Masaryk University Brno
Department of Physical Electronics

Atmospheric Pressure Plasmas – Basics and Applications

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Lecture II: Diagnostics of non-thermal atmospheric pressure plasmas

– Electrical characterization
– Optical emission spectroscopy, fast optical/spectroscopic methods
– Surface charge measurements

"Macroscopic" diagnostic

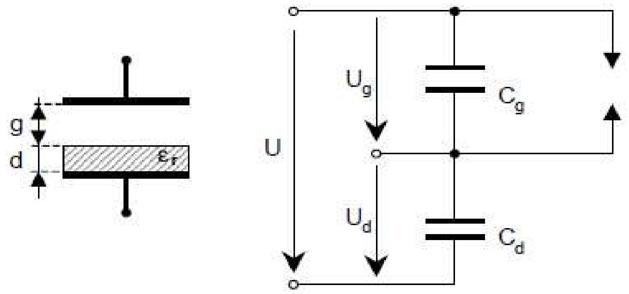
… to be performed AT LEAST on reactors

- Electrical characterization
  - Voltage and current oscillography
  - Power measurements → Specific Energy Density
- Gas analysis (chemistry)
  - Flame Ionization Detection (FID): Total hydrocarbons (THC)
  - Fourier transform infrared spectroscopy (FTIR): IR-active species
  - Gas Chromatography – Mass Spectrometry (GC-MS)

… and if possible
- Optical and spectroscopic methods
  - Optical emission spectroscopy: indirect and average information!
  - Fast imaging: Distribution of MDs → local power density

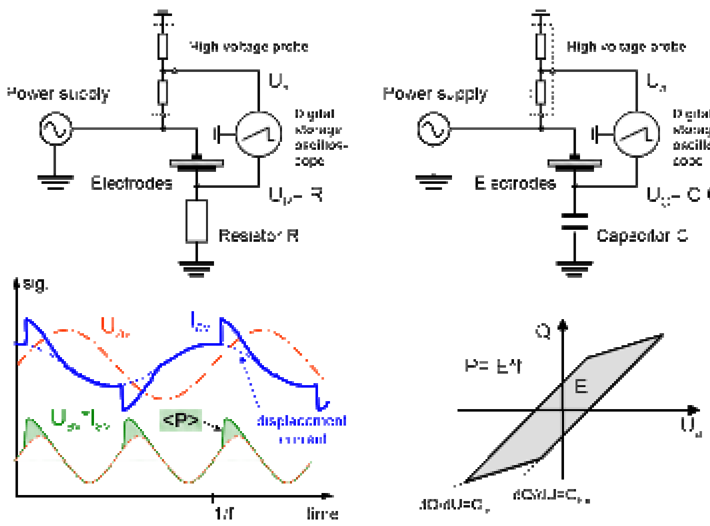
Electrical characterization of DBDs

Equivalent circuit (the simplest!)



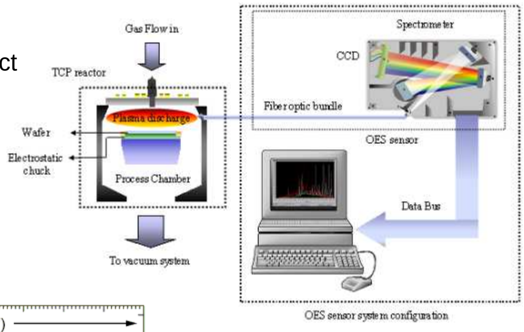
Electrical characterization of DBDs

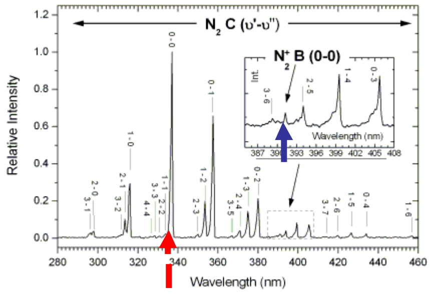
U-I-Oscillography | **U-Q-Lissajous figure**



Optical emission spectroscopy

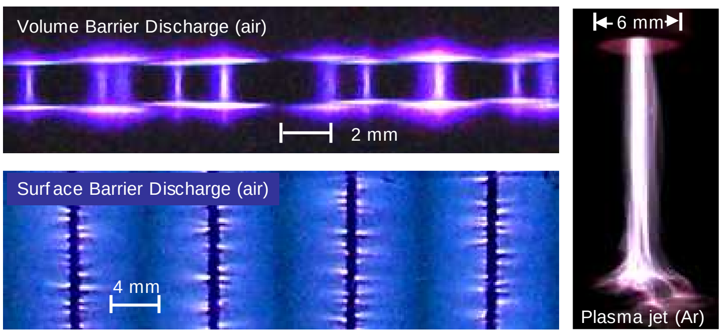
- Simple, non-intrusive
- Emission of plasma (indirect information)
  → gas/excitation temp.
  → electrons (Stark tech.)
- Monitoring of processes
  → intensity
  → spectrum performance





Filamentary plasmas

- Atmospheric pressure
  → high collision rates (rapid ionization, quenching)
  → streamer breakdown mechanism favoured (Raether/Meek criterion)
  → small dimensions (Paschen law)



- **Electrical breakdown in several individual ionization channels**
- **Filaments = repetitive, but transient Microdischarges (MDs)**

Discharge physics and plasma chemistry

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Timescales

Timescales	
10^{-12} s ...	Electric Field
	Breakdown
10^{-9} s ...	Electrons & Ions
	Excited Species
10^{-6} s ... 10^{-3} s	Chemical Reactions
10^{-3} s ... 10^{1} s	Heat and Mass Transfer

Discharge-PHYSICS

- Plasma parameters (E/n, n_e)
- Densities of active species (n_X, n_+, n_-)
- Excitation and relaxation processes

→ MDs as „tiny chemical reactors“
→ MD-multitude determines overall chemistry

Plasma-CHEMISTRY

- Yield of (by-)products
- Efficiency of decomposition etc.

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The challenge

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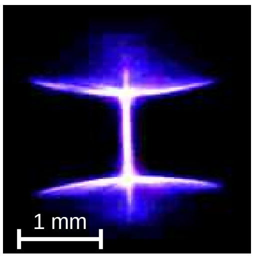
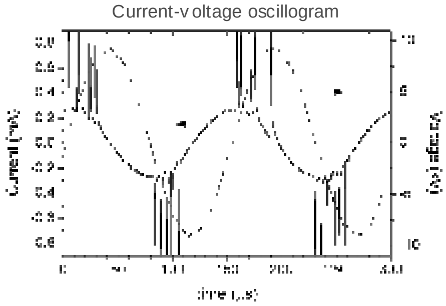


Current-voltage oscillogram



- **Small scale (diameter, discharge gap)** ________ *10 µm ... 5 mm*
- **Transient and short lived** ________ *10 ns ... 1 µs*
- **Erratic appearing** ________ *Triggering ?*
- **Low emission intensity** ________ *Spectral resolution ?*

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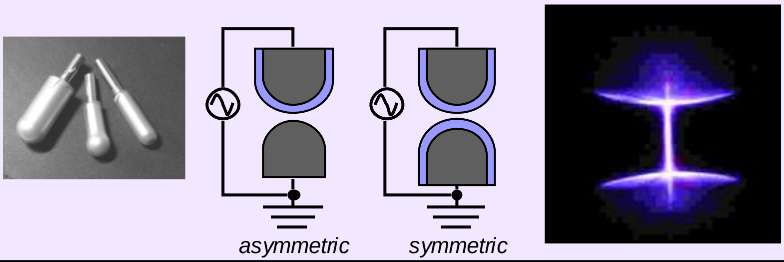
Methods overview

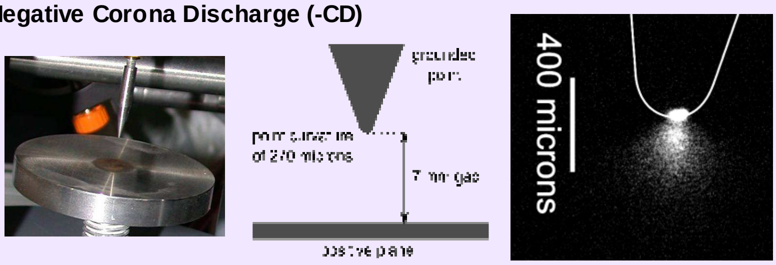
- Current pulse measurements (Current probes/Rogowski coils)
  - \+ Mandatory information, but often difficult to measure
  - \- No spatial information
- Optical and spectroscopic methods
  - \+ Passive methods, easy to apply, "intuitive"
  - \+ Independent from gas and discharge type
  - \- Limited to emission → indirect information
- Laser diagnostics *(LIF, TALIF → Volker Schulz-von der Gathen)*
  - \+ Direct information on density, field, …
  - \- Specified diagnostic systems etc.
- Mass spectrometry (*Achim von Keudell, Jan Benedikt,*)
  - \+ Direct and un-specified excess
  - \- Gas sampling → limited to stable compounds
- Surface charge measurements
  → Quantitative measurement of deposited charges
- Simulation (Fluid, hybrid, …)
  → Needs experimental verification

Microdischarge investigation: Single filaments

Volume Barrier Discharge (VBD)



Negative Corona Discharge (-CD)



Fast current measurements

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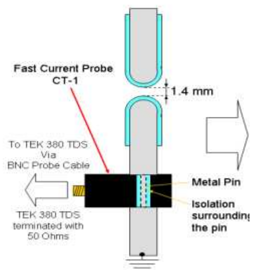

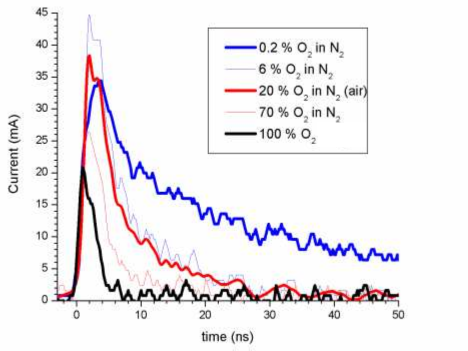

▪ duration:	1-10 ns
▪ transported charge:	100-1000 pC
▪ current density:	100-1000 A cm^2

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ICCD-camera (short exposure time photos)

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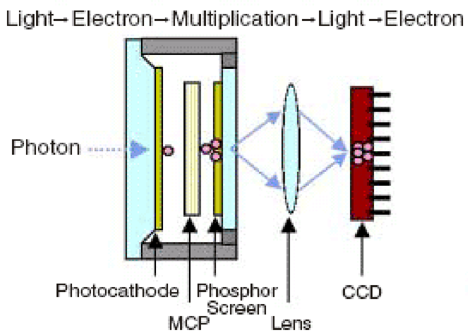

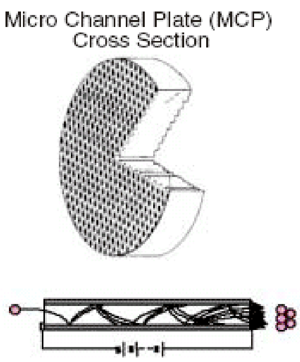

Principle	Image intensification by micro-channel plate; CCD-Sensor
Parameters	Δt down to 2 ns (new: down to 80 ps, Lavision fast gated ICCD) Gain 10^5 … 10^6
Pecularities	→ Temporally resolved measurement only if pulsed driven → Photos of individual MDs or discharge channels

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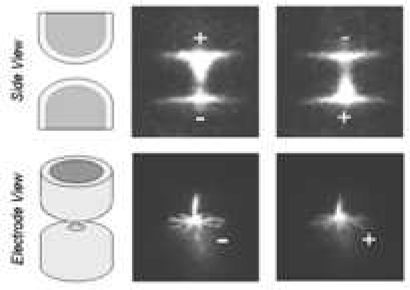
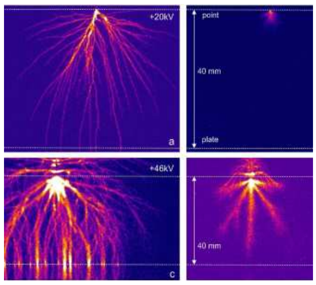
ICCD-camera (short exposure time photos)

Volume Barrier Discharge (VBD)

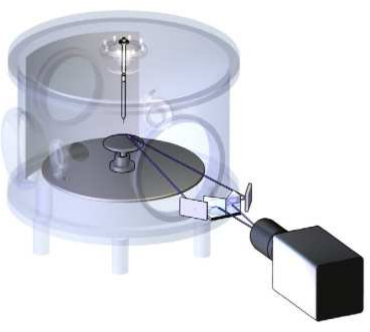


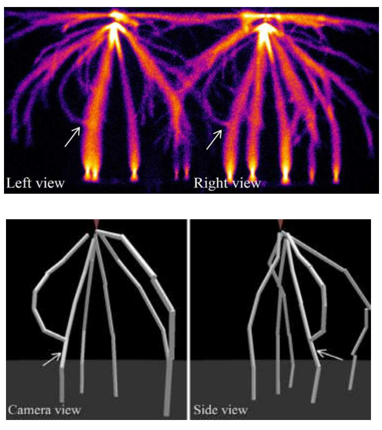
Positive Corona



T.M.P. Briels et al. J. Phys. D: Appl. Phys. (2008)
R. Brandenburg et al. J. Phys. D: Applied Phys. (2005)

Stereoscopic ICCD-imaging (pos. corona)





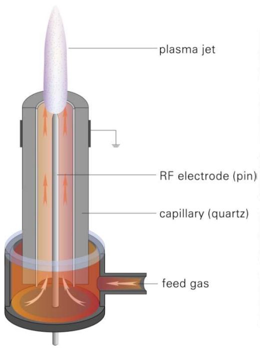
Discharge channels analyzed in full 3D

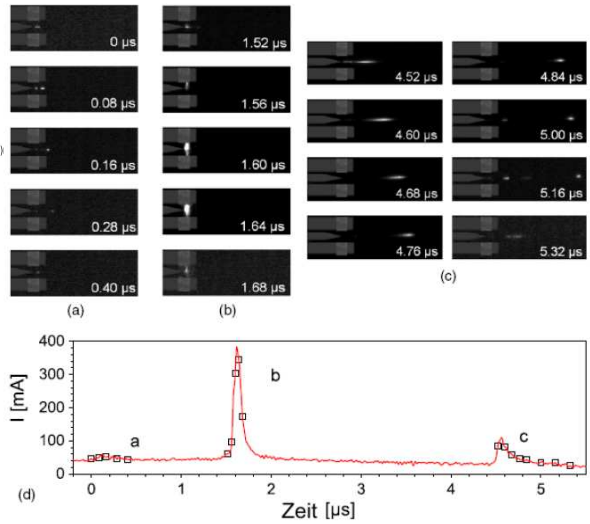
→ Reconnection and merging of discharge channels

→ Branching angles

E.M. van Veldhuizen et al. Eur. Phys. J. - Appl. Phys. **47**, 22811 (5p) (2009)

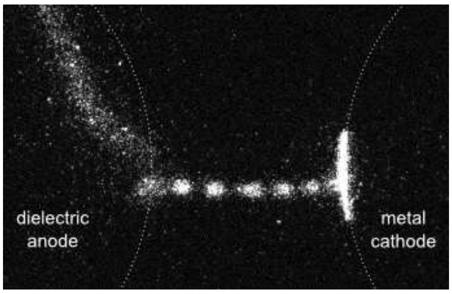
Plasma bulltes (Plasma jet)

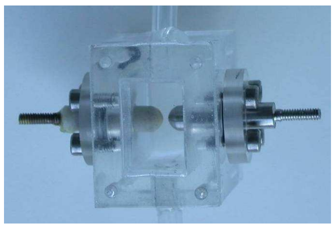




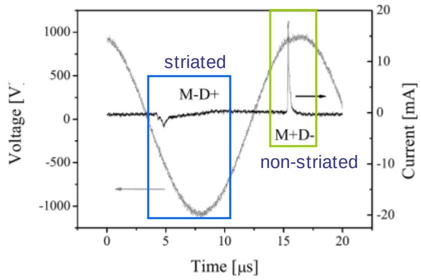
E. Kindel, H. Lange et al.; GD 2008 Cardiff

Striated MD in asymmetric volume BD in Ar





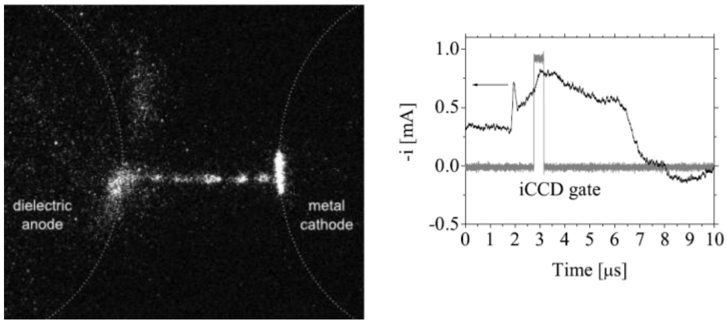
- Appearence of striated channel dependent on argon gas purity (argon flow rates above 100 sccm) and applied voltage amplitude
- Moste stable striated regime at 2 kV$_{p\text{-}p}$ (f= 60 kHz; T= 16 µs)

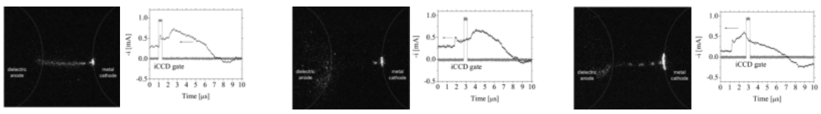


T. Hoder et al. Phys. Rev. E 2011

Reconstruction of temporal development

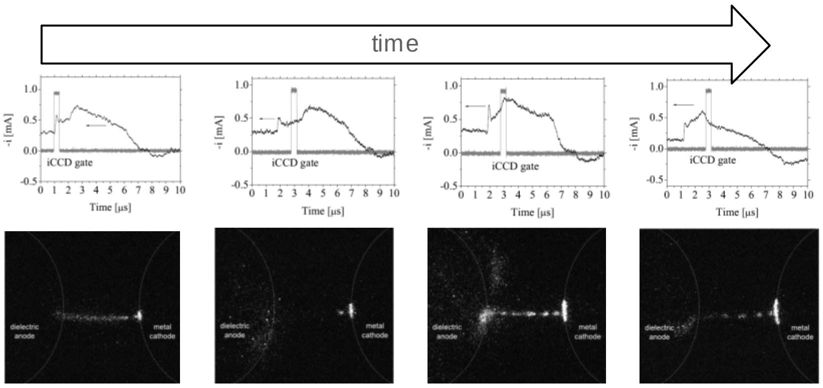
- Simultaneous recording of current and ICCD-photo (gate-signal)
- “Sorting” of ICCD-photos according to relation between ICCD-gate and current pulse





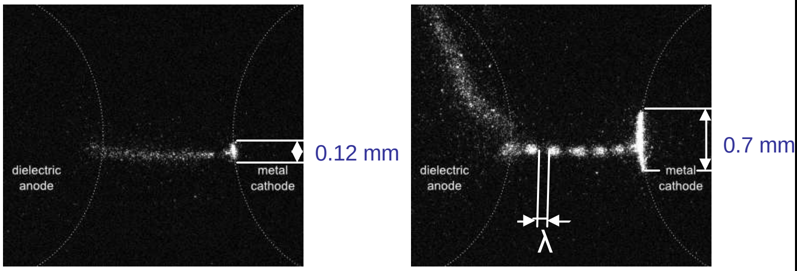
Spatio-temporally resolved development

1. glow-discharge-like structure
2. striated column and extended cathode layer
3. striated structure decay towards cathode



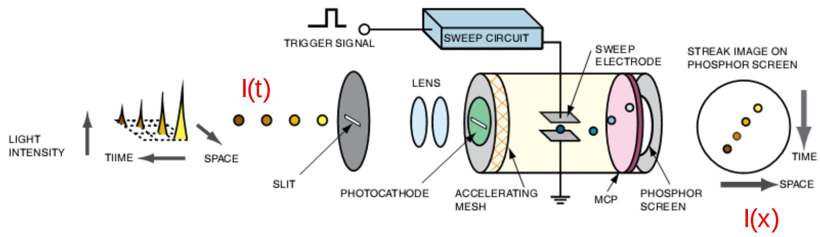
MD striation mechanism

- Scaling parameters from scaling law theory for low pressure discharges:
  i = 0.8 mA, r = 60 µm, λ = 200 to 300 µm
  → i/r ≈ 13 A/cm, p·r = 5 Torr·cm, 3 ≤ λ/r ≤ 5
  Similar to striations in low pressure glow discharges
- Different diameter of the cathode layer - channel constriction
  → different current densities at the cathode layer and in the channel
  → electron density gradient → local disturbance & **spatial electron relaxation**
- Energy dissipation length $\lambda_e(U)$ = 196 µm (theory*) corresponds to distance between the neighboring striations λ



*D. Loffhagen, M. Becker; INP Greifswald

Streak camera (optoscope)



Principle	Temporal profile transformed into spatial profile by defined deflection in streak tube and (I)CCD
Parameters	Δt down to 1 ps Gain 10^5 … 10^6
Pecularities	→ Temporally resolved investigation of individual MDs → One spatial dimension

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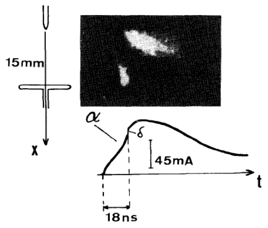
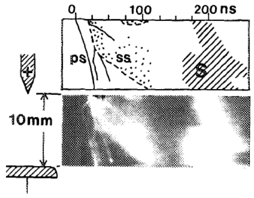
Streak photos of positive coronas

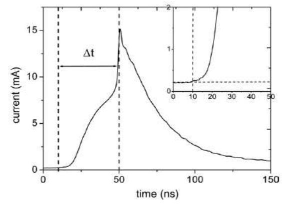
Marode 1974



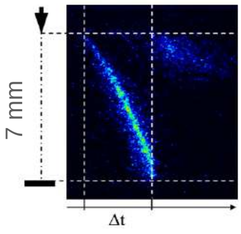
Sigmond 1983



Eichwald 2008



- Primary streamer (ps) and secondary streamer (ss)
- Return stroke (return streamers) and spark (S) formation

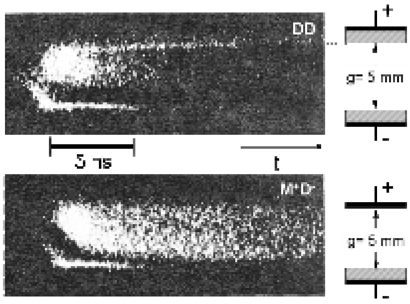


~ 50 ns

E. Marode; Journal of Applied Physics, Vol. 46, No.5 (1975); Raizer "Gas discharge physics" (Springer)
O. Eichwald et al.; J. Phys. D: Appl. Phys. 41 (2008) 234002 *R.S. Sigmond; J. Appl. Phys. 56 (5),1 (1984)*

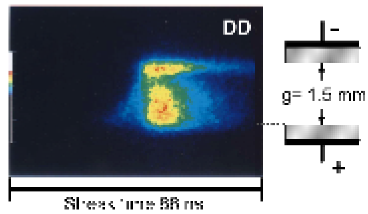
Streak photos in volume BD

Air



Optical streak

Kr/He/Cl_2 @ 400 mbar



Electro-Optical streak

C. Heuser, Diss. RWTH Aachen; G. J. Pietsch, Contributions to Plasma Physics 41, 620-628 (2001);
R.-J. Zahn S. Müller, 8th Int. Symposium on Science & Technology of Light Sources, Greifswald (1998).

Pulsed driven volume BD in N_2/O_2

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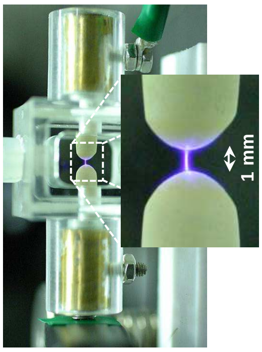
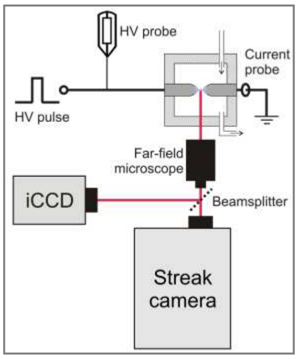
Discharge cell



- Dielectric: Al_2O_3($\varepsilon_r \approx 9$), about 0.5 mm thick
- **„Square wave“HV-pulses: U_P= 7 … 10 kV; dU/dt ~ 250 V/ns; f = 10 kHz**

Diagnostics



- Simultaneous measurement with ICCD and streak camera
- Electrical diagnostics

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Electrical measurements

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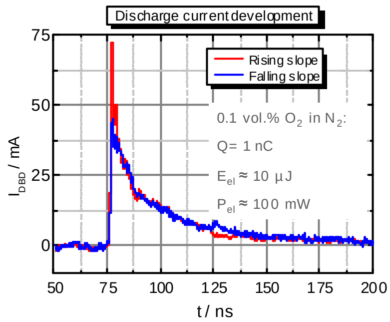
Voltage
Current



- One MD in the rising and in the falling slope of pulsed high voltage

- Similar current pulses at both slopes
- Decreases current pulse amplitude and duration with increasing $[O_2]$

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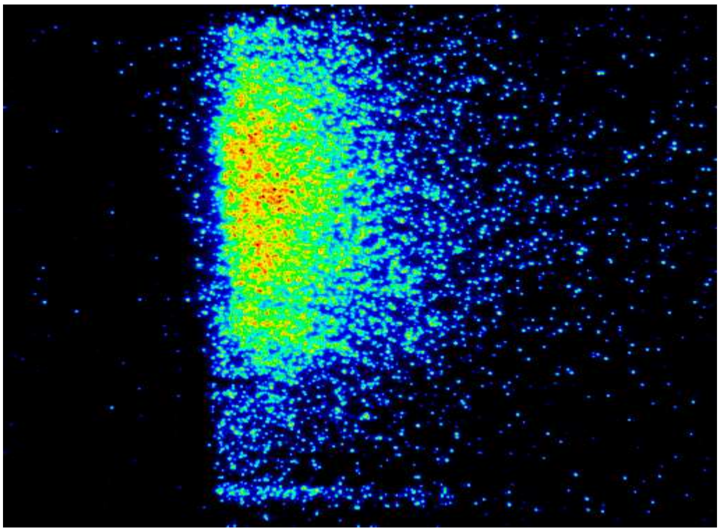
Streak-Camera imaging: single MD



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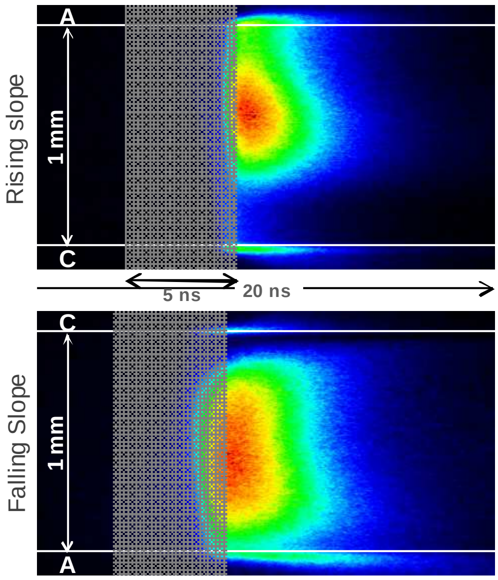
Streak-camera imaging: 1,000 MDs acc.



- Cathode directed ionisation front / streamer
- Glow region after streamer passage

Polarity-Difference:

- Longer MD duration in case of falling slope
- Larger dark space in case of rising slope

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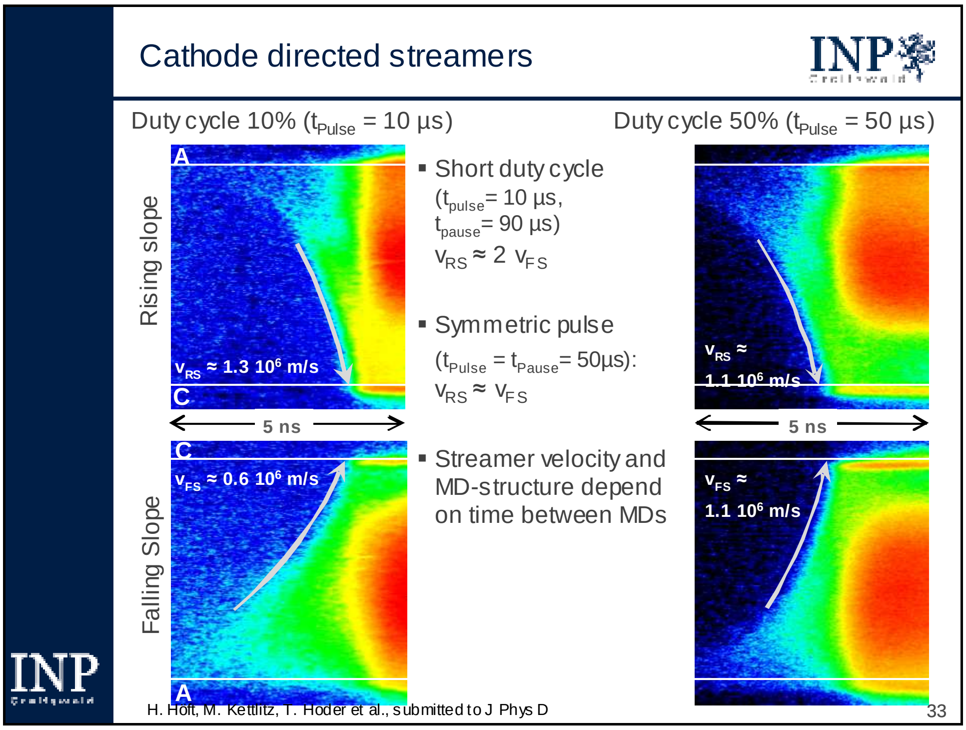
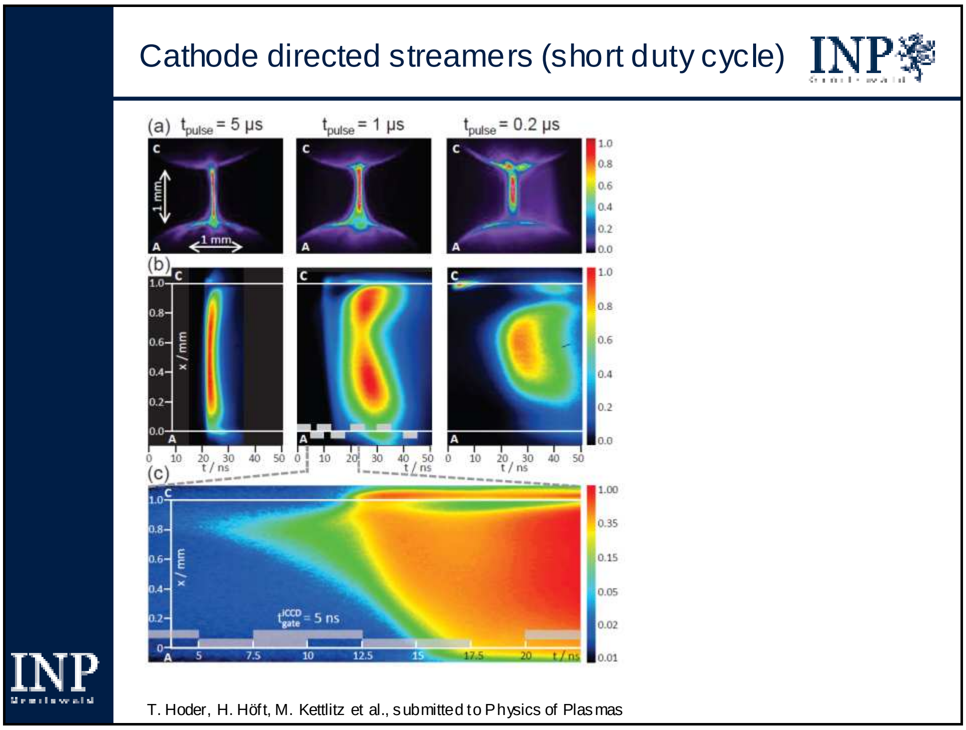

Cathode directed streamers
Duty cycle 10% (t_Pulse = 10 µs)
Duty cycle 50% (t_Pulse = 50 µs)
Rising slope
Falling Slope
v_RS ≈ 1.3 10^6 m/s
v_FS ≈ 0.6 10^6 m/s
v_RS ≈ 1.1 10^6 m/s
v_FS ≈ 1.1 10^6 m/s
5 ns
Short duty cycle (t_pulse = 10 µs, t_pause = 90 µs) v_RS ≈ 2 v_FS
Symmetric pulse (t_Pulse = t_Pause = 50µs): v_RS ≈ v_FS
Streamer velocity and MD-structure depend on time between MDs
H. Höft, M. Kettlitz, T. Hoder et al., submitted to J Phys D
33


Cathode directed streamers (short duty cycle)
(a) t_pulse = 5 µs
t_pulse = 1 µs
t_pulse = 0.2 µs
(b)
(c)
x / mm
t / ns
t_gate^ICCD = 5 ns
T. Hoder, H. Höft, M. Kettlitz et al., submitted to Physics of Plasmas

Cross-Correlation Spectroscopy (CCS)

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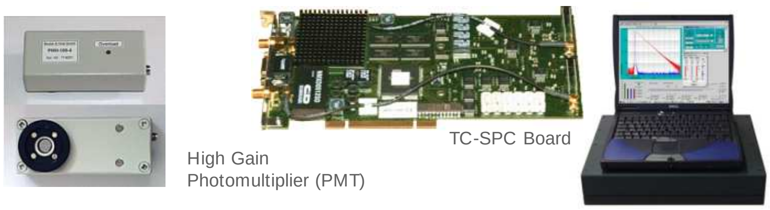
Principle	Time-correlated single photon counting (TC-SPC) with reference signal from MDs itself
Parameters	Δt down to 12 ps Gain up to 10^8 $\Delta\lambda$ about 0.03 nm
Pecularities	→ highest sensitivity → temporally and spectrally resolved investigation of repetitive, but erratic appearing discharge events → averaging over many MDs (stability required) → 2D spatial resolution possible



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CCS principle

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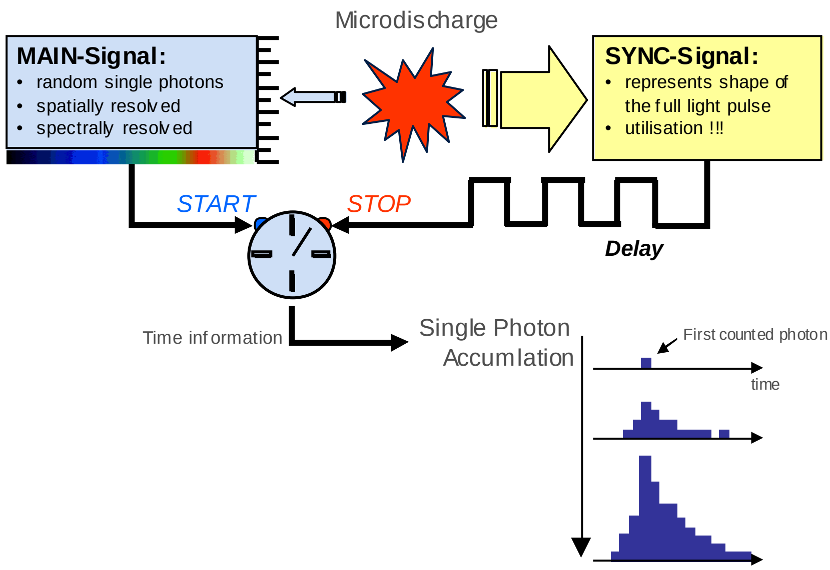

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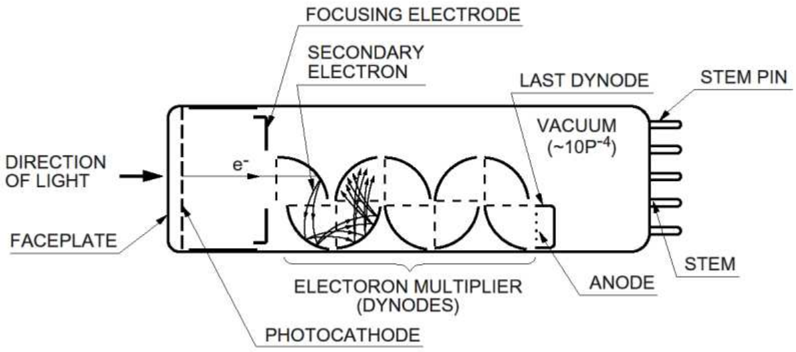
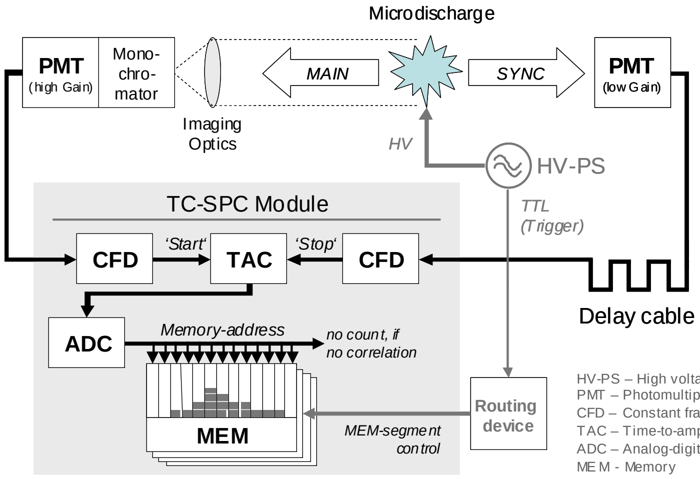
High-Gain Photomultiplier



Gain of up to 10^8

W. Becker, Becker-Hickl GmbH Berlin

CCS set-up



HV-PS – High voltage power supply
PMT – Photomultiplier
CFD – Constant fraction discriminator
TAC – Time-to-amplitude convertor
ADC – Analog-digital convertor
MEM - Memory

Emission spectrum in air

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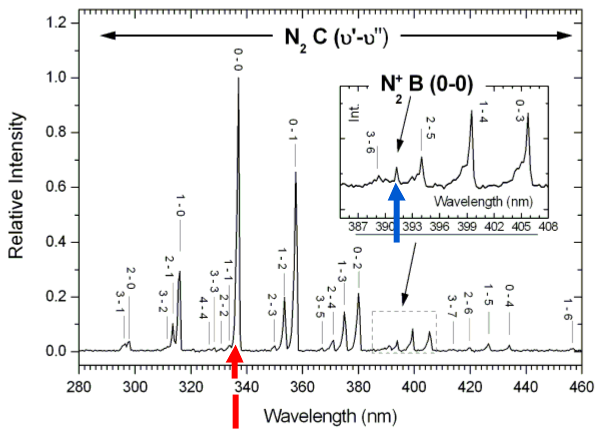

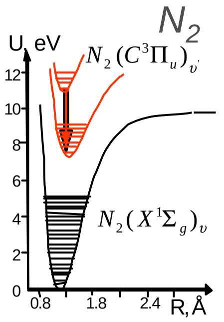

2. positive Sys. SPS $N_2(C^3\Pi_u)_{\upsilon'=0} \rightarrow N_2(B^3\Pi_g)_{\upsilon''=0} + h\nu$ $\lambda = 337nm$ $E_{C,0} = 11eV$

1. negative Sys. FNS $N_2^+(B^2\Sigma_u^+)_{\upsilon'=0} \rightarrow N_2^+(X^2\Sigma_g^+)_{\upsilon''=0} + h\nu$ $\lambda = 391nm$ $E_{B,0} = 19eV$

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Microdischarge development (VBD)

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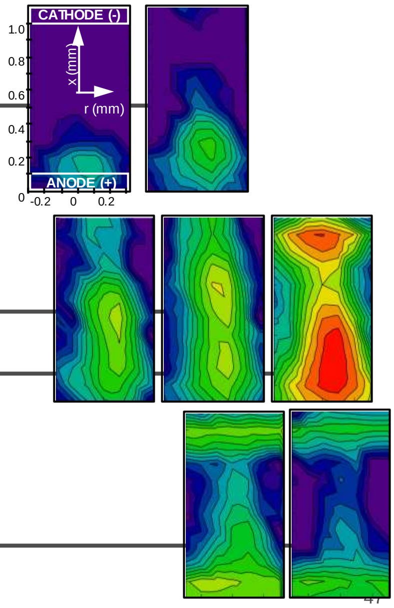
1. Pre-breakdown phase:
   several 100 ns,
   localised (residual surface charges)
2. Breakdown phase:
   cathode directed
   ionization front (2ns),
   anode glow and surface discharge
3. Relaxation (decay) phase:
   compensation of external E-field
   outward directed propagation of
   surface discharges



R. Brandenburg et al. J. Phys. D: Applied Phys. (2005)

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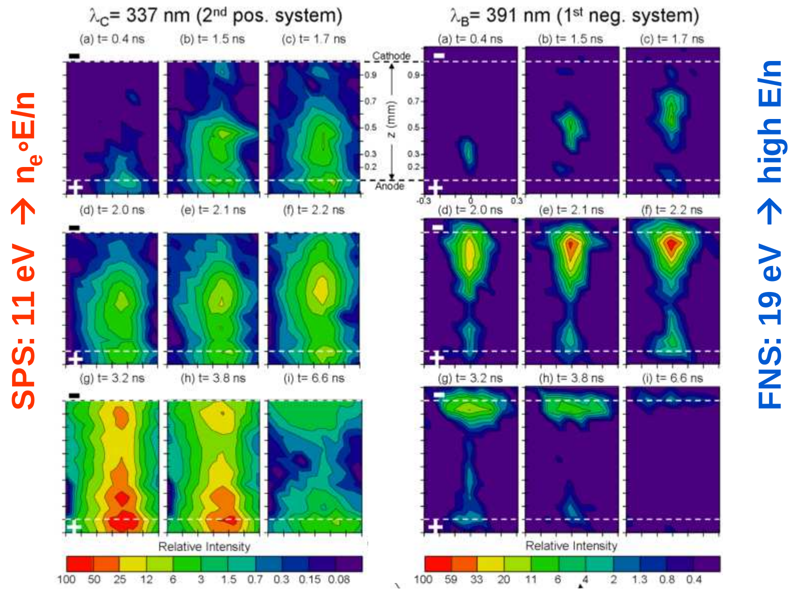
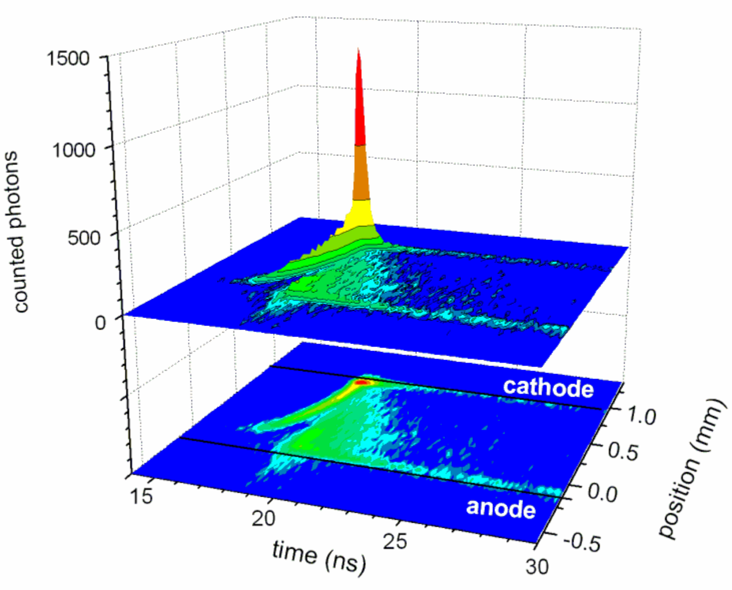
Microdischarge development (VBD in air)

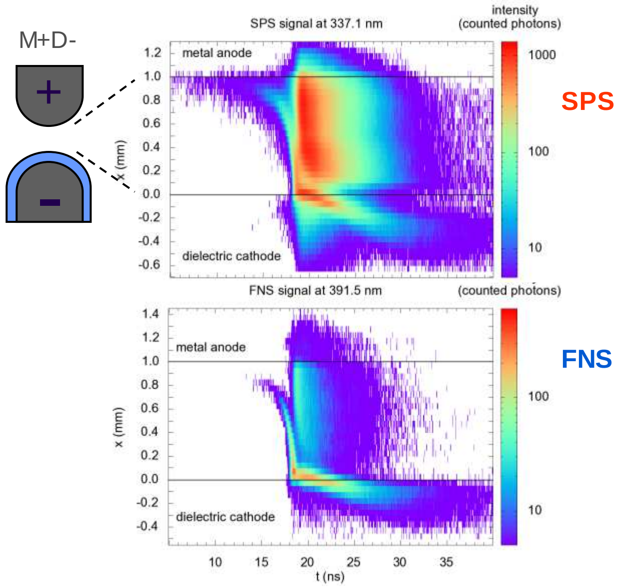


R. Brandenburg et al, IEEE Trans. Plasma Sci. (2008)

Development along MD-axis in the volume



Asymmetric volume barrier discharges

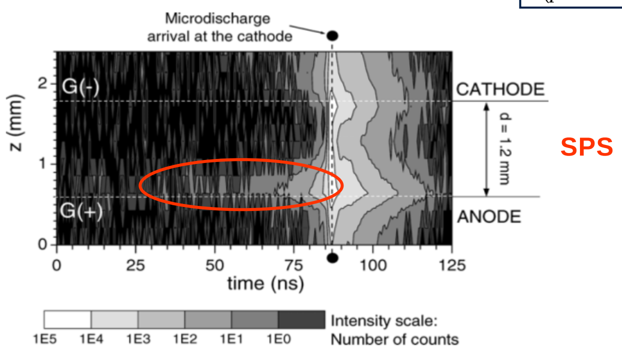


T. Hoder et al. J. Phys. D: Appl. Phys. 43 (2010) 124009

Pre-breakdown (Townsend) phase

- Pre-breakdown phase of several 100 ns
- Raether-Criterion not fullfilled

$$\int \alpha_{eff}\, dx < 18$$
$$(pd \approx 100\, Torr \cdot cm)$$

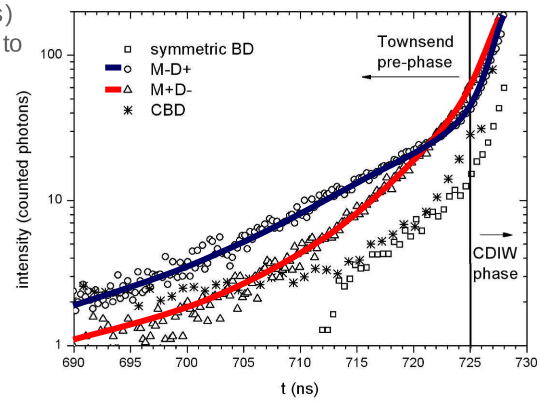


- Townsend-breakdown, localised due to minor field inhomogenity by residual surface charges (valid for repetitive mode)
- Accumulation of positiv ions during Townsend phase → streamer start

Yu. Yurgelenas et al.; Plasma Phys. and Controlled Fusion (2005)

Pre-breakdown (Townsend) Phase

Intensity (photons) measured closed to anode



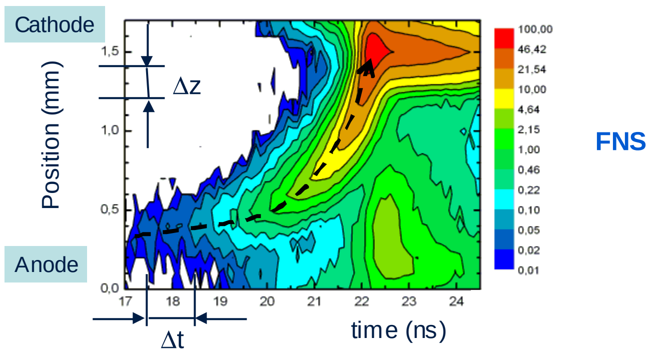
△ Dielectric cathode (M+D-): Emission of residual surface electrons
→ Shorter Townsend-prephase and stepest luminosity increase

○ Dielectric anode (M-D+): Positive residual surface charge
→ Local field increase and this enhanced pre-phase

T. Hoder et al. J. Phys. D: Appl. Phys. 43 (2010) 124009

Cathode directed ionisation front

- Cathode directed propagation of increasing field maximum (positive streamer)

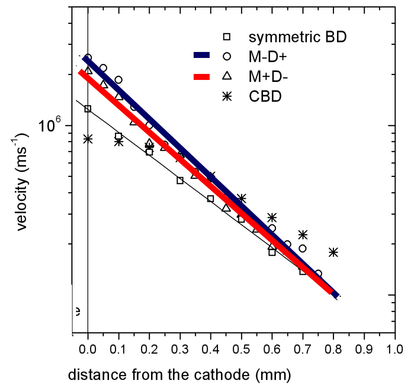


- Velocity depends on distance from cathode (v = 10^5 … 2 10^6 m/s),
- No v- dependence on (N_2-O_2) gas composition in symmetric VBD
- Velocity dependent on discharge configuration (sym. vs asym. VBD)

K.V. Kozlov et al.; J. Phys. D: Appl. Phys. (2005)

Ionization front (pos. streamer)

INP Greifswald



△ Dielectric cathode (M+D-): Emission of residual surface electrons
→ More effective γ-processes → Pos. charging of D → slower streamer

○ Dielectric anode (M-D+): → More effective α-processes (bulk)
No reversed field by surface charge deposition and secondary electron emission → Faster streamer

T. Hoder et al. J. Phys. D: Appl. Phys. 43 (2010) 124009

Evaluation of plasma parameters (model)

INP Greifswald

$$\frac{dn_{B,C}}{dt} = k_{B,C}\left(\frac{E}{n}\right)\cdot n_{N_2}\cdot n_e - \frac{n_{B,C}}{\tau_{eff}^{B,C}}$$

$$I_{B,C}(z,t) \propto n_{B,C}(z,t)$$

- local field approximation
- „strong“ and monotonous function ($E_{C,0}$= 11 eV << $E_{B,0}$=19 eV)

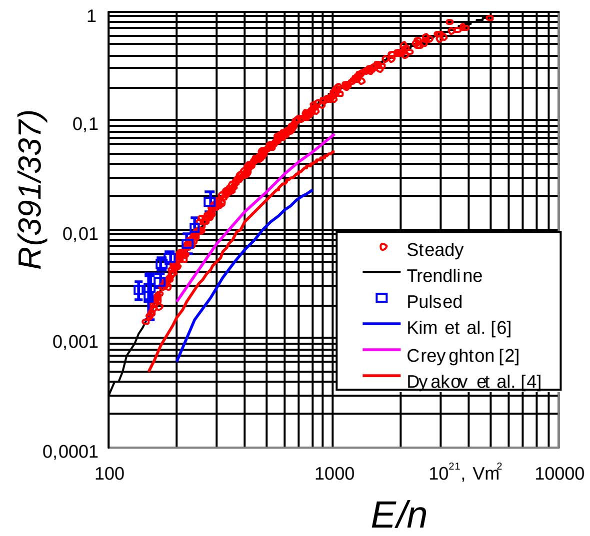
$$\frac{k_B}{k_C}\left(\frac{E}{n}\right) = C\cdot\left(\frac{A_{00}^B}{A_{00}^C}\right)\cdot\frac{\dot{I}_B + I_B/\tau_{eff}^B}{\dot{I}_C + I_C/\tau_{eff}^C}$$

Theory

Experiment

→ E/n (z,t) → particle balance equ. → $\frac{n_e(z,t)}{n_e^{max}}$

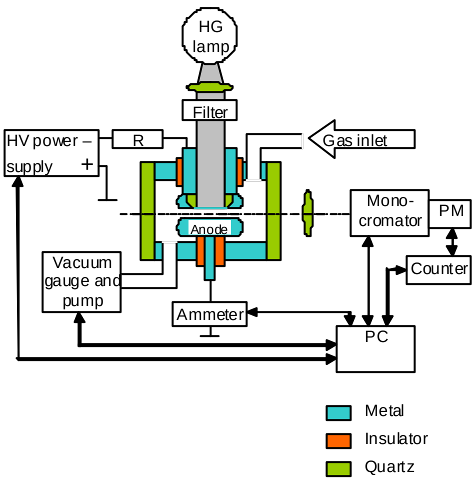
Evaluation of plasma parameters (model)

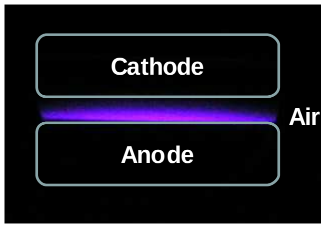


P. Paris; J Phys D (2005); University of Tartu

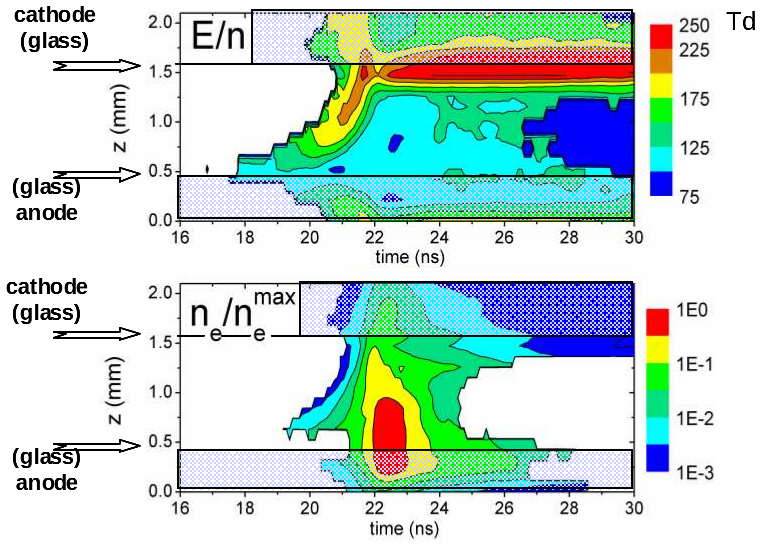
Model independent calibration in progress

Based on Townsend discharge (cell from Universtity of Tartu)





Plasma parameters



K.V. Kozlov et al : J. Phys. D: Appl. Phys. 2001

1Td = 10^{-17} V cm^2

E/n; n_e → O-Atom generation

Calculation based on experimental results

electronic dissociation

$O_2 + e \xrightarrow{k_d} O + O + e$

k_d(E/n (z,t)) • n_e(z,t) • n_{O2}

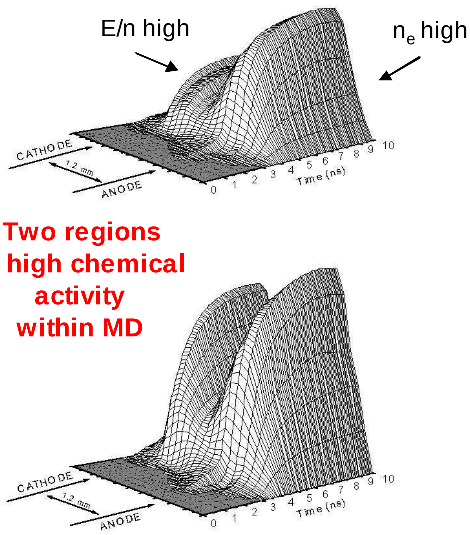
experiment

PENNING dissociation

$N_2 + e \xrightarrow{k_e} N_2^* + e$

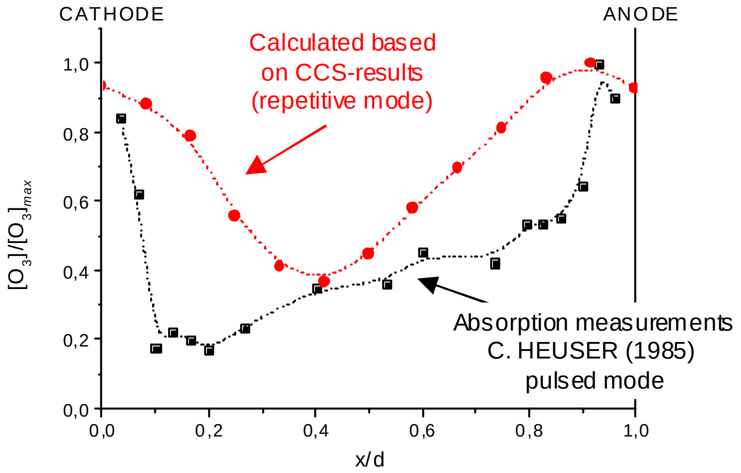
$N_2^* + O_2 \rightarrow N_2 + O + O$

k_e(E/n (z,t)) • n_e(z,t) • n_{N2}

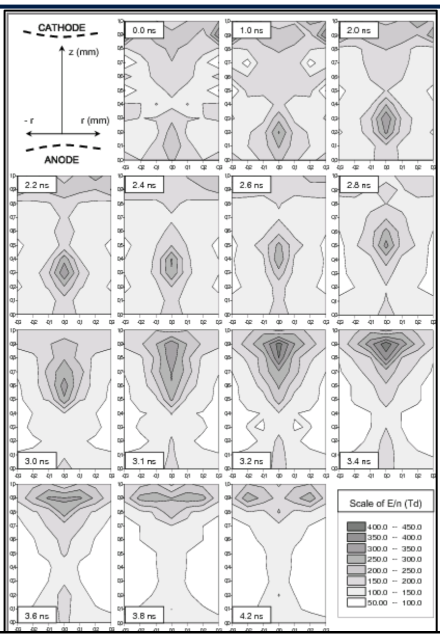


Calculated O_3 Concentration Profiles

→ raw assumption: complete O to O_3 conversion



E/n - 2D, symmetric BD



1Td = 10^{-17} V cm^2

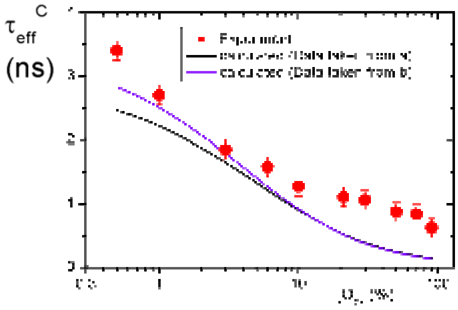
K. V. Kozlov and H.-E. Wagner, Contrib. Plasma Phys. (2007)

Time constants

- In regions of relaxating plasma: decay process for estimation of effective lifetimes

$$\frac{1}{\tau^{C}_{eff}} = \frac{1}{\tau^{C}_{rad}} + \boxed{K^{C}_{N_2} n_{N_2} + K^{C}_{O_2} n_{O_2}}$$

Quenching!

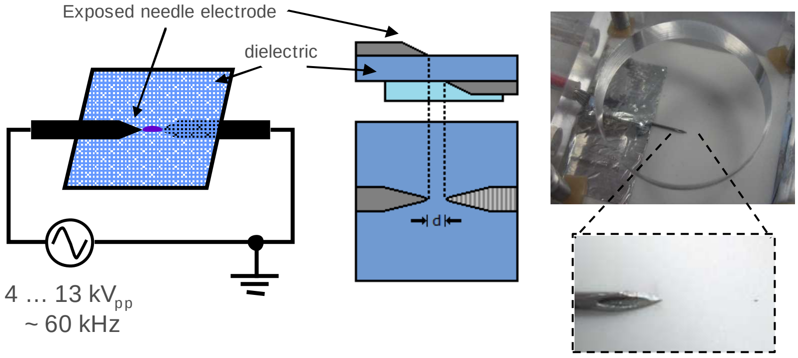


$$K^{C}_{N_2} << K^{C}_{O_2}$$

a) Pancheshnyi et al., Chem. Phys. 262 (2000) 349;
b) b) Mitchell, J. Chem. Phys. 53, 5 (1970) 1795

K.V. Kozlov et al : J. Phys. D: Appl. Phys. 2005

SBD configuration for MD studies



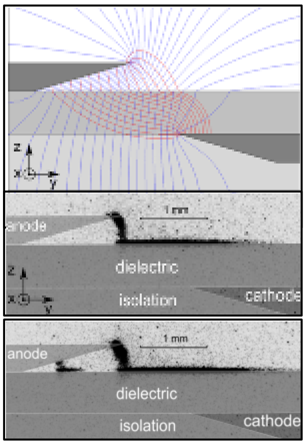
→ **Localization & stabilization for time-consuming CCS measurements**

- Two needle electrodes (Ø 0,4 mm, chrome- nickel- steel- alloy)
- Elektrode gap d= 1.15 mm

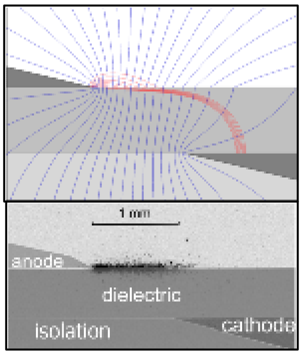
Dielectric material: Al_2O_3 , 0.6 mm thickness
Gas: dry air

Discharge generation

Field configuration: Calculated stream lines and potential



Volume discharge and surface discharge

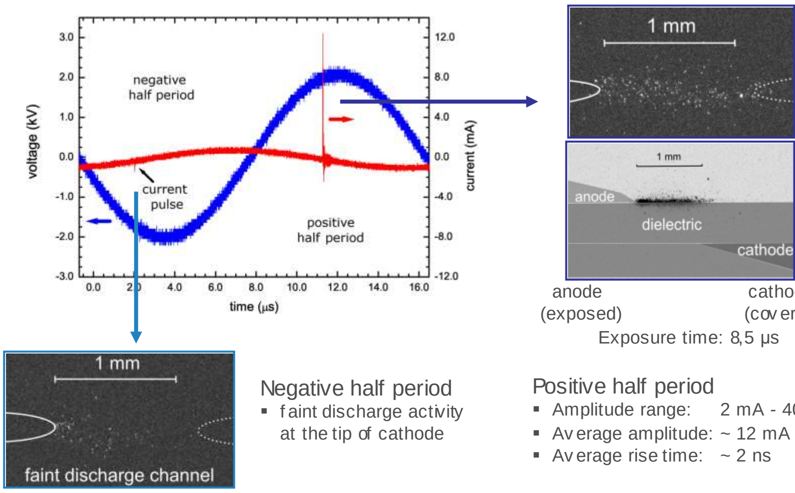


Surface discharge

T. Hoder, H. Grosch et al., EPJD 2010; IEEE Trans. Plas. Sci. 2011

Surface Barrier Discharges (SBD)

Applied Voltage closed to burning voltage → one MD per half period (HP)



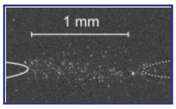
cathode (exposed) anode (covered)
Exposure time: 8,5 µs

anode (exposed) cathode (covered)
Exposure time: 8,5 µs

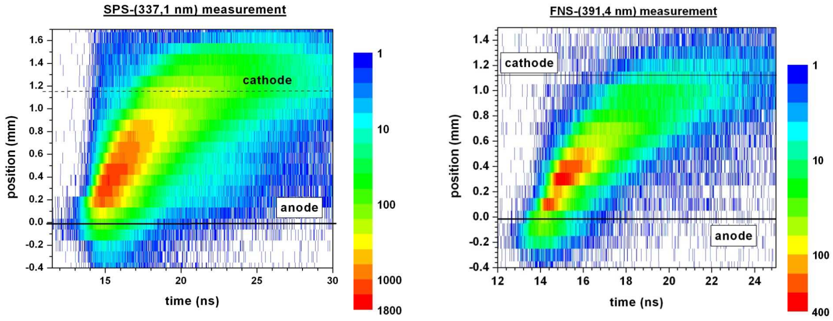
Negative half period
- faint discharge activity at the tip of cathode

Positive half period
- Amplitude range: 2 mA - 40 mA
- Average amplitude: ~ 12 mA
- Average rise time: ~ 2 ns

CCS results



Positive HP: exposed electrode= anode



- Pre-breakdown phase
- Cathode directed ionising front („streamer“) with **decrasing** velocity ($v = 3.0 \cdot 10^5$ m/s $-1.5 \cdot 10^5$ m/s)

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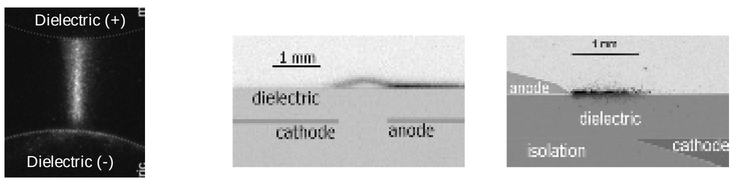
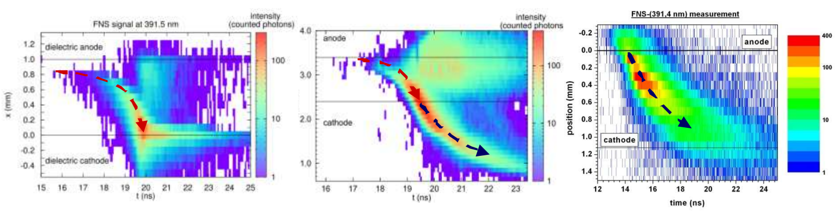
Comparison of different BDs

Symmetric VBD | **Coplanar Discharge** | **Surface Discharge**





	Symmetric VBD	Coplanar Discharge	Surface Discharge
v_{max}	10^6 m/s	10^6 m/s 10^5 m/s on dielectric	10^5 m/s
v-slope	increasing	increasing decreasing on dielectric	decreasing

T. Hoder et al.; J. Phys. D: Appl. Phys. 2010; H. Grosch et al., EPJD, 2010

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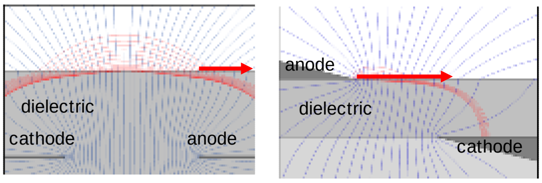
MD propagation on dielectric barrier

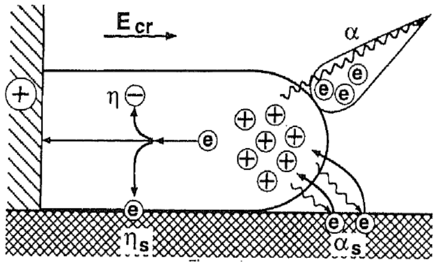
Coplanar Discharge **Surface Discharge**

External electric field:
- decreases along MD path

Red: Streamlines
Blue: Equipotential lines

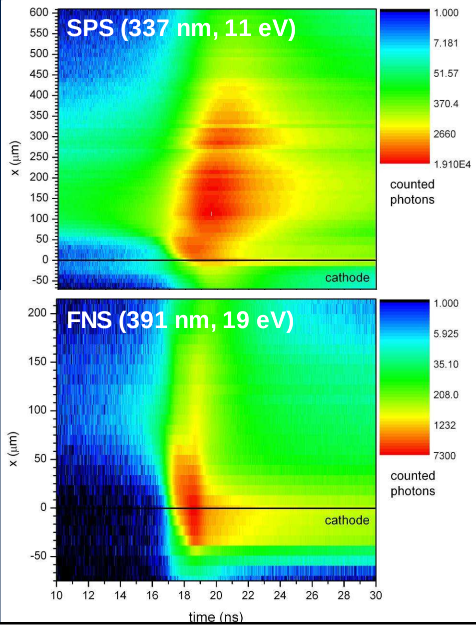


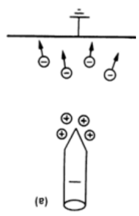
Surface processes:
- negative residual charge (e^-)
- surface ionization α_S (detrapping, photo effect, ion impact)
- surface attachment η_S



Niemeyer, L.; IEEE Trans. Dielectr. Electr. Insul. (1995), Vol. 2 No. 4, 510-528

Trichel pulse corona (negative corona)



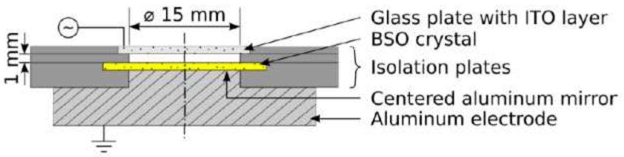


1. Electron multiplication phase (120 µm)
2. pos. streamer
3. anode directed streamer

T. Hoder et al., prep. Appl. Phys. Lett.

Surface charge measurements

The discharge cell



- surface charge measurement on dielectric ⇒ utilization of the optoelectronic Pockels-effect ⇒ BSO-crystal ($Bi_{12}SiO_{20}$)
- E-field causes anisotropy of the crystal induced by **applied voltage** and **surface charges**

M. Bogaczyk, H.-E. Wagner, Uni. Greifswald

Summary

- Fast optical and spectroscopic methods = powerfull tools for discharge diagnostics
- CCS as high sensitive method for spectroscopic investigation
  → Microdischarge development with high resolution ($\Delta t, \Delta x, \Delta\lambda$)
  → Estimation of plasma parameters (E/n; τ_{eff}, $n_e/n_{e,max}$)
- Microdischarge development in barrier discharges:
  (1) Townsend-prephase
  (2) cathode directed ionization front (pos. streamer)
  (3) decay phase
- Quantified determination of positive and negative surface charges by Pockels-effect
  → positive and negative surface charge density profiles significantly different due to the electron mobility
  → positive and negative charges can exist simultaneously
  → memory-effect important for discharge re-ignition

Outlook

Finished
- E/n-calibration of CCS device for systematic determination of plasma parameters (corona discharge)

Future work:
- To correlate fast spectroscopic and optical investigation with measurements of surface charges
  → structure and development (diffuse vs. filamentary)
  → role of surface processes (e.g. exoemission)
- Study of the correlation between plasma physics and chemistry
  → “From the microdischarge to the plasmareactor”

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- BMBF: “ForMaT - InnoPlas”

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