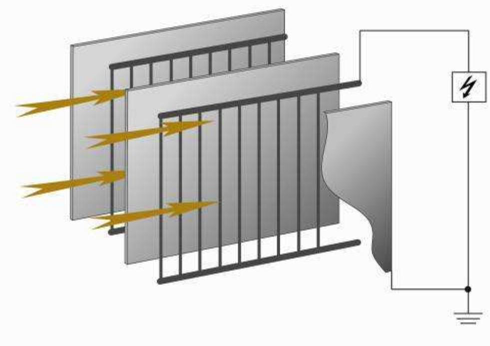


Corona discharge

Wire-in-cylinder
Coaxial electrode



Multi-wire-plate
arrangement



Corona onset – Peek' law

$$E_c = 30\,\delta\left[1 + \frac{0.3}{(\delta R)^{1/2}}\right]$$

$\delta = N / N_0$
R = Wire Radius

$$M = \exp\left(\int(\alpha-\eta)dx\right) = 10^4$$

$M \approx 3\cdot 10^4$ Townsend-Breakdown

$M = 10^8$ Streamer-Breakdown

an explanation for the low magnitude of Q. We conclude that the most likely cause of the low value of Q is the onset of indirect ionization processes, such as from metastable–metastable collisions, which then enables the discharge to be maintained at a value of E/N significantly lower than the critical E/N for which ionization equals attachment.

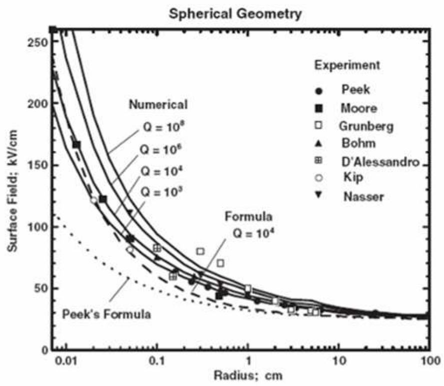
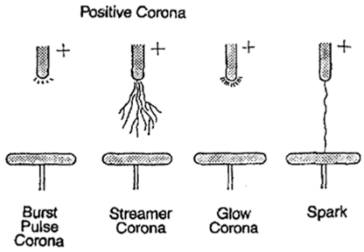
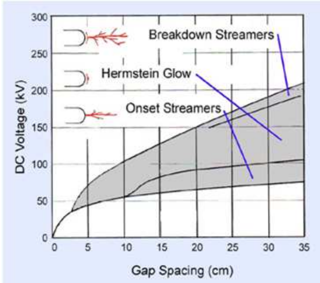


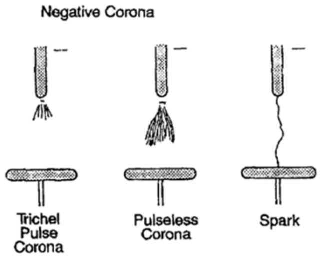
Figure 4. Experimental data points for corona onset from points and spheres as a function of point radius. Also shown as curves are theoretical predictions obtained numerically and also from predictions using Peek's formula for wires, equation (1), and the formula given by equation (7).

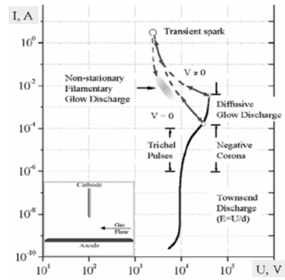
J.J. Lowke and F. D'Alessandro J. Phys. D: Appl. Phys. 36 (2003) 2673-2682

Modes of corona discharges



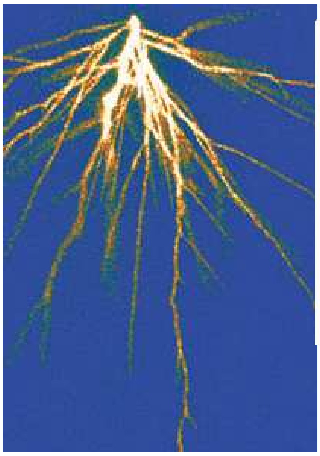


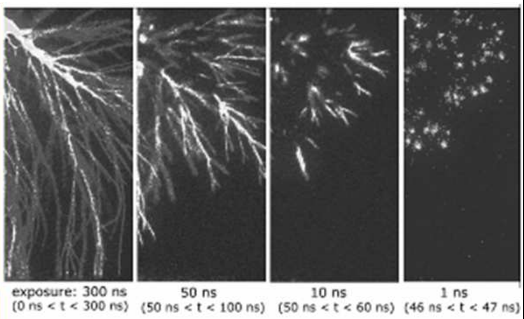




Chang et al. IEEE Trans. Plasma Sci. ***19****(1991)*

Streamer branching

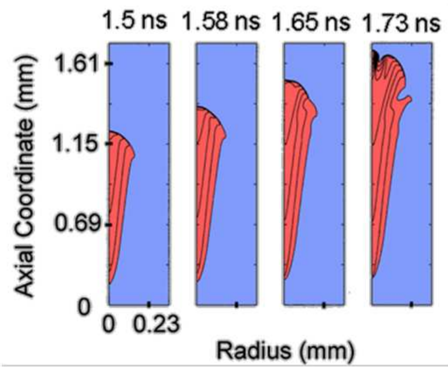


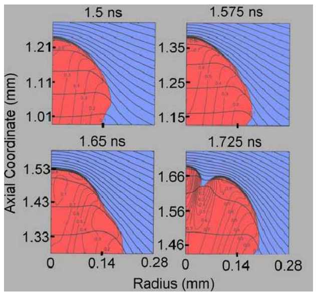


E.M. van Veldhuizen, W.R. Rutgers; J. Phys. D: Appl. Phys. 35 (2002) 2169-2179; J. Phys. D: Appl. Phys. 36 (2003) 2692-2696

Streamer branching simulation

Electron density contour plots (maximum $10^{14} \ldots 10^{15}$ cm^{-3})





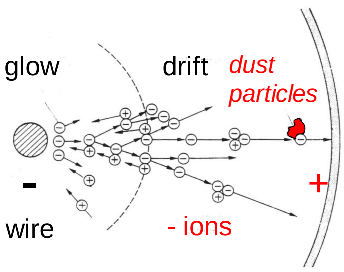
Branching by Laplace instability at streamer head

U. Ebert et al. (TU Eindhoven/CWI Amsterdam)
http://homepages.cwi.nl/~ebert/publications.html;
A. Rocco et al., Phys. Rev. E. 66(2002),

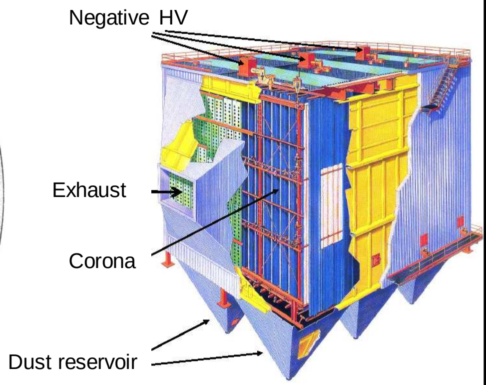
Electrostatic Precipitators

Electro filter in power stations (dust filter)

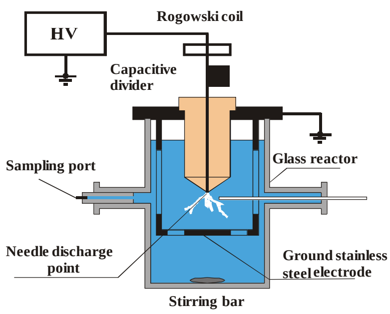
- standard technique



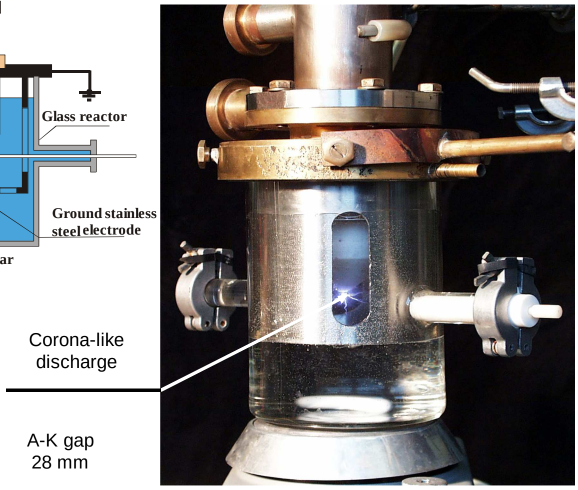
attachment: A+e ⟶ A⁻



Electrohydraulic discharges



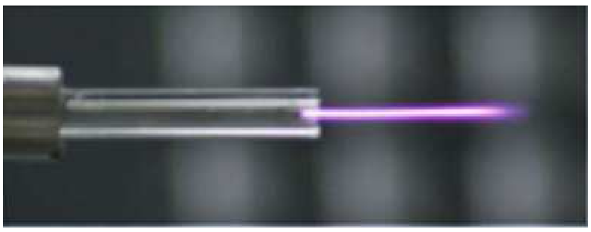
P. Sunka et al, IPP Prague



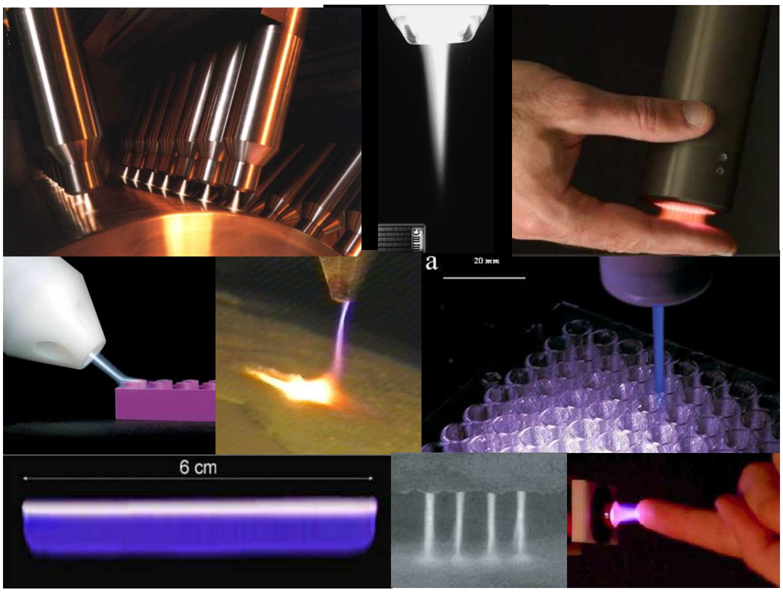
P. Lukes et al.; Plasma Sources Sci. Technol. 17 (2008)

Atmospheric plasmas and microplasmas

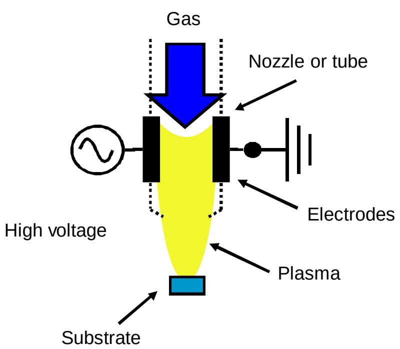
6. Plasma jets



Diversity in design, operation ...



Plasma jet principle



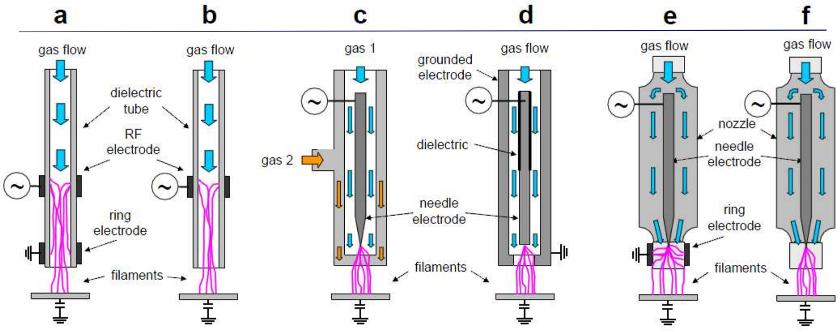
Gas flow transports plasma outside electrode configuration

- non-thermal plasmas
- pulsed dc ... GHz
- Power 1 ... 1 kW

"Remote-type"
- active plasma between electrodes
- plasma jet = effluent or afterglow (long lived species)
- potential free

"Active-type"
- active plasma between electrodes and between nozzle and substrate
- plasma jet contains free electrons
- current transport through substrate

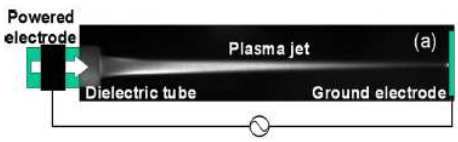
Plasma jet Configurations

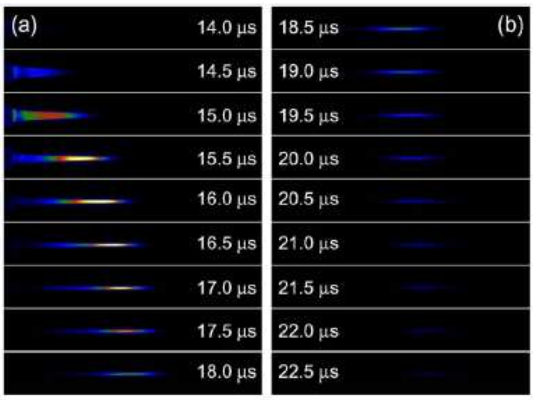


a) using 1 powered and 1 grounded ring electrode
b) without grounded ring electrode
c) combination of 2 tubes whereas the inner tube is streamed with a noble gas for discharge ignition and the outer tube with a precursor
d) composed of two coaxial electrodes with a dielectric in between
e) consisting of an inner RF driven needle electrode and a grounded ring electrode
f) without grounded ring electrode

Ehlbeck, Pollack, Winter, et al,. J Phys D 2011

Plasma bullets



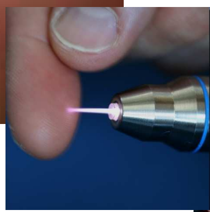


- hypersonic train of plasma bullets
- travelling ionisation fronts

J. Shi et al; Phys. Plasmas **15**, 013504 2008

kINPen

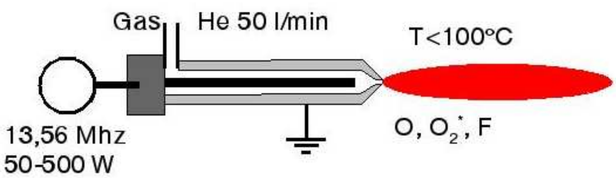
- P = 5 … 40 W
- f = 13 MHz / 27 MHz
- gas: Argon, N_2, ….
- Q = 1 … 20 slm



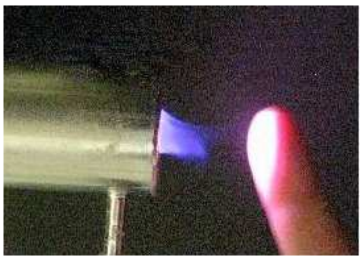
- compact and modular
- low power consumption
- penetrates in small structures
- non-thermal plasma

R. Foest et al., Plasma Phys. Control. Fusion 47 (2005) B525-B536

APPJ - Atmospheric pressure plasma jet

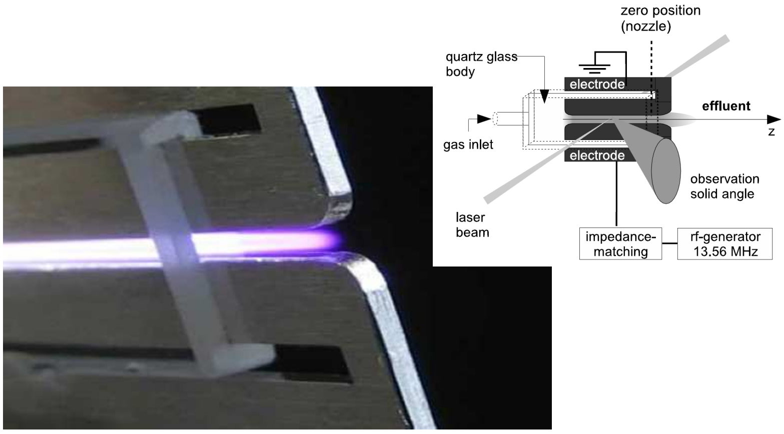


Helium:
>> low breakdown voltage
>> high heat conductivity



A. Schuetze et al., IEEE Trans. Plas. Technol. 26 (1998)

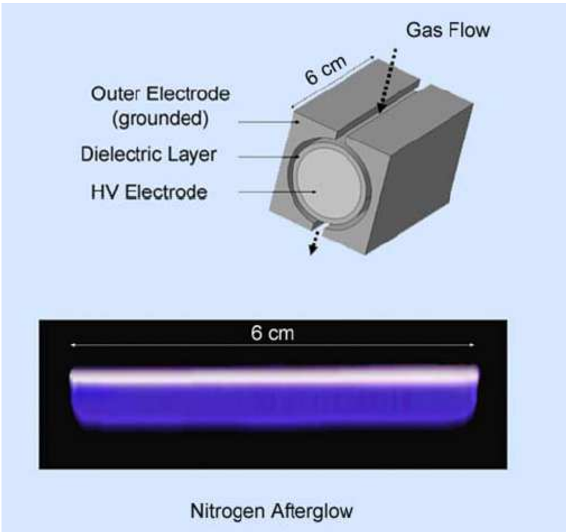
µ-APPJ (RF-driven; He, Ar)



- α-mode: dominated by ionization processes in the bulk
- γ-mode: secondary electron emissions from electrode surface

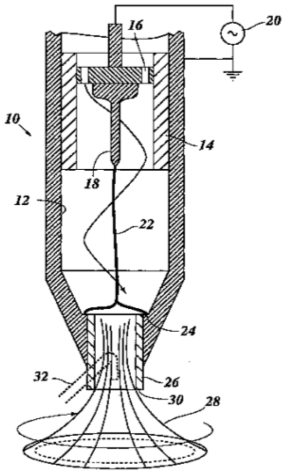
V. Schulz-von der Gathen et al. (RU Bochum / Uni. Essen)

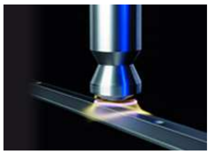
Linear plasma jet source

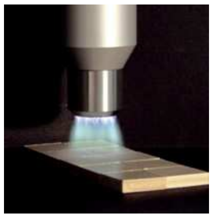


AcXys

Openair-Plasma (Plamatreat)



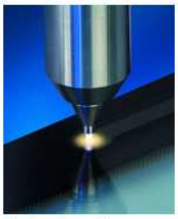




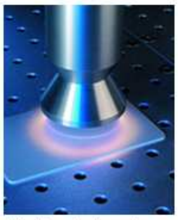
Plasmatreat

Openair-Plasma (Plamatreat)

- Pretreatment prior to painting, printing, bonding, …
- Cleaning
- Activation
- Coating



Cleaning glass with Openair® plasma



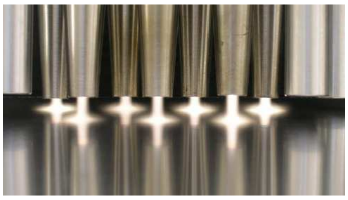
Activation of polypropylene before further processing

Coatings by means of plasma polymerization

Plasmatreat

Plasma and Corona treaters

Plasma-Blaster

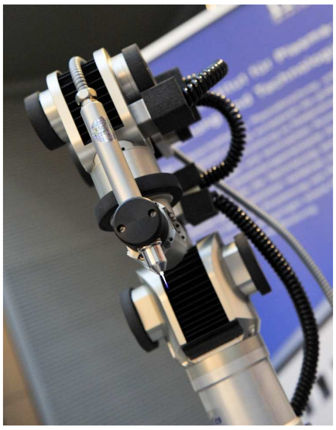


„Korona-GUN“

Change of surface energy to improve adhesion

Dr. Gerstenberg GmbH Tigres

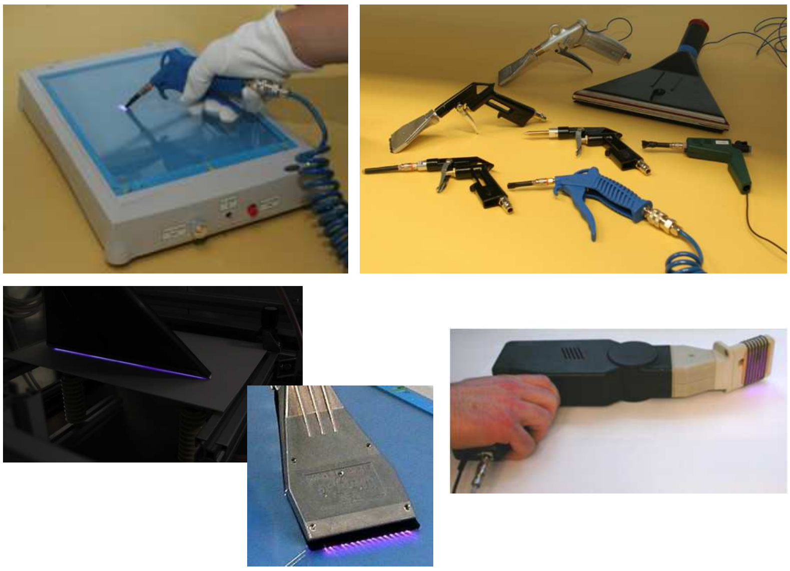
Treatment of complex workpieces



kiNPen Plasma jet

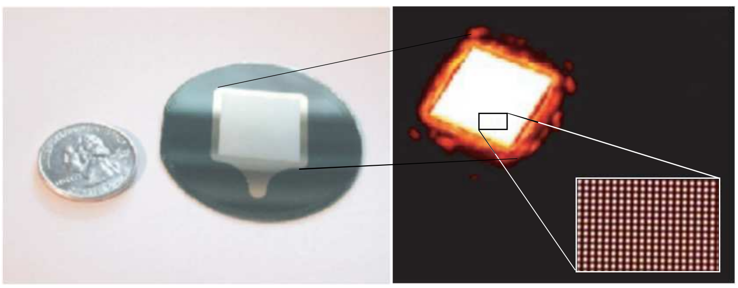
neoplas tools

New concept: Conplas



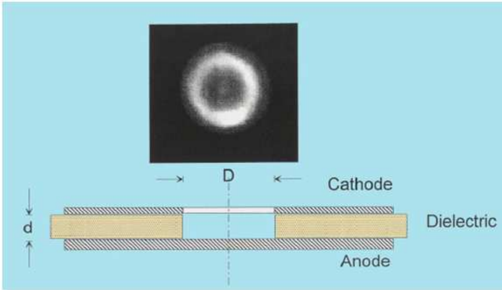
Atmospheric plasmas and microplasmas

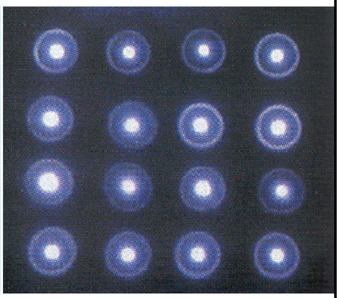
7. Microplasma arrays



pictures composed from: G. Eden et al.; J. Phys. D: Appl. Phys. 38 (2005) 1644–1648

Microhollow cathode discharges (MHC)



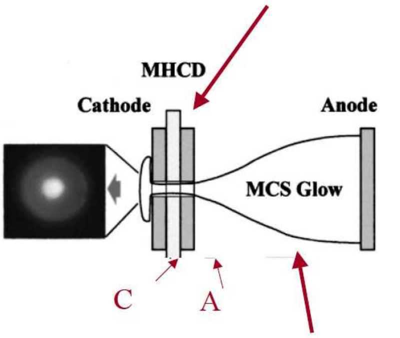


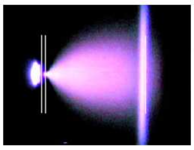
D: 0.1 … 0.25 mm **d about 150 µm**

- MHC concept extends hollow cathode discharge operation to atmospheric pressure
- nonequilibrium plasma
  (T_g about 2000 K, n_e: $10^{15}cm^{-3}$ … 5 $10^{16}cm^{-3}$; T_e: 0.5 – 5 eV)
- many similarities with a glow discharges (thin localized cathode fall region; moderate gas temperature)

K.H. Schoenbach et al. Appl. Phys. Lett. **68** 1, 13-15 (1996)

MHCD as plasma cathode

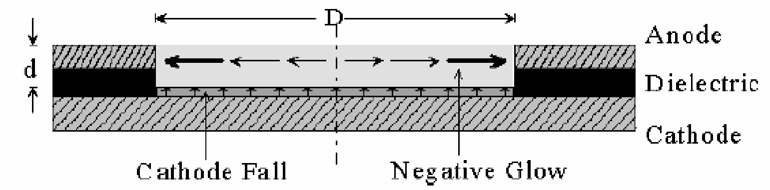




R.H. Stark and K.H. Schoenbach, JAP **85,** 2075 (1999).

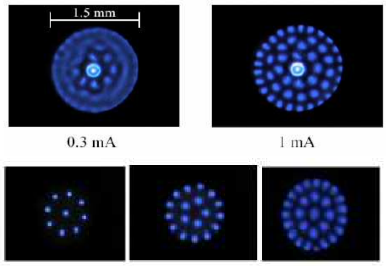
Cathode boundary layer (CBL)

INP Greifswald



D about 1.5 mm **d about 150 µm**

- hole diameter D of MHC widened to about 1.5 mm
- varying number of self-organized bright discharge spots, originating in the cathode fall region

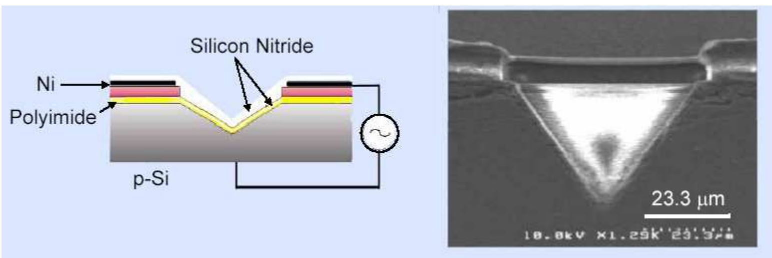


INP Greifswald

K.H. Schoenbach et al. Plasma Sources Sci. Technol. 13, 177-185

Pyramidal barrier discharge

INP Greifswald

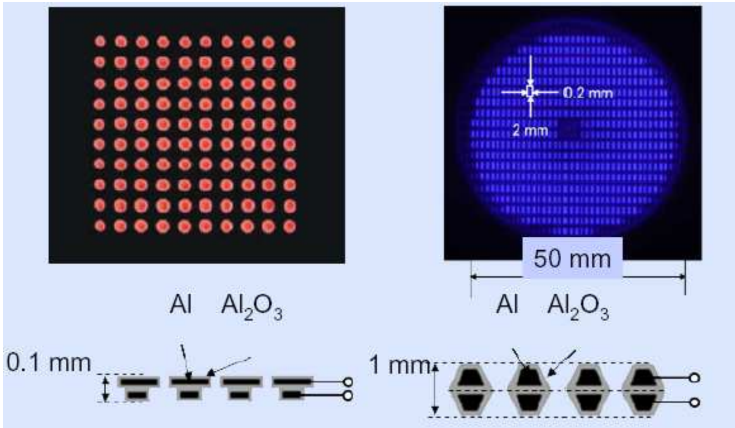


- **use of p-type Si(100) wafers**
- **micromachining technologies: lithographical patterning; anisotropic wet etching or reactive ion etching**
- **area of inverted pyramids: 100 x 100 µm^2 down to 10 x 10 µm^2**
- **flexible arrays possible**
- **specific local power loading up to 250 kW cm^{-3}**

INP Greifswald

J. G. Eden et al., J. Phys. D: Appl. Phys. **36**(2003), 2869

Coplanar/coaxial type microplasma sources

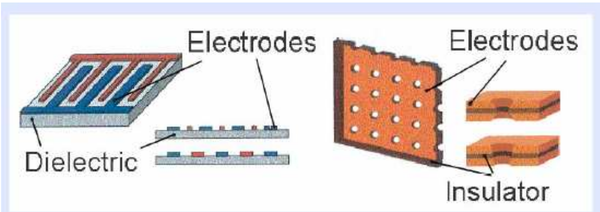


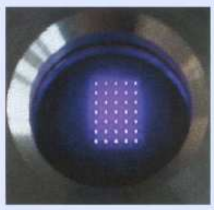
- **Al foils or Al structures that can be covered with a thin alumina coating serving as a dielectric layer, e.g perforated 70 µm thick Al foils with Al_2O_3 films of 10 µm thickness**

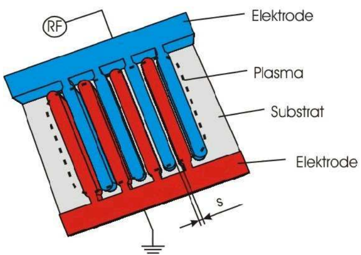
S.-J. Park et al. Appl. Phys. Lett. **86**, (2005);
K. Tachibana et al. Plasma Phys. Control. Fusion **47**, (2005)

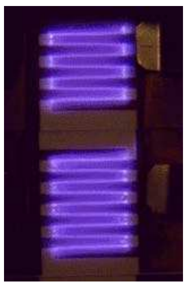
RF capacitively coupled microplasmas

Micro-Structured Electrode Arrays (MSEs)



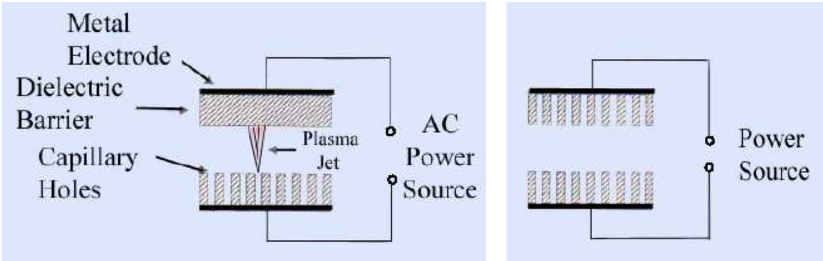






M. C. Penache Penache, Ph.D. Thesis, U of Frankfurt 2002; N. Lucas et al. IMT Braunschweig

Capillary plasma electrode discharge



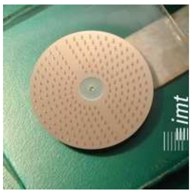
- one or both dielectric plates with parallel thin capillary channels
- frequency above a few kHz: sudden, capillary plasma jets emerge from capillary holes, overlaping and merging to a volume plasma with electron densities by orders of magnitude higher then those observed in diffuse BDs
- each hole acts as a current limiting micro-channel preventing overall current density from increasing above threshold for glow-to-arc transition.

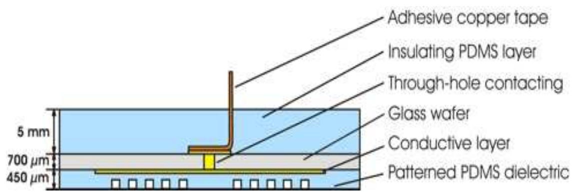
E. E. Kunhardt IEEE Trans. Plasma Sci. **28**(2000), 189 - 200

Microplasma stamps

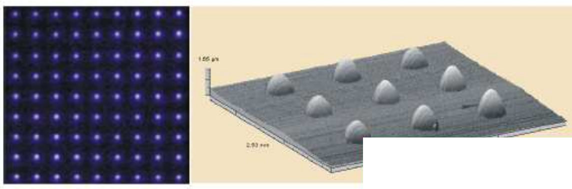
Microstructured Surface Treatment

- micron-scale area-selective surface modification processes
- BD-principle: patterned / structured dielectric
- structure size: 150 … 500 µm





(PDMS: poly-dimethylsiloxane)



N. Lucas, C.-P. Klages et al.; Proc. 3rd Int. l Workshop on Microplasmas, Greifswald, 2006, p. 180-183; Proc. 5th euspen Int. Conference, Montpellier/France, 2005, vol. 2, p. 665-668.

Downscaling limitations

New physics at high pressures and small dimensions

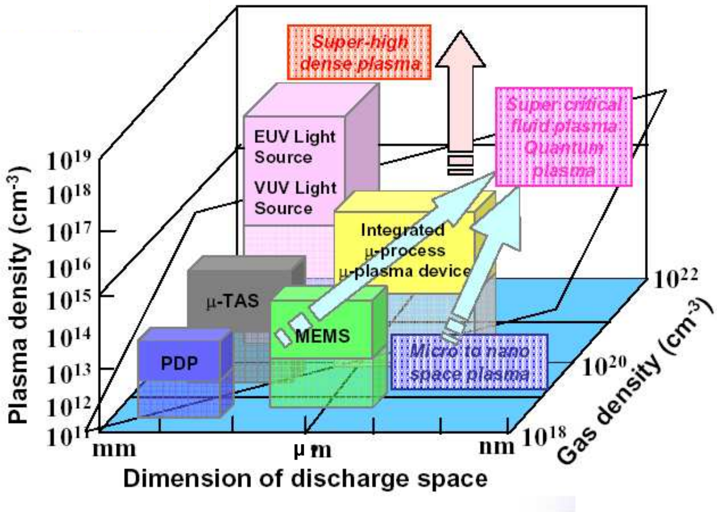
- new breakdown criteria
- large surface-to-volume ratio

>> role of plasma-surface processes
(e.g. ion-enhanced field emission and quantum tunneling lower breakdown voltage in left branch of Paschen curve)
>> scaling laws no longer apply
(e.g. when cathode fall thickness ≈ linear plasma device dimensions)
>> Debye length ≈ plasma dimension (no shielding of plasma volume)

- plasma generation, maintenance and control of parameters

- control of instabilities
- pattern formation and self organisation

New Applications

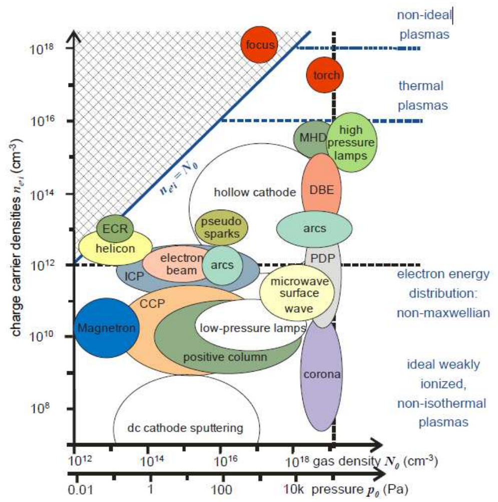


MEMS: Micro electromechanical systems

Tachibana, Kyoto University; IEEJ Trans. 2006; 1: 145-155

Summary

Atmospheric pressure plasmas exist in a wide range of parameters (LTE and non-LTE) and configurations ...



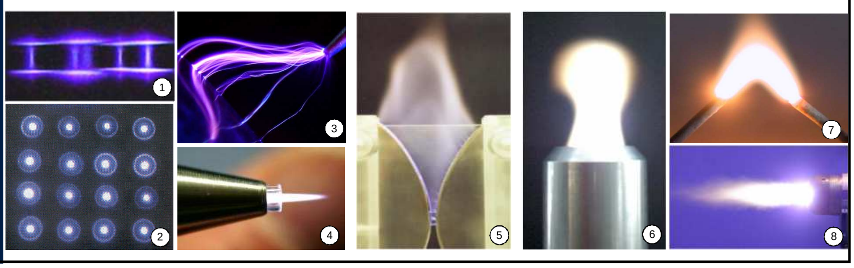
„reactive" neutral-dominated plasmas

H. Kersten, Uni Kiel

Classification

Non-Thermal (NT) Plasmas		Thermal Plasmas
"Cold" Non-Thermal Plasmas	Translational ("Hot NT") Plasmas	Thermal Plasmas
$T_i \approx T_g \approx 300 \ldots 400$ K $T_i << T_e < 10^5$ K (10 eV)	$T_i << T_e \leq 10^4 \ldots 10^5$ K $T_i \approx T_g \leq 4\ 10^3$ K	$T_i \approx T_g \approx T_e$ $T_x < 5\ 10^3 \ldots 10^4$ K

- **Barrier discharges** (1)
- **Coronas** (2)
- **Microplasma-Arrays** (3)
- **Plasma jets** (4)
- **Gliding Arc** (5)
- **Plasma Torch** (6)
- **Microwave Driven Plasmas**
- **Arc** (7)
- **Arc jet** (8)



Atomspheric plasmas and microplasmas

Further reading

„Non-equilibrium air plasmas at atmospheric pressures“ eds. K.H. Becker, U. Kogelschatz, K. H. Schoenbach, R.J. Barker; Institute of Physics Publishing: London (2005), Distributor: Francis & Taylor, CRC Press

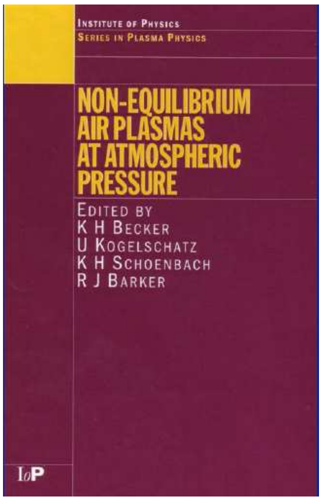
„Electrical breakdown of gases“ eds. J.M. Meek, J.D. Craggs; John Wiley & Sons: Brisbane (1978)

„Fundamentals of gaseous ionization and plasma electronics“ E. Nasser; Wiley-Interscience: New York (1971)

„Plasma chemistry“ A. Friedman; Wiley-Interscience: New York (1971)

„Gas discharge physics“ Yu.P. Raizer; Springer-Verlag: Berlin (1991)

J.R. Roth „Industrial Plasma Engineering”, Vol. 1 and 2, IOP Publishing Ltd 1995



INP Greifswald

Atomspheric plasmas and microplasmas

Further reading

U. Kogelschatz: “Atmospheric-pressure plasma technology” Plasma Phys. Control Fusion 46, 2004; B63-B75

A. Fridman, A. Chirokov, A. Gutsol : “Non-thermal atmospheric pressure discharges” J. Phys. D- Appl. Phys. 38, 2005; R1-R24

H.-E. Wagner, R. Brandenburg, K.V. Kozlov et al “The barrier discharge: basic properties and applications to surface treatment” VACUUM 71, 3, 2003; 417-436

M. Laroussi and : “Arc-Free Atmospheric Pressure Cold Plasma Jets: A Review” Plasma Proc. and Polymers 2007, 4, 777–788 DOI: 10.1002/ppap.200700066

E. E. Kunhardt “Generation of large-volume, atmospheric-pressure, nonequilibrium plasmas IEEE TRANSACTIONS ON PLASMA SCIENCE, 28, 1, 2000; 189-200

K. Tachibana: “Current status of microplasma research” IEEJ Trans. 2006; 1: 145-155

F. Iza et al.: “Microplasmas: Sources, particle kinetics, and biomedical applications” Plasma Proc. and Polymers 2008; DOI: 10.1002/ppap.200700162

U. Kogelschatz: “Applications of Microplasmas and Microreactor Technology”; Contrib. Plasma Phys. 47, No. 1-2, 80 – 88 (2007) / DOI 10.1002/ctpp.200710012