Workshop - April 10-12, Casa Valguga – Vale dos Vinhedos – Bento Gonçalves/RS

Atmospheric plasmas and their applications to surface treatment: shedding light on microwave sources .

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LABORATOIRE DE SCIENCE ET GENIE DES SURFACES

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INPL

Outlook

- Introduction
- Some examples of atmospheric pressure plasmas
- The resonant cavity system
- Physics of microwave plasmas
- Applications of atmospheric plasmas for materials treatment
- Conclusion

Why study atmospheric pressure plasmas?

- The physics of atmospheric pressure plasmas are not completely known (scientific interest)
- High potential for “low-cost” industrial applications (industrial interest)
- Environmental friendly alternative for some wet treatments

Advantages of atmospheric pressure plasmas:

- High reactivity
- Vacuum equipments are not necessary
- Easily set up for in-line continuous treatment (at least for flat surfaces)
- Low equipment cost

Drawbacks of atmospheric pressure plasmas:

- Small plasma volume
- Treatment homogeneity (principally for 3D parts)
- Highly influenced by fluid dynamics usually requiring high gas flow

Excitation power supply can be:

- DC or AC
- Frequencies going from 0 up to some GHz
- Continuous or pulsed mode

Some well known examples of atmospheric pressure plasmas are:

- Dielectric Barrier Discharge (DBD)
- Corona discharge
- Micro-plasmas
- Microwave plasmas

In different sources the plasma parameters and/or properties can be strongly different

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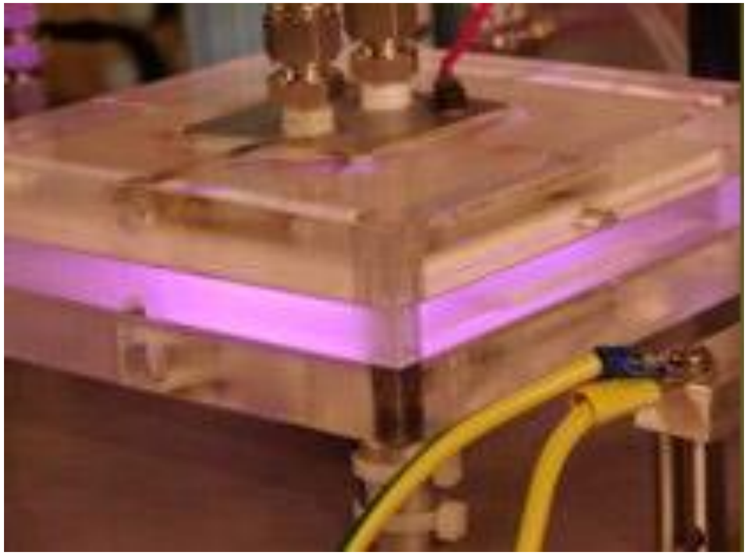
Examples of atmospheric pressure plasmas

DBD (Dielectric Barrier Discharges)

Essential Characteristics:

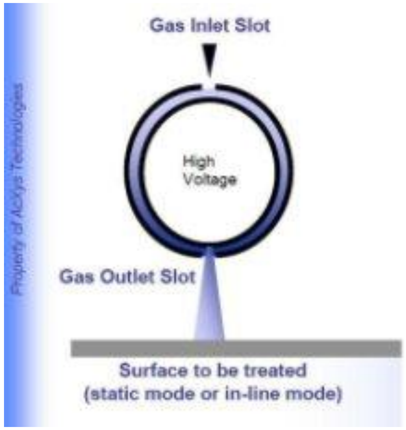
- Discharge created between two electrodes (gap < 1 cm)
- One or both of the electrodes are insulating to avoid arcing
- Low gas temperature
- High voltage (some KV in AC or pulsed DC)
- Different operation modes
  - *Homogeneous*
  - *Filamentary*



Glow discharge DBD (interesting for surface treatment)

http://www.risoe.dk/

Remote plasma (AcXys Atmospheric Plasma)



http://www.acxys.com/

Filamentary DBD

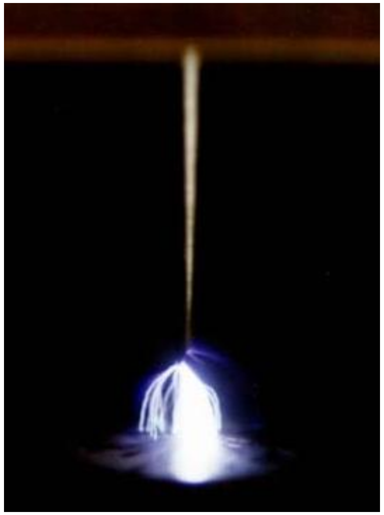
Cooper et all. 18th International Symposium on Plasma Chemistry, Kyoto, Japan, August 26-31, 2007

Examples of atmospheric pressure plasmas

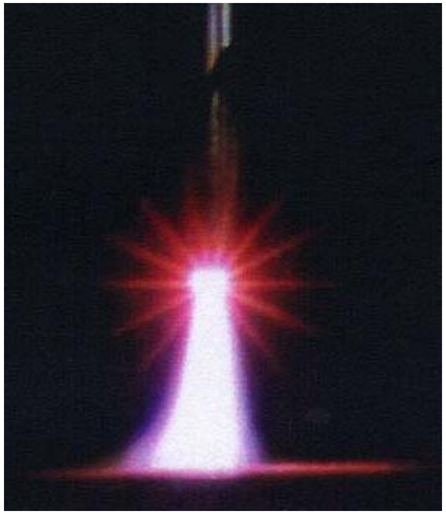
Corona

Essential Characteristics:

- Usually discharge is created between an electrode and a pointed shape, resulting in a highly concentrated electric field at its tip
- High voltage
- Pulsed discharge (to avoid arc formation)
- Two possible operation modes



positive corona



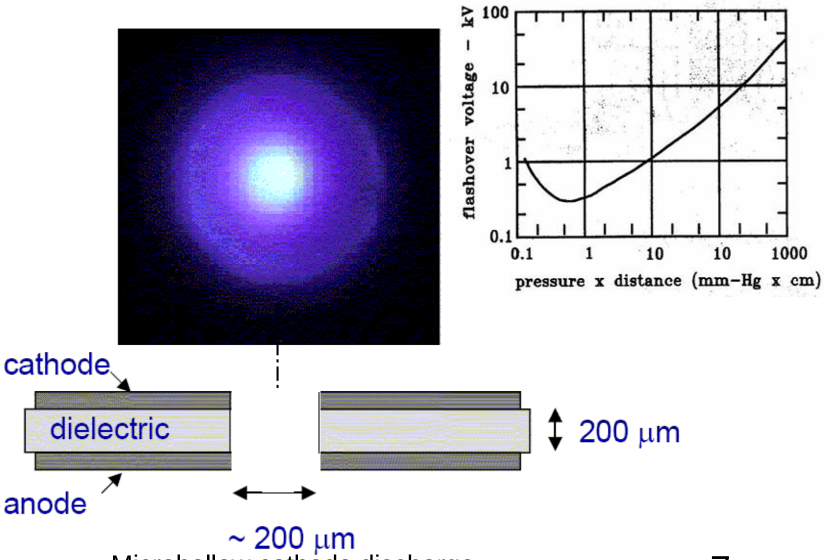
negative corona

C. Tendero et all. Spectrochimica Acta Part B 61 (2006) 2 – 3010

Micro-discharge

Essential Characteristics:

- Low voltage (usually < 500 V)
- Based on the Paschen's law (minimum pd for breakdown)
- Discharge created between two electrodes (usual gap of ~100 µm)
- Intermediate gas temperature



Microhollow cathode discharge

L. Pitchford, http://www.mrct.cnrs.fr/PF/Bonascre/bona2006/MicroPlasmas.pdf

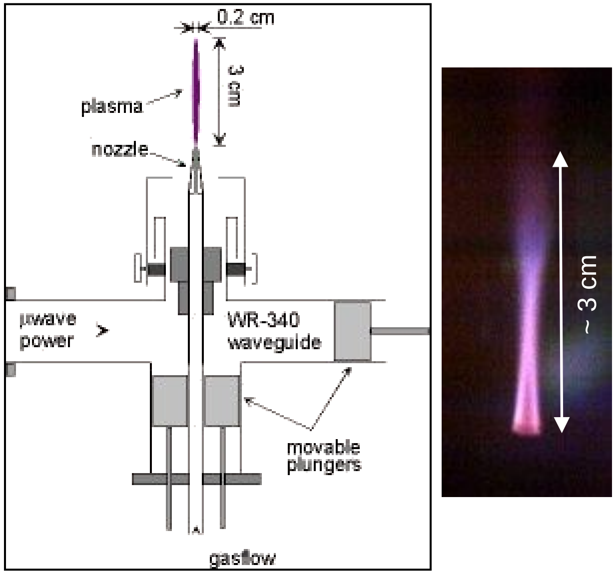
Examples of atmospheric pressure plasmas

Microwave plasmas

Essential Characteristics:

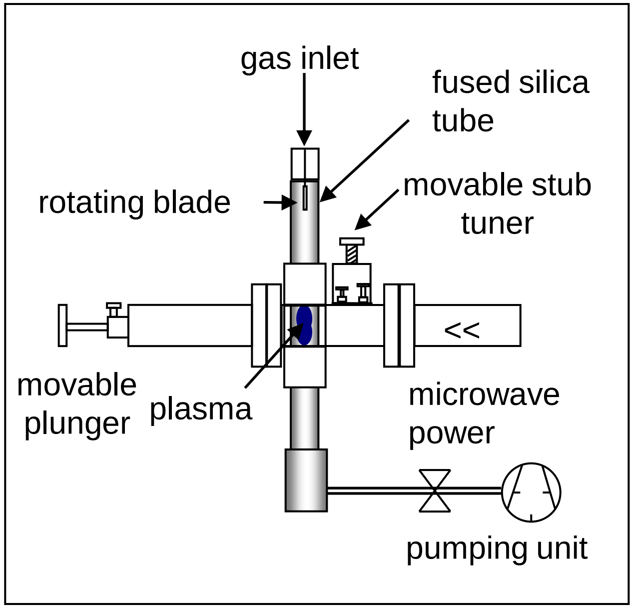
- Electrodeless discharge
- Plasma can be created without contact with surfaces (no sputtering and no contamination)
- High gas temperature can be achieved
- Different operation modes and excitation geometries are possible

TIA Torch



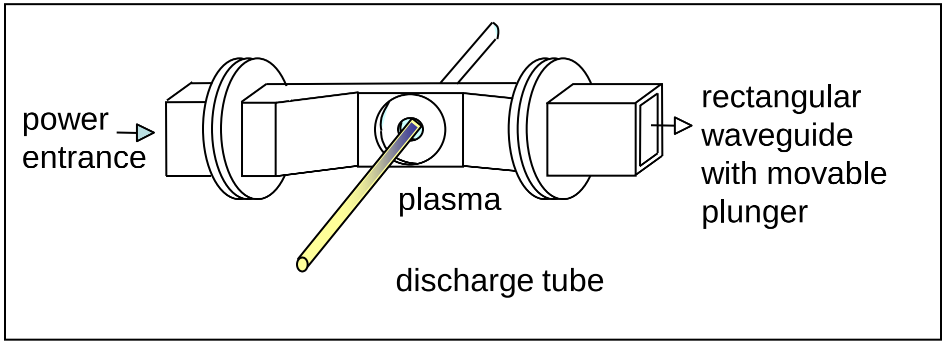
microwave is guided until the torch tip

Resonant cavity



microwave is confined into the cavity

Surface wave plasma



microwave propagates on the surface, between the plasma and the discharge tube

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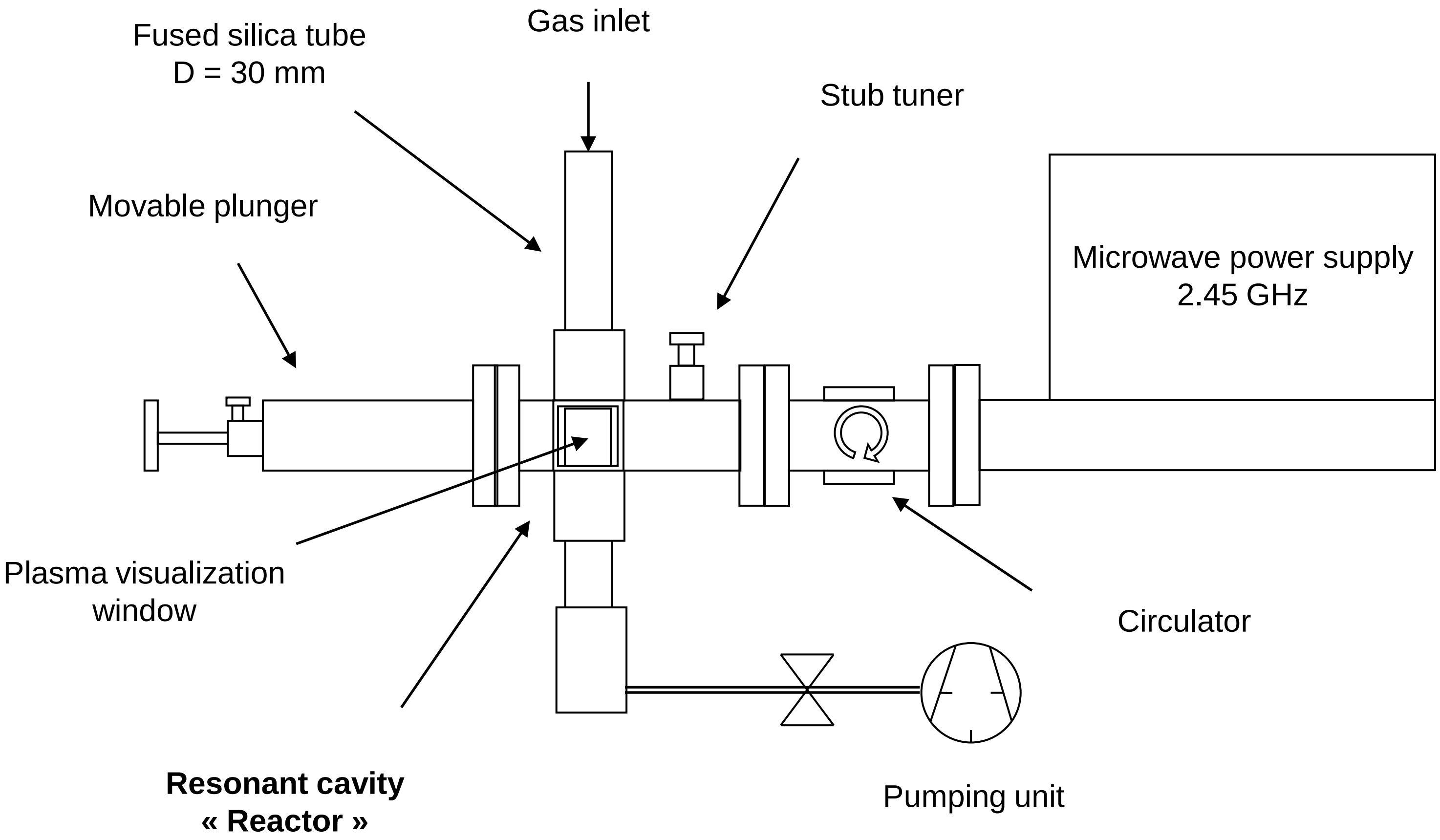
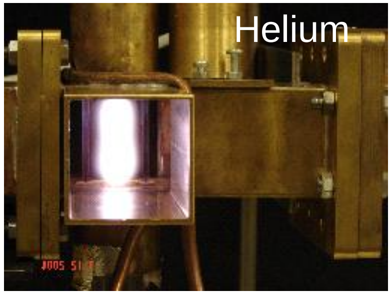
The microwave resonant cavity



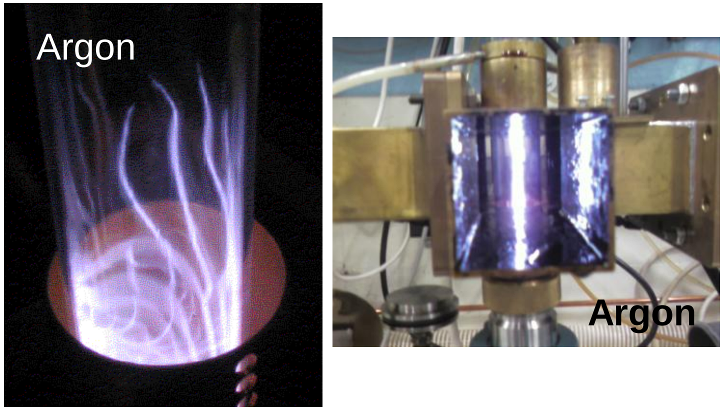
- The stub tuner and the movable plunger are adjusted to obtain the resonance of the cavity, consequently the electric field will increase into the cavity
- The discharge tube goes through the center of the cavity where the electric field is maximum
- The electric field transfers its energy to electrons that excite the gas

The resonant cavity

Examples of plasmas generated in a resonant cavity

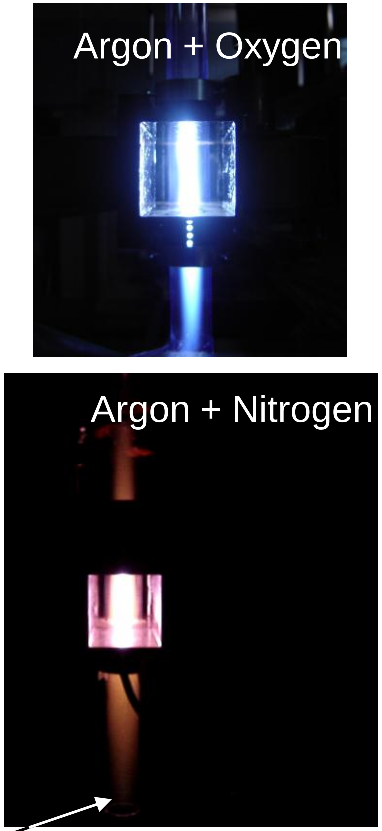


Homogeneous



Filamentary

Torch like



- Three different operation modes
- Introduction of solid samples into the cavity perturbs microwave propagation and consequently the plasma
- Surface treatments are carried out in the post discharge

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Plasma physics of microwave plasmas

Some particularities of atmospheric pressure microwaves plasmas generated in resonant cavity:

- Different phenomena are strongly coupled so the plasma physics is very complex
- In this low volume plasmas high gradients are present (for example temperature gradients can be higher than 1000 K/cm)
- High gas temperature
- Plasma does not fill the discharge tube (contraction)
- In some conditions plasma can be filamentary
- Locality of electron energy dissipation is not always verified (difficult to model)

The comprehension of plasma physics is fundamental for a better understanding of plasma treatments and for the development of innovative applications

In our group we have chosen to start the studies of these plasmas by helium plasmas.

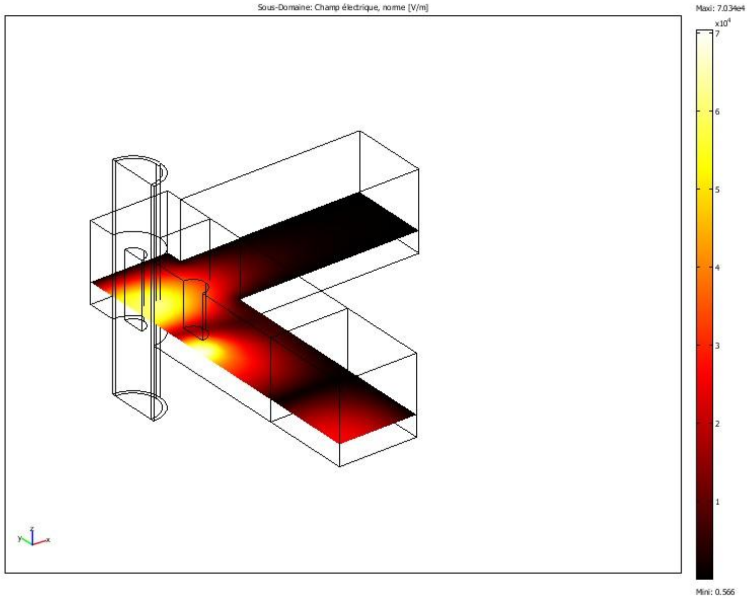
Homogeneous atmospheric pressure plasmas are more easily generated in helium and the locality of electron energy dissipation can be applied. Studies on argon plasmas are in progress.

Electromagnetic modeling

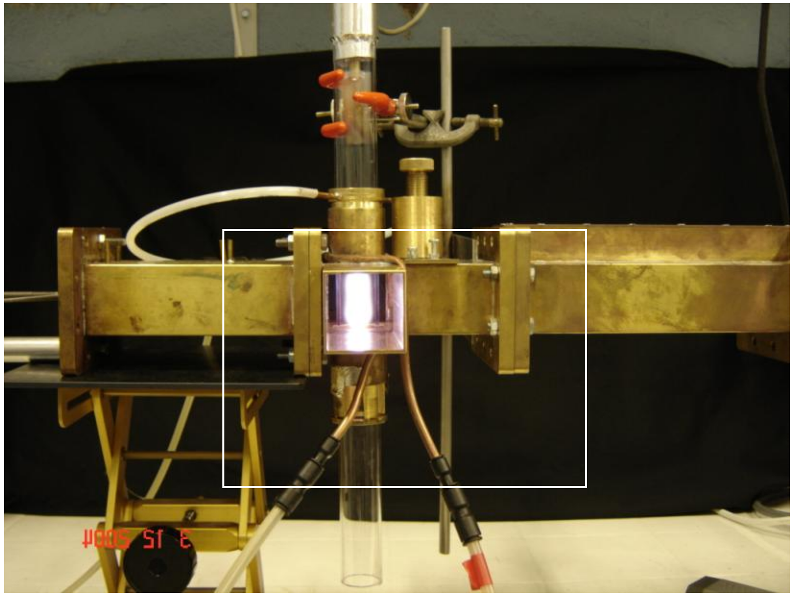
With the plasma dimensions and the cavity settings (stub and plunger position) we can estimate the electron density by solving Maxwell equations (numerical solution using Comsol Multiphysics^{TM})

The plasma is described as a cylinder.

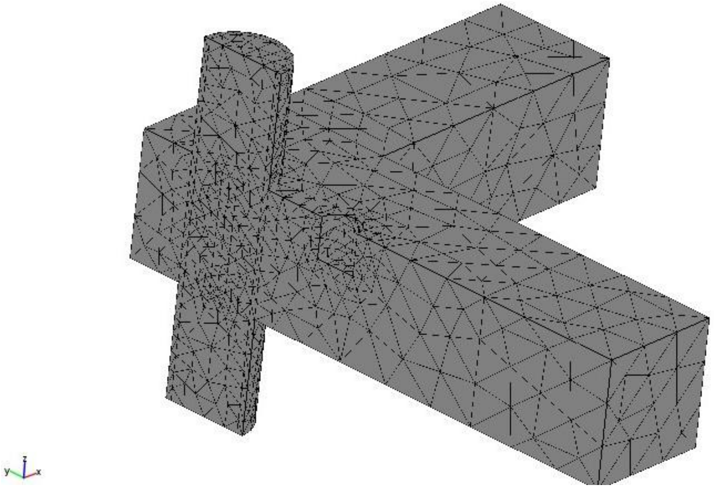
The electron density is taken into account by the plasma permittivity.



Electric field in a plan crossing the center of the cavity



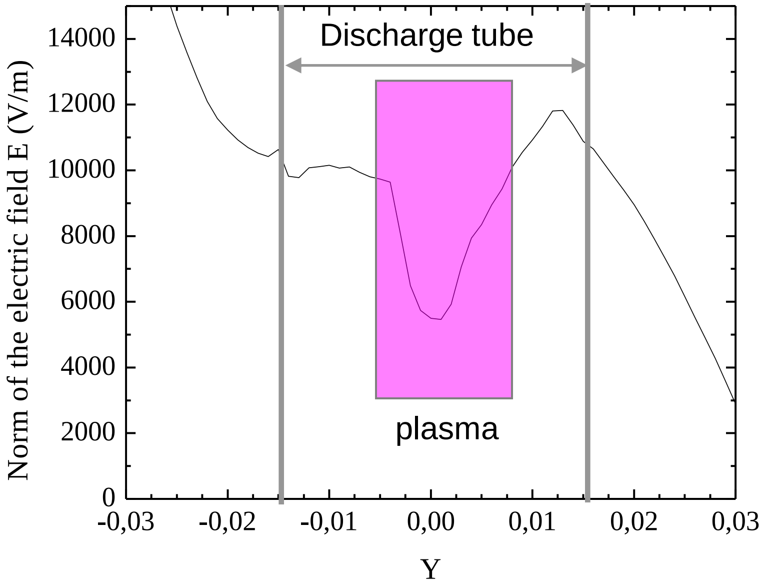
Modeled region



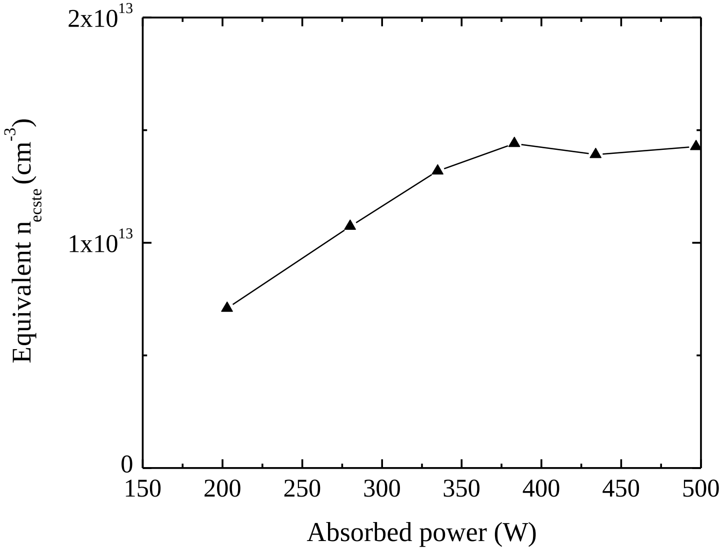
Numerical mesh

Electromagnetic modeling

Electric field across the discharge tube



Electron density as a function of power



- ✓ The electric field decreases in the plasma region due to the energy absorption by the plasma
- ✓ The reduced electric field (E/N) in the center of the plasma at 300 W is 2.2 Td (1 Td = 10^{-17} Vcm^2)
- ✓ The electron density increases slightly with power being approximately 10^{13} cm^{-3}

CR – Modeling (for pure helium)

Boltzmann equation (171 excitation processes)

Kinetic model (454 elementary reactions)

} Coupled solution

Problems :

- ✓ Rate constants
- ✓ Excitation cross section

} Some data are not known with enough precision

⇒ It is necessary to adjust some of them

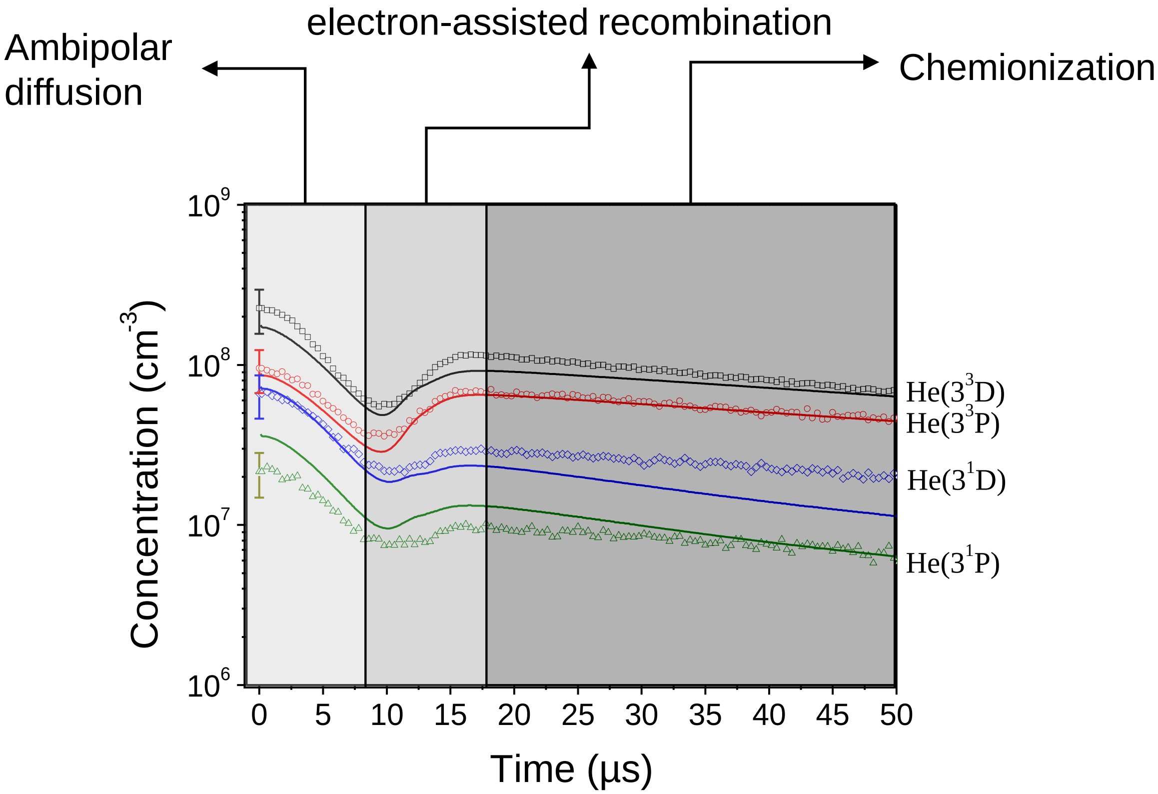
⇒ After adjusting some constants a consistent set of rate constants and excitation cross sections is obtained

Adjusting method (based on experimental data):

- ✓ The electric field is obtained from the solution of Maxwell equations
- ✓ The adjustment of constants are done by comparing the results from the model and the experimental data in steady state plasmas and time post discharges

CR – Modeling (results)

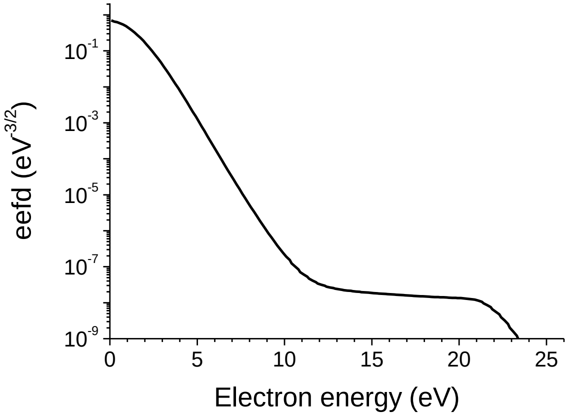
Evolution of n=3 helium states during the time post discharge of a pulsed plasma



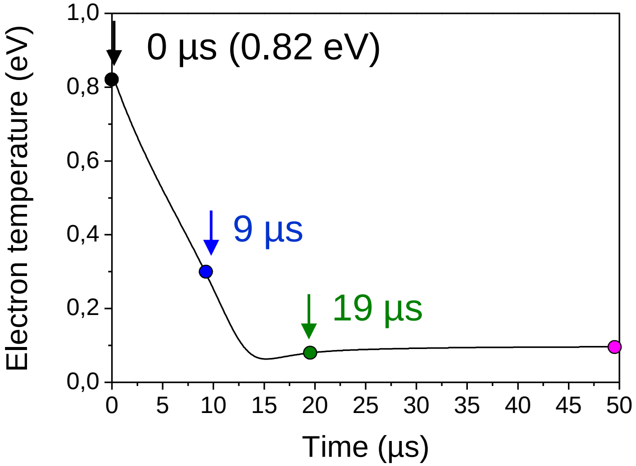
- ✓ The time evolution can be described in three parts (well described by the model)
- ✓ The gradient length for ambipolar diffusion determined by the first slope is 0.9 mm
- ✓ The rate constant for recombination and chemionization were determined for our working temperature (2450 K)

CR – Modeling (results)

Electron distribution function in steady state



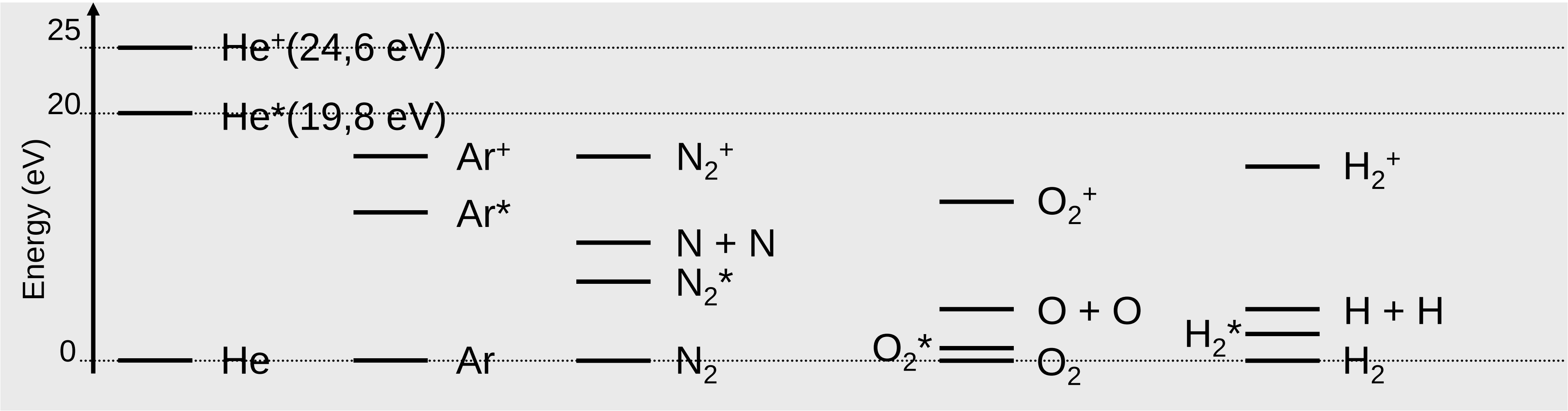
Mean electron energy in the post discharge



- ✓ The electron distribution function is strongly non-Maxwellian
- ✓ The mean electron energy in steady state plasma is 0.82 eV
- ✓ The mean electron energy reaches a local minimum value at 15 μs, that coincides to the maximum in emission of n=3 helium states

Influence of impurities

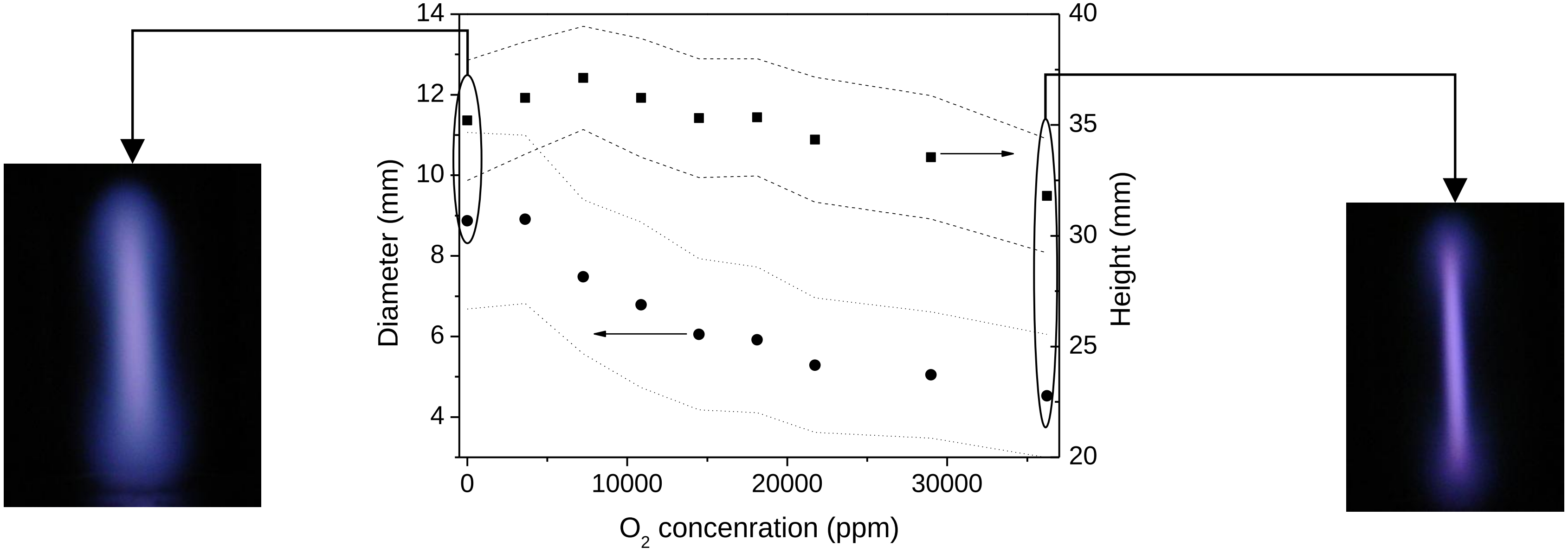
Comparison of the energy of the first excited state of helium and the energy level of different “impurities”



- ✓ The first helium excited state is metastable and lies at high energy
  - The ionization process is stepwise (metastable being the intermediate step)
    - Impurities can be excited more easily than helium
      - Helium discharges are very sensitive to impurity content
- ✓ We decided to investigate this aspect in our experimental conditions

Influence of impurities (Plasma dimensions)

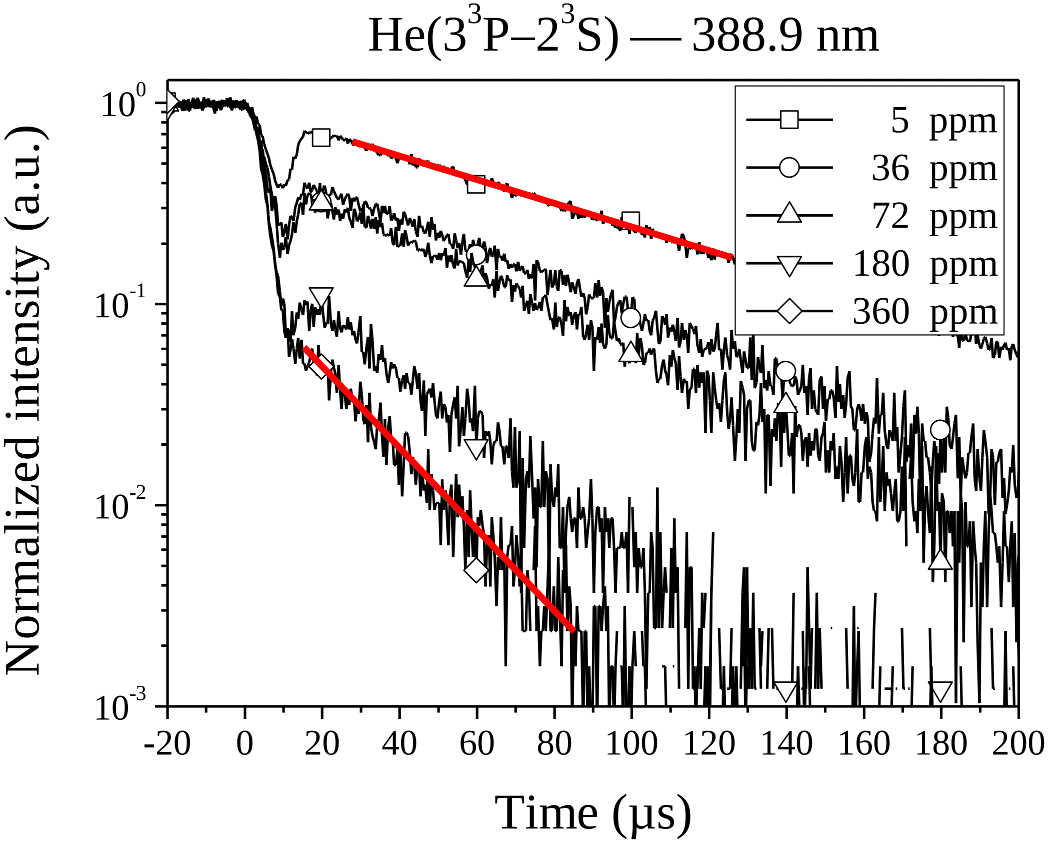
Variation of plasma dimensions as a function of O_2 concentration

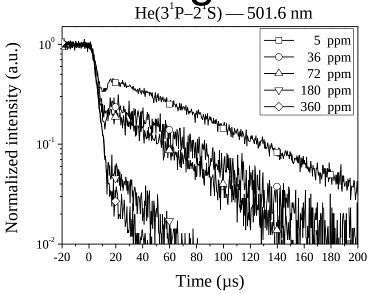


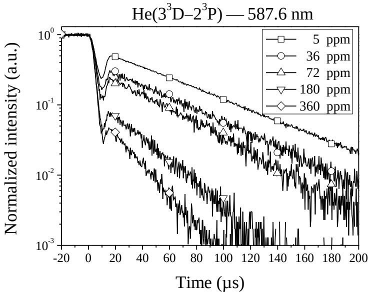
- ✓ The plasma volume decreases for high oxygen concentration (This is probably due to changes in the main sustaining mechanism, change in α)

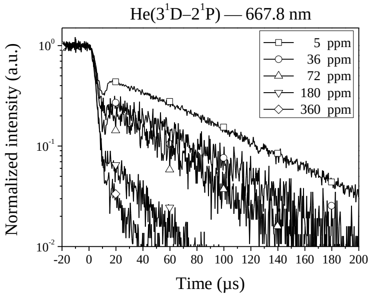
Influence of impurities (Post-discharge measurements)

Evolution of n=3 helium states emission during the time post-discharge


He(3^3P–2^3S) — 388.9 nm


He(3^1P–2^1S) — 501.6 nm

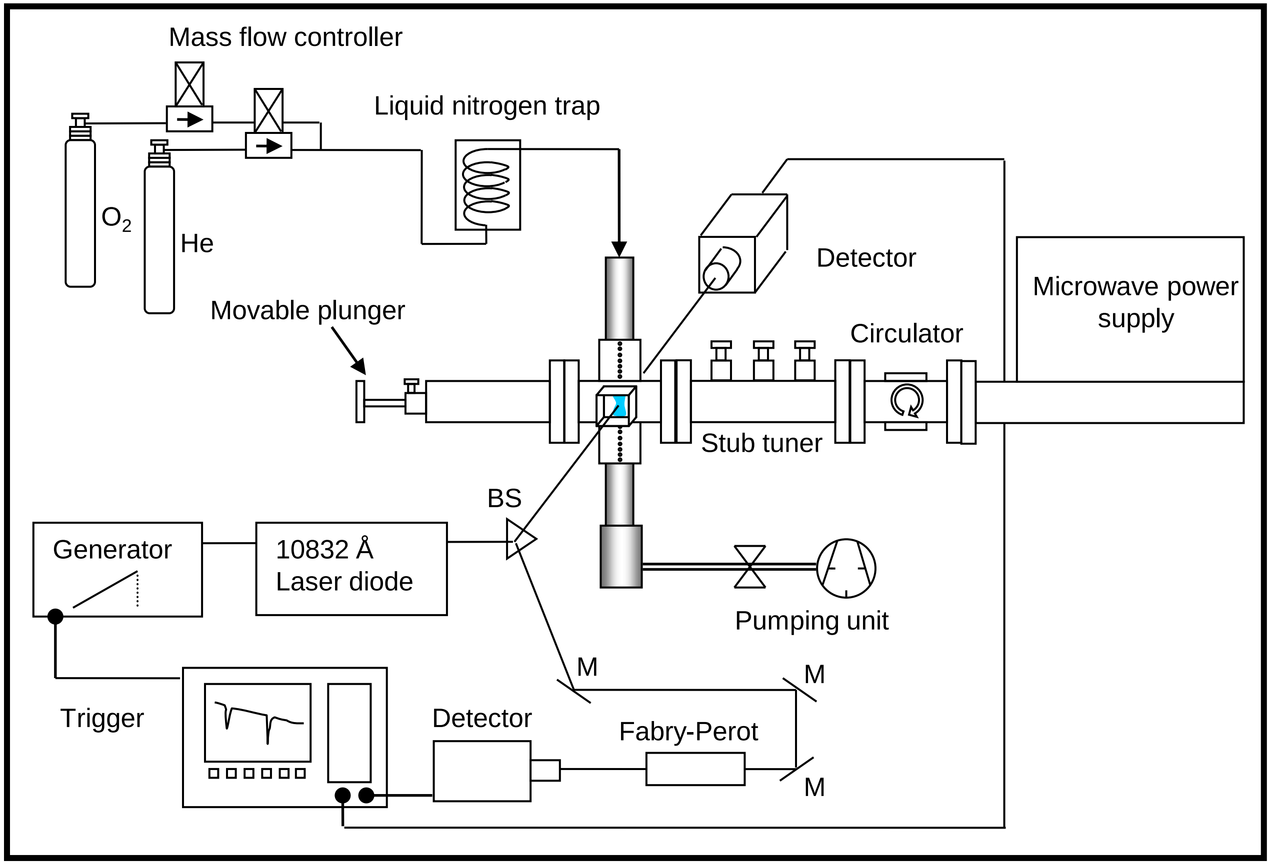

He(3^3D–2^3P) — 587.6 nm


He(3^1D–2^1P) — 667.8 nm

- ✓ The last step of the time post-discharge presents an exponential decay and the slope (destruction frequency) increases with the oxygen concentration

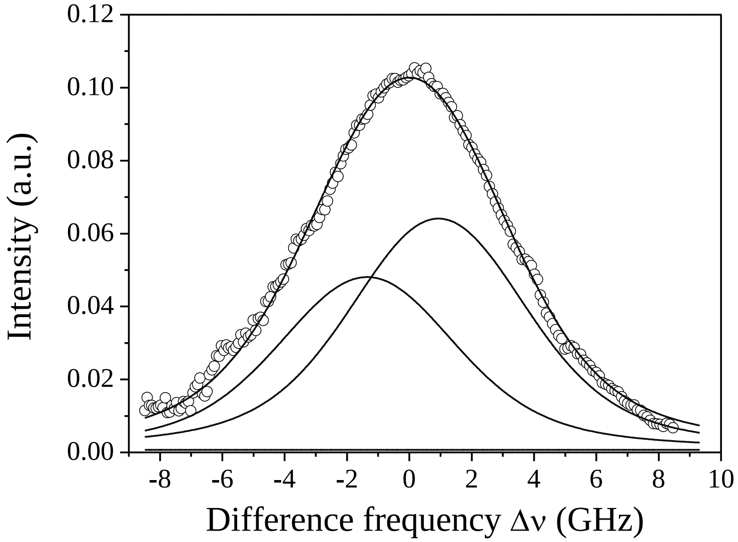
Influence of impurities (measurements of He(2^3S))

Laser Atomic Absorption Spectrometry: measurements of He(2^3S)

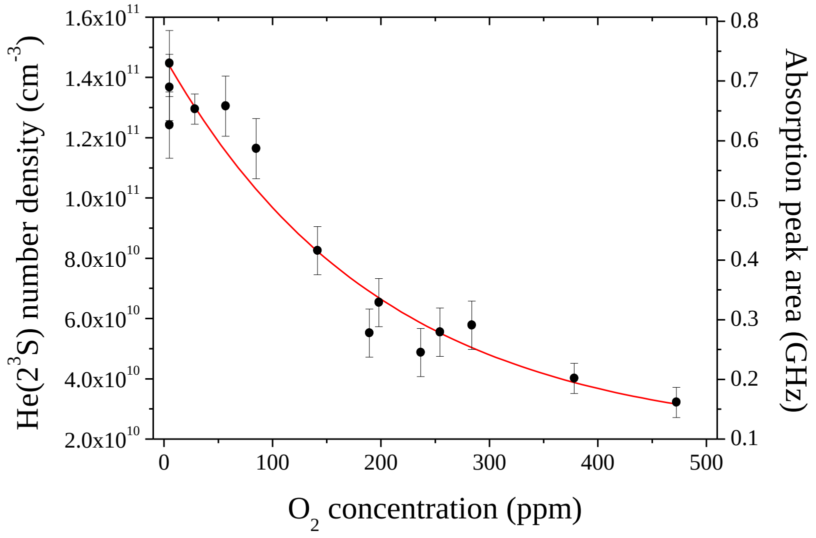


A tunable laser beam crosses the plasma and the transmitted intensity is measured. Knowing the plasma absorbance, the density of the absorbing species can be determined.

LAAS measurements of He(2^3S)



R P Cardoso et al. J. Phys. D: Appl. Phys. 39 (2006) 4178

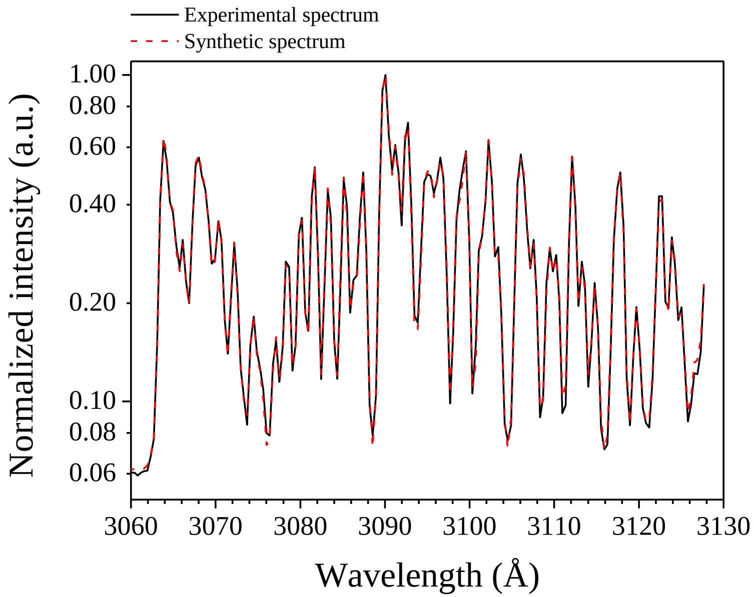


- The peak area is directly related to the He(2^3S) concentration.
- The absorption peak can be fitted by a Voigt profile
  - Gaussian = Doppler broadening (related to temperature)
  - Lorentzian = Pressure broadening (Stark broadening being negligible)

✓ The He(2^3S) metastable concentration decreases by a factor of 3 for an impurity addition of 300 ppm.

Gas temperature

Emission of OH (306.4nm : $A^2\Sigma^+$; v=0 - $X^2\Pi$; v'=0) 270 W

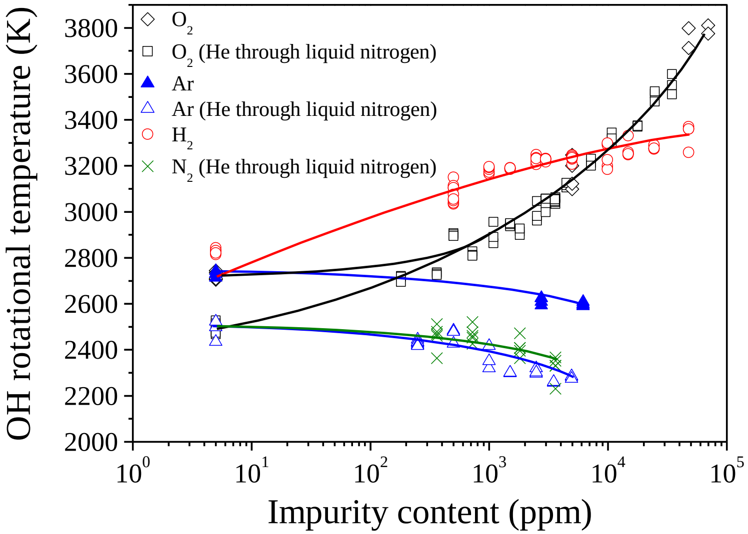


R P Cardoso et al. J. Phys. D: Appl. Phys. 40 (2007) 1394

- ✓ At atmospheric pressure the rotational temperature can be considered in equilibrium with the gas temperature
- ✓ The rotational temperature is measured by the synthetic spectrum method

Gas temperature

Evolution of gas temperature as a function of impurity content and nature measured by the synthetic spectrum method using OH emission



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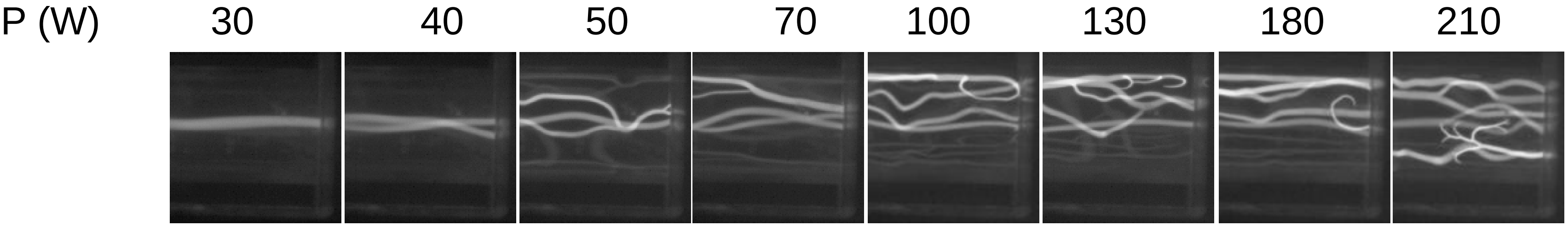
- ✓ In pure Helium, the gas temperature is about 2500 K
- ✓ Two different behaviors are observed, depending on the nature of the impurity.
  For Ar and N_2 the temperature remains approximately constant
  For O_2 and H_2 the gas temperature increases with the impurity concentration
- ✓ For the case where the impurity is oxygen and hydrogen the increase in the gas temperature is related to the contraction of the discharge (higher power density)

The resonant cavity plasma

Filamentation: breaking of single plasma filament into filaments of smaller diameter

Discharge filamentation is related to the limited penetration of the HF electric field into the plasma at high enough electron density (skin effect)

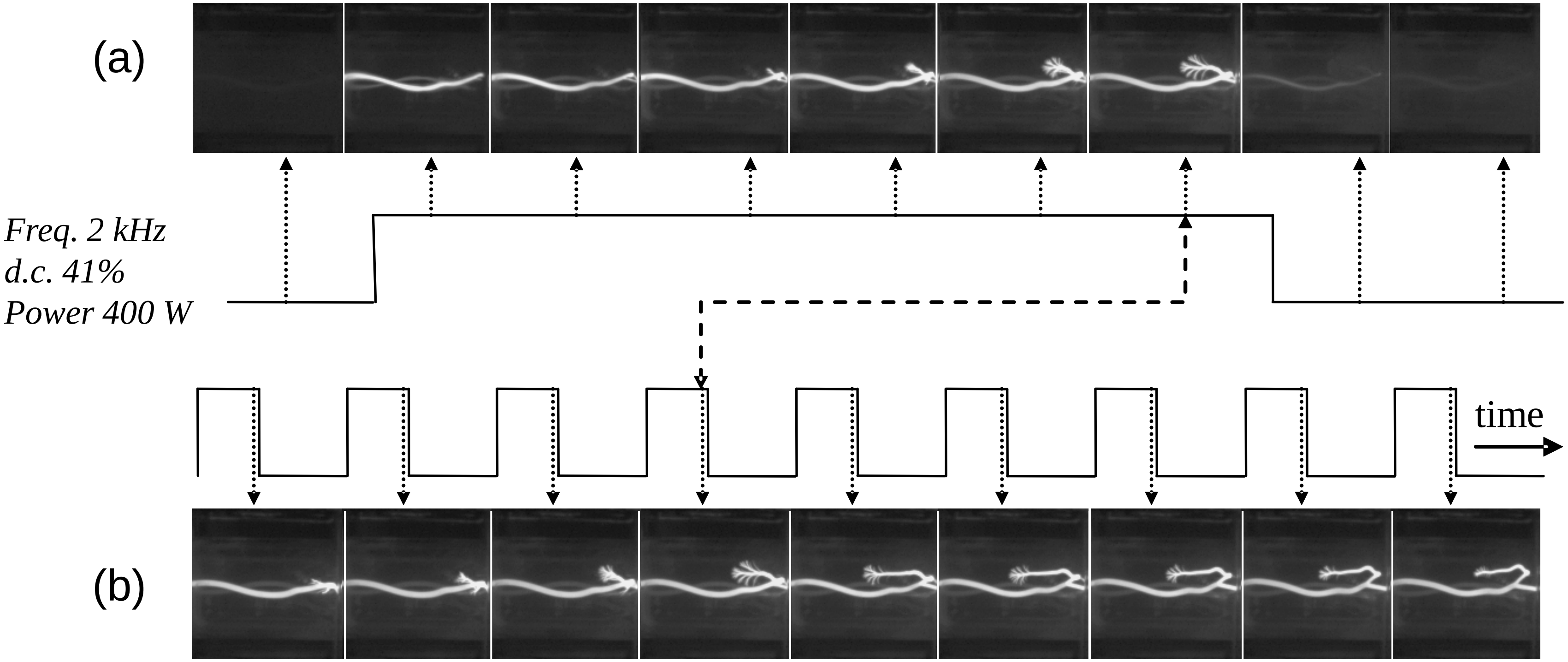


Photographic sequence of continuous argon atmospheric pressure discharges for different input powers. Exposure time is 10µs.

- The number of filaments is approximately a linear function of power

The resonant cavity plasma

Memory effect in an Ar pulsed plasma



Freq. 2 kHz
d.c. 41%
Power 400 W

Photographic sequences showing: (a) the filament evolution during a plasma pulse and (b) the last photo before cutting the argon atmospheric pressure discharges in a sequence of pulses. The interval between two photos is 31µs and the exposure time is 10µs.

- We can see that different pulses are not completely independent
- The memory effect is associated to hot gas channel formed during the on pulse

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Applications of atmospheric pressure plasmas

Some applications for surface treatment

- Adhesion enhancement
- Surface cleaning
- Wettability control
- Coating
- Etching

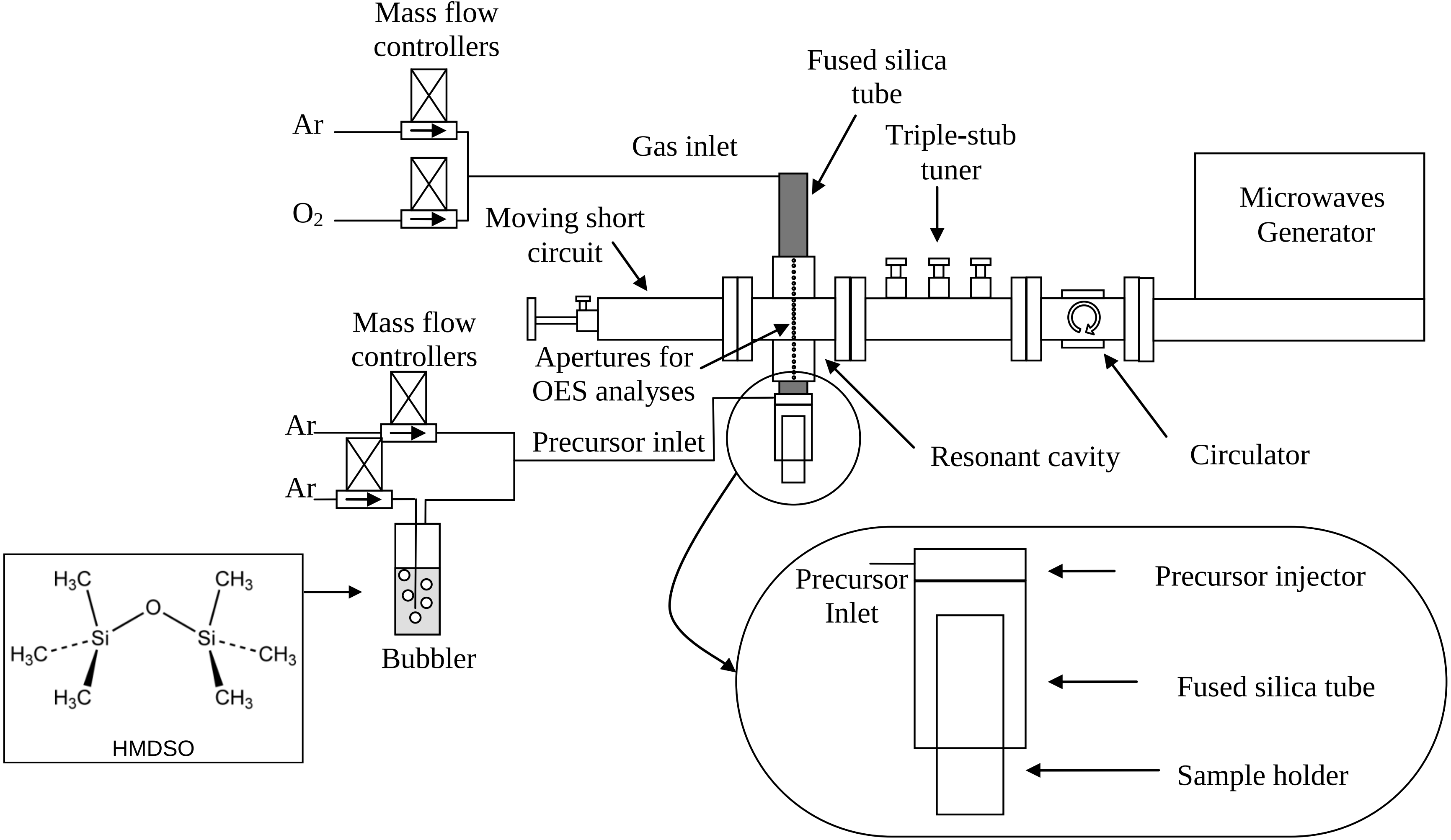
Other possible applications

- Exhaust gas treatment
- Powder production
- Powder treatment
- Sterilization

In the literature, a very few applications of AP-MW plasmas are found in surface science

The most important one, by far, is PECVD
(applying remote plasma – problem of powder formation)

Thin film processing (SiO_x deposition)

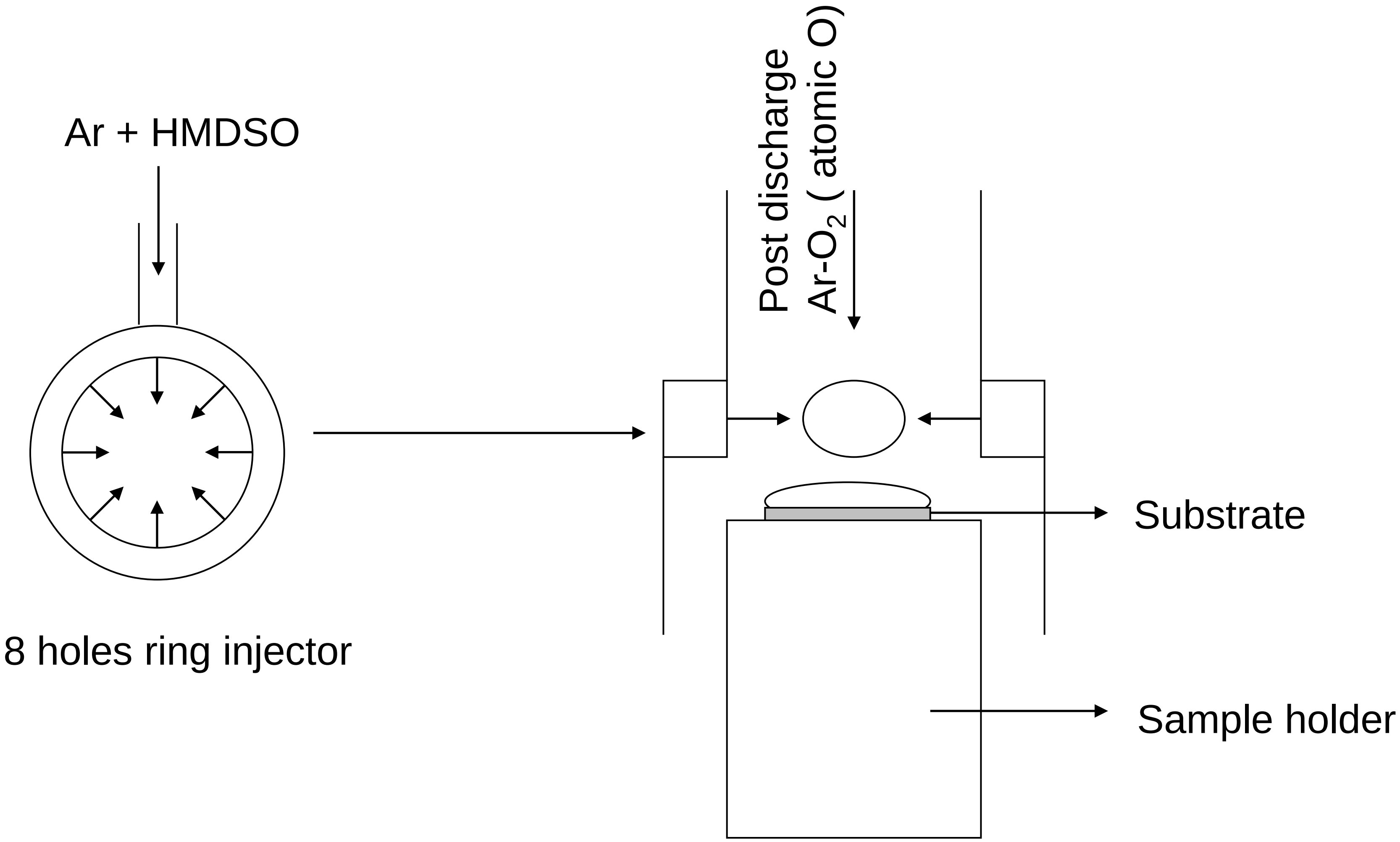


✓ Gas mixture is Ar-O_2 (for economical reasons)

✓ Hexamethyldisiloxane(HMDSO) mass flow is controlled by the argon flow through the bubbler

✓ The sample holder is temperature controlled

Thin film processing (SiO$_x$ deposition)



Ar + HMDSO

Post discharge

Ar-O_2 (atomic O)

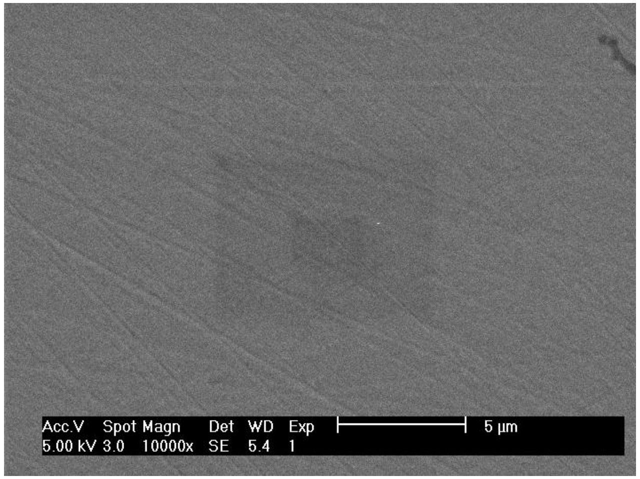
Substrate

Sample holder

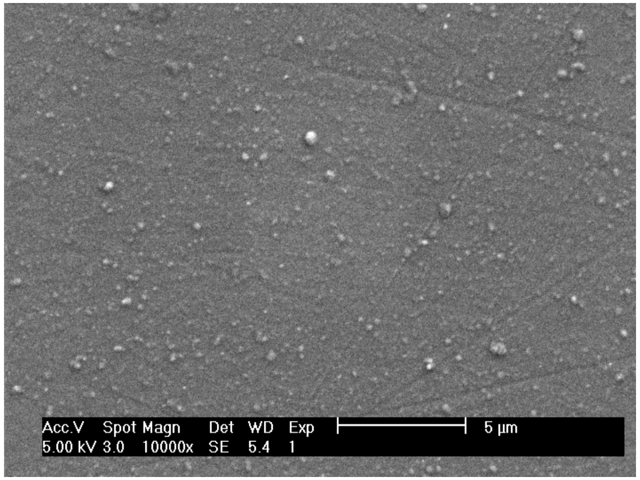
8 holes ring injector

Thin film processing (SiO$_x$ deposition)

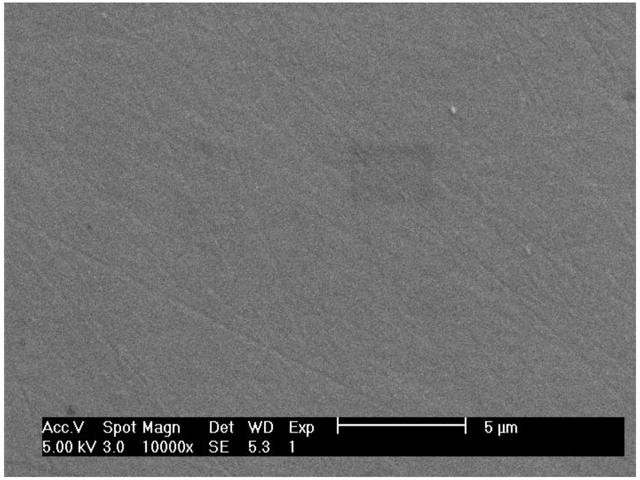
Surface topology by SEM



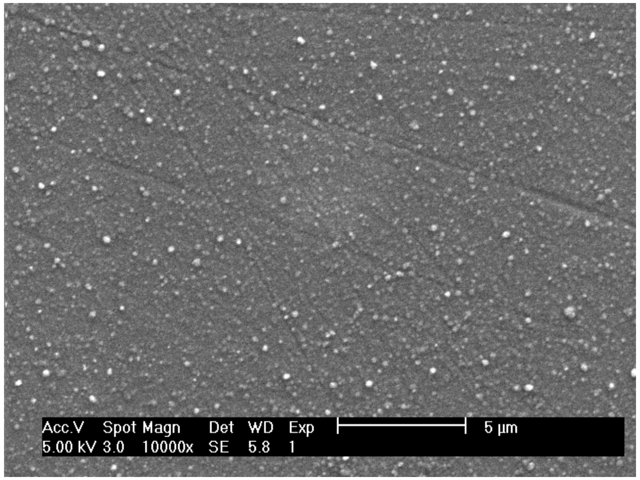
65 ppm of HMDSO



261 ppm of HMDSO



130 ppm of HMDSO

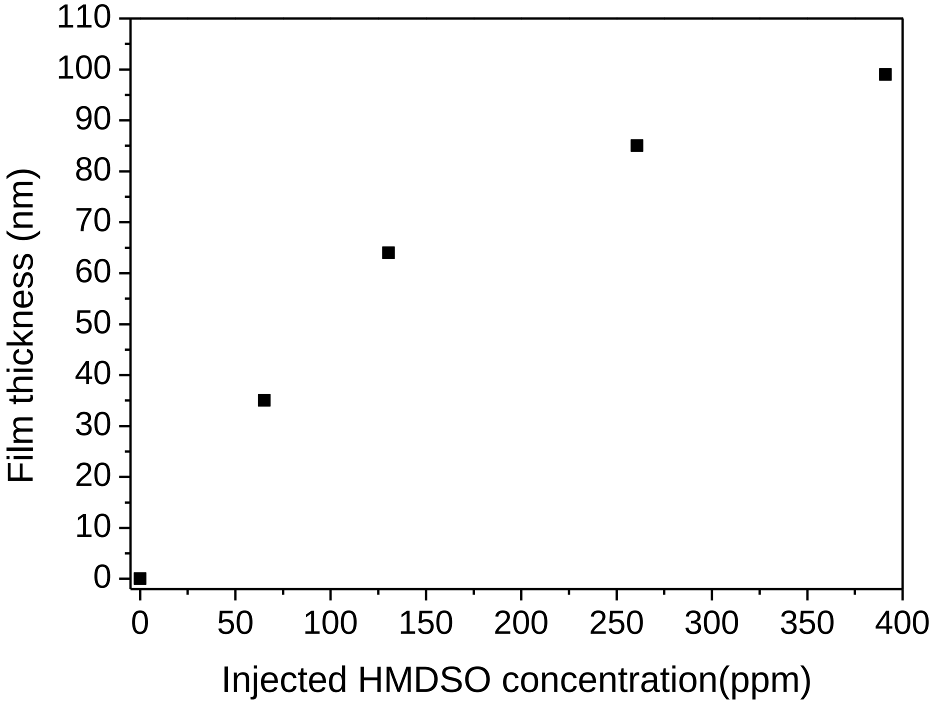


391 ppm of HMDSO

✓ For high HMDSO concentration particles are embedded in the film

Thin film processing (SiO_x deposition)

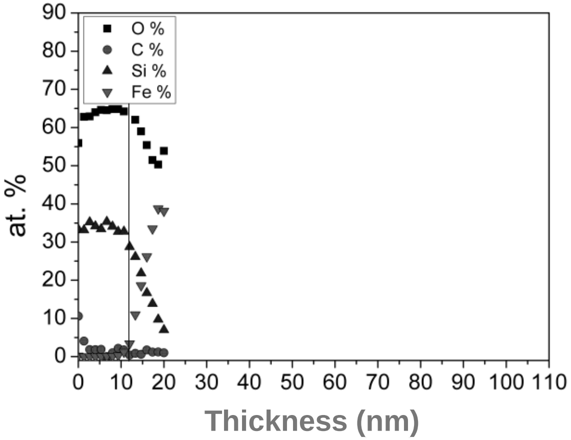
Thickness measurements by SNMS (Secondary Neutral Mass Spectrometry)



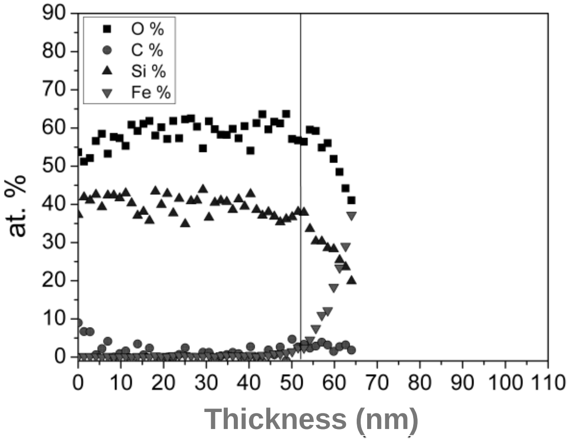
- ✓ For high HMDSO concentration the film thickness tends to saturation (due to precursor consumption by homogeneous reactions – powder formation)

Thin film processing (SiO_x deposition)

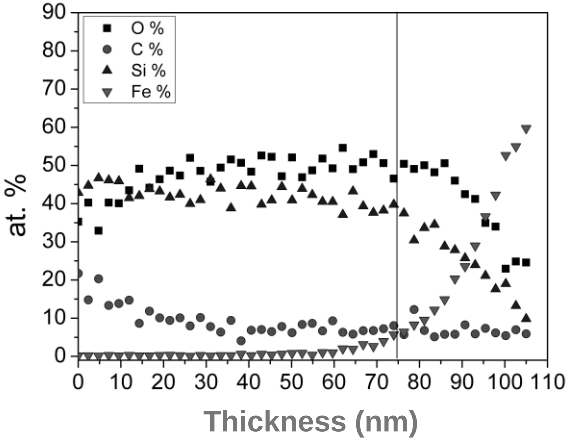
Concentration profiles measured by SNMS (Secondary Neutral Mass Spectrometry)



573 K



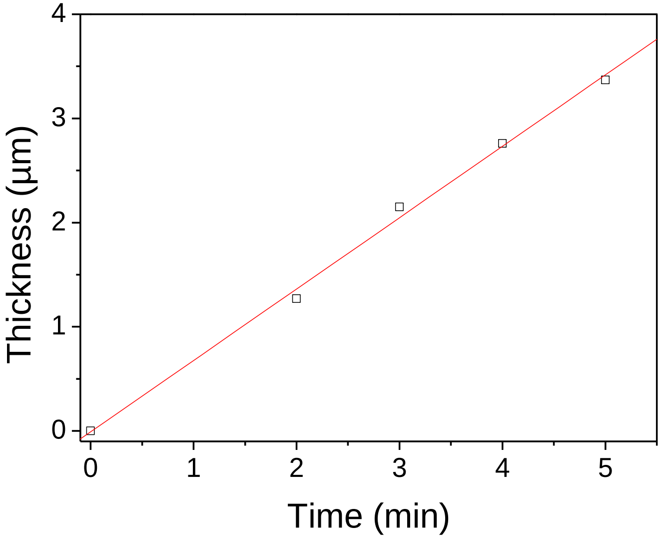
483 K

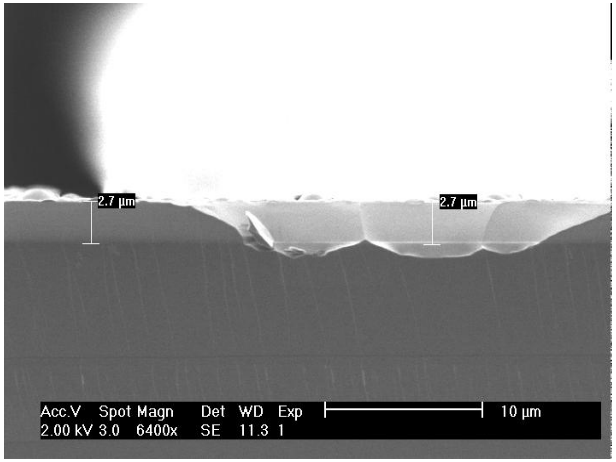


303 K

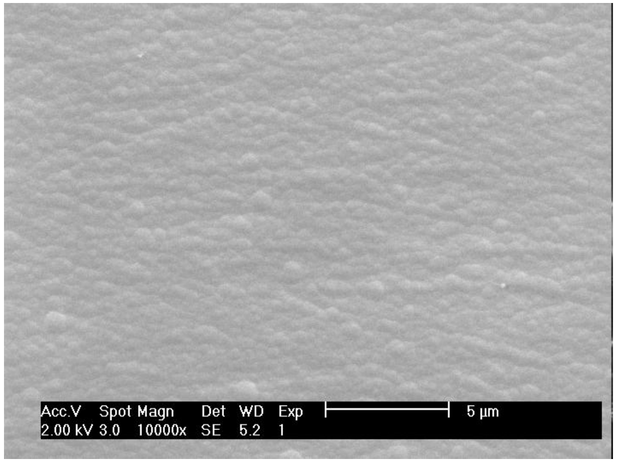
- ✓ Carbon content in the film varies from 0 to 10% depending on the sample temperature
- ✓ The film thickness diminishes for high temperature (thermal diffusion (Soret effect) and/or adsorption/desorption)
- ✓ Deposition rate varies from 1 to 10 nm/min

Thin film processing (SiO$_x$ deposition)





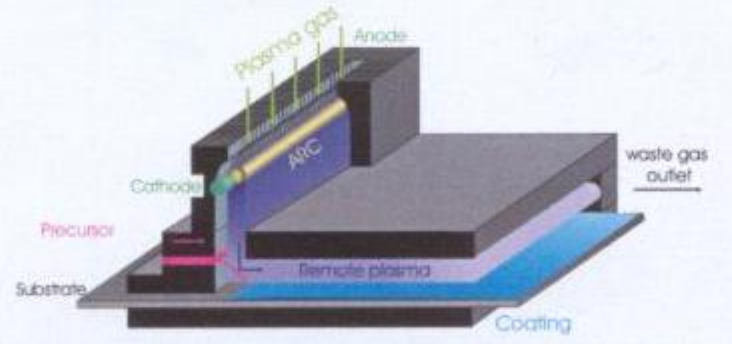
Dense film



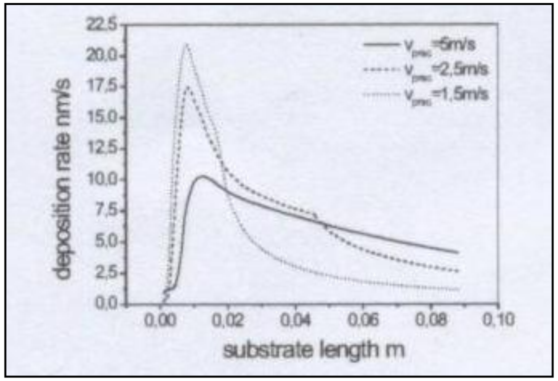
Relatively smooth topography

Maximum deposition rate of 1 µm/min (Patent pending)

Linear extended DC arc plasma source

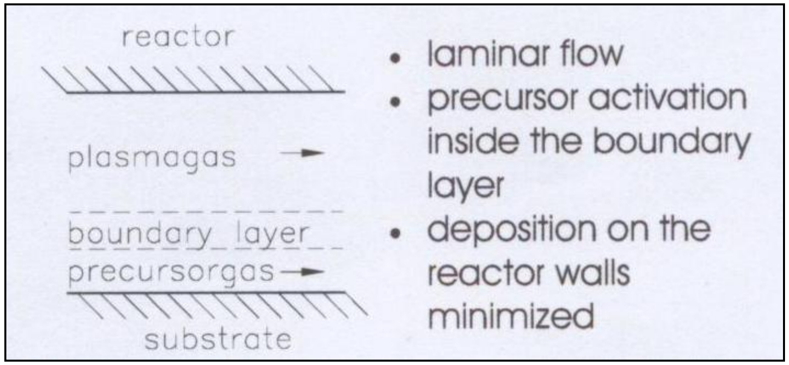


G. Mäder et al., PSE (2006) Garmisch Partenkirchen



Maximum deposition rate ~ 1.6 µm/min

Main problem
Avoid the synthesis of powders!



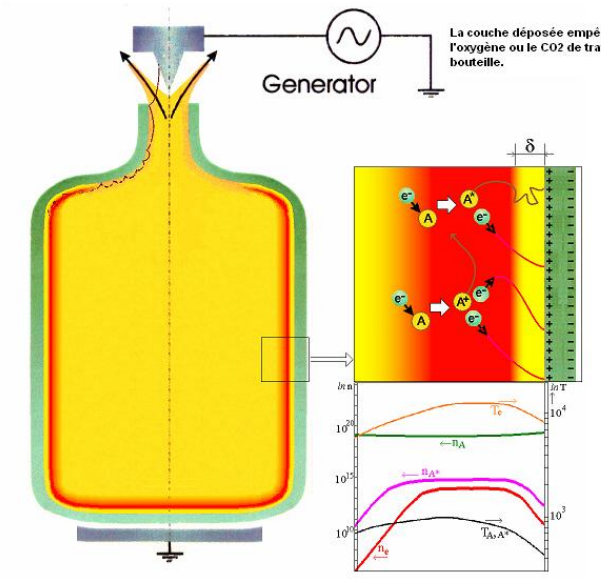
- laminar flow
- precursor activation inside the boundary layer
- deposition on the reactor walls minimized

According to the author the origin of the high deposition rate is the fluid flow structure

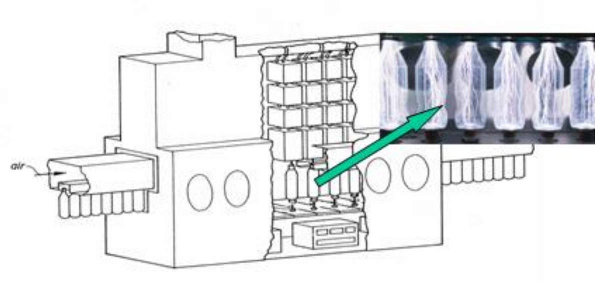
Other applications for film deposition

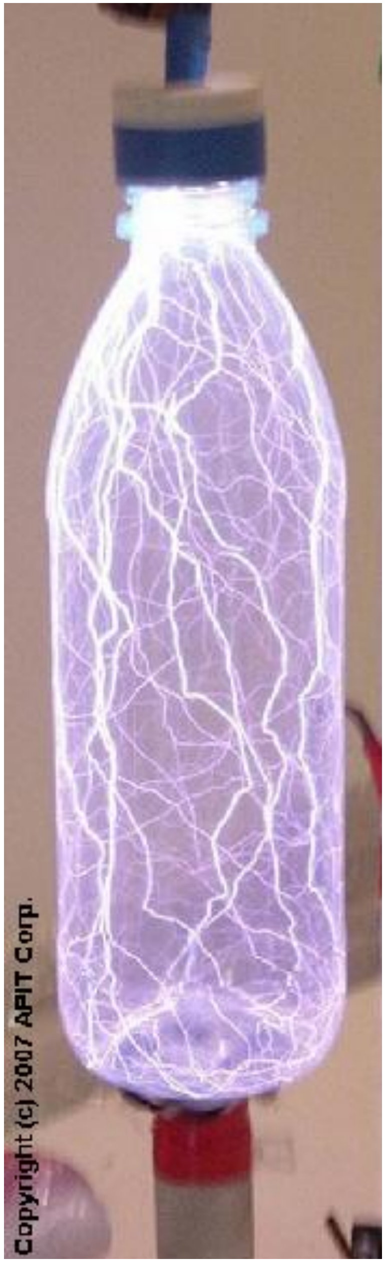
APITcorp

Objective: reduce gas linkage by deposition of a diffusion barrier
Film homogeneity is not an important parameter so it is possible to apply filamentary discharges



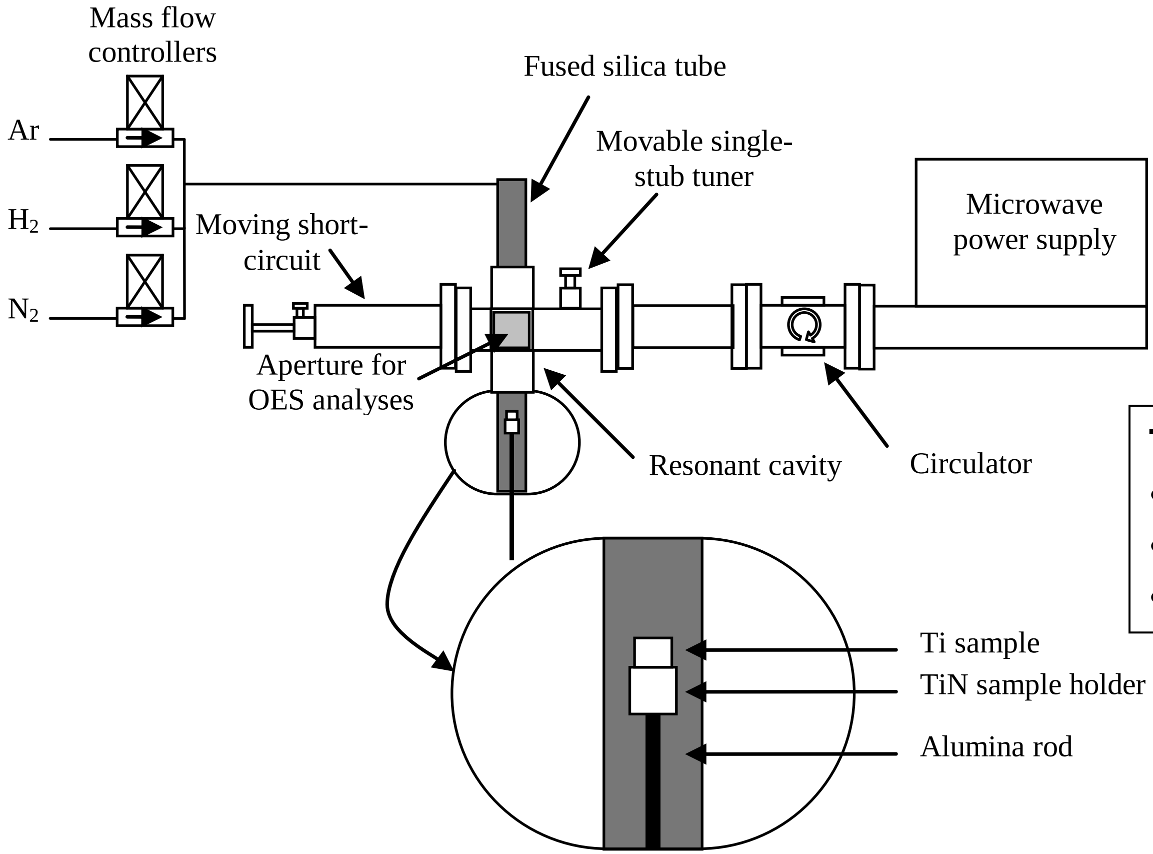
La couche déposée empêche les gaz tels que l'oxygène ou le CO2 de traverser l'enveloppe de la bouteille.





www.apitcorp.com

High temperature Ti Nitriding



Typical treatment parameters:

- Microwave power: 500 W
- Treatment time: 1h
- Gas mixture: Ar–N_2–H_2

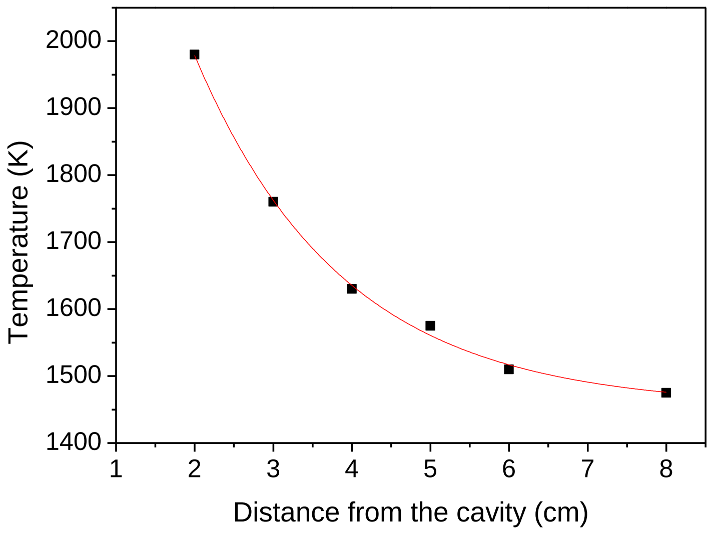
- Treatments are carried out in the near post-discharge
- Treatment temperature is set by fixing the distance from the cavity to the sample

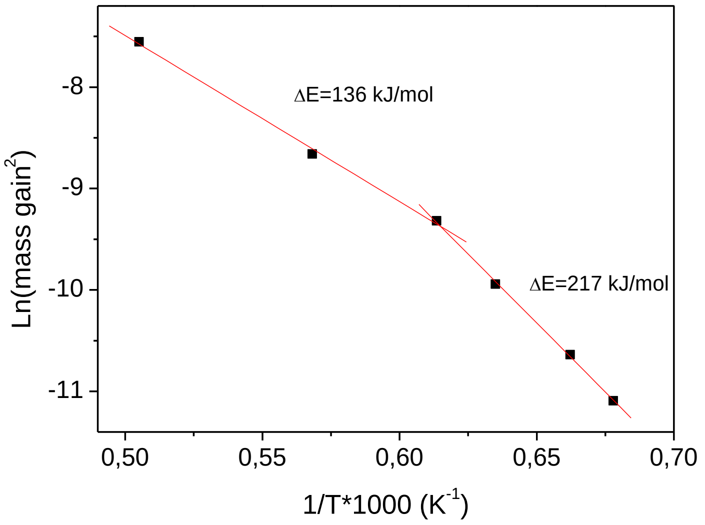
Samples:

- Commercial–grade titanium (99.6 wt.%)
- Cylindrical shape (height: 4.5 mm, diameter: 6 mm)

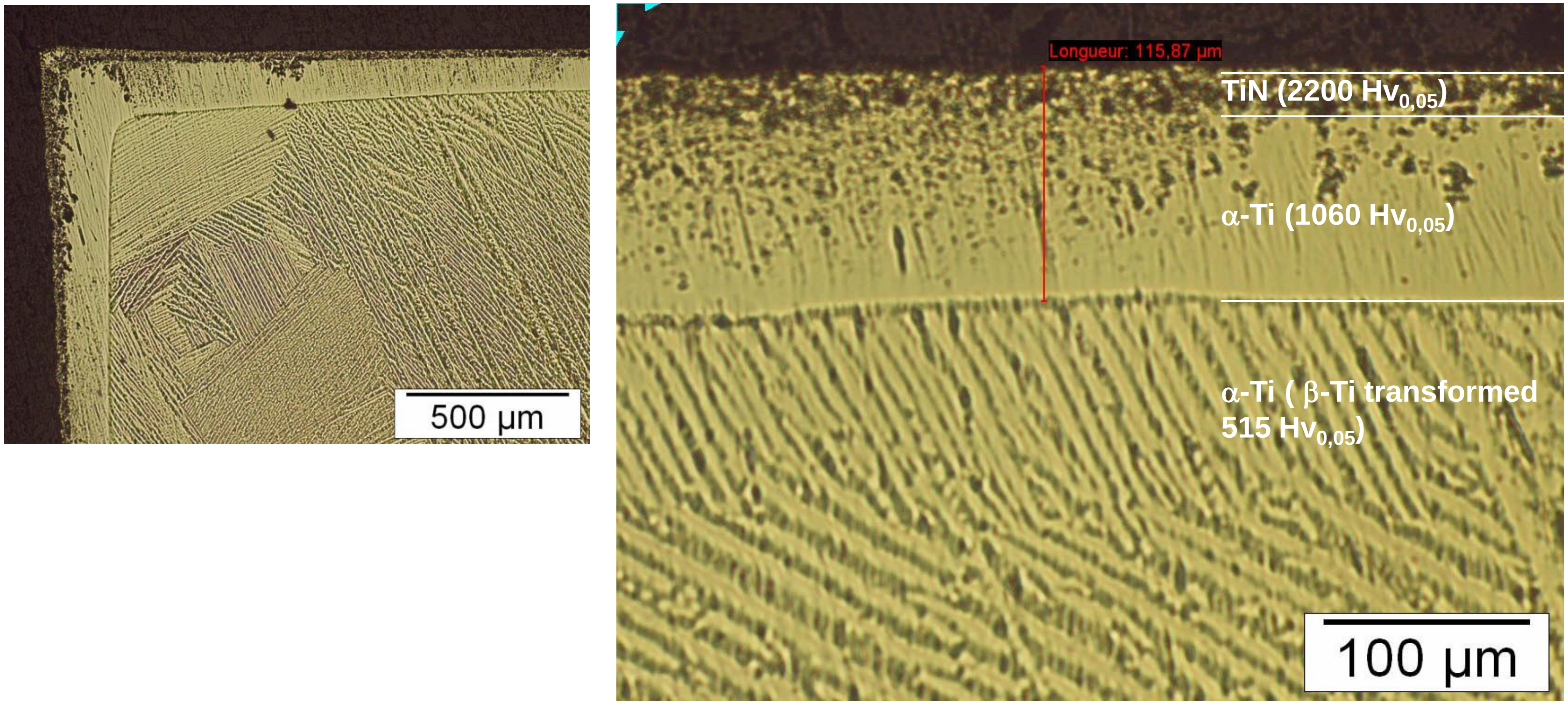
Sample temperature measurement by multi-wavelengths visible pyrometry

Arrhenius plot (Treatment kinetics)





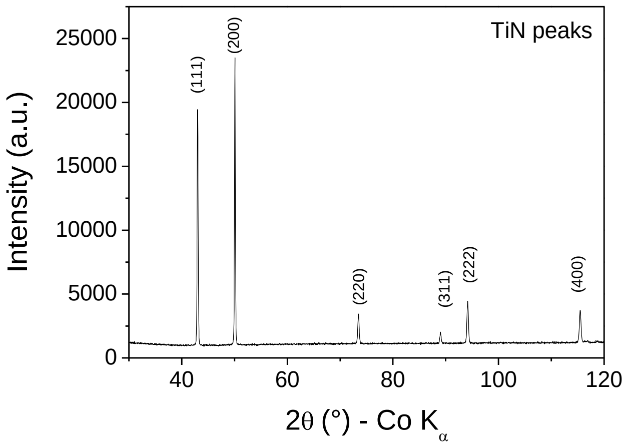
- ✓ Temperatures between 1450 and 2000 K can be reached for 500 W
- ✓ The treatment kinetics is limited by the diffusion of nitrogen through the TiN layer (ΔE = 217 kJ/mol agrees with N diffusion in TiN)
- ✓ ΔE = 136 kJ/mol slope is not related to the diffusion. In fact over a given temperature the sample cannot be considered as semi-infinite

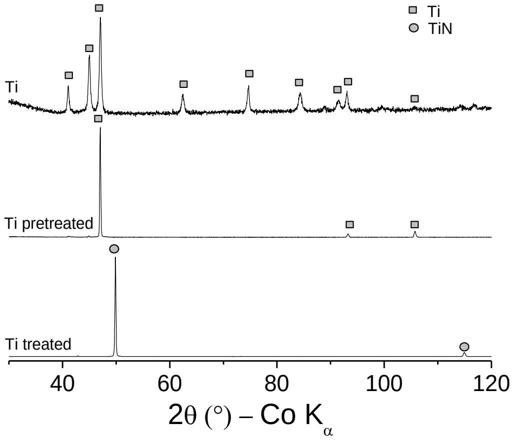


Microstructure of a treated sample. Gas mixture: 86.3%Ar – 13.3%N2 – 20.4%H2, total flow 7.53 slm, power 500W, distance from the cavity 3 cm (1750K)

- ✓ Three layers can be observed
- ✓ Microstructure is the same for all treated samples

X-ray diffraction patterns (effect of pretreatment)





- ✓ Sample surface is TiN
- ✓ TiN layer micro-structure is strongly related to the structure of the untreated sample
- ✓ After pretreatment (1h at 1550 K in Ar-H_2) we cam produce strong oriented TiN layers

Outlook

- Introduction
- Some examples of atmospheric pressure plasmas
- The resonant cavity system
- Physics of microwave plasmas
- Applications of atmospheric plasmas for materials treatment
- **Conclusion**

Conclusion

- We can now describe (at least partially) the physics of the microwave atmospheric pressure plasmas.

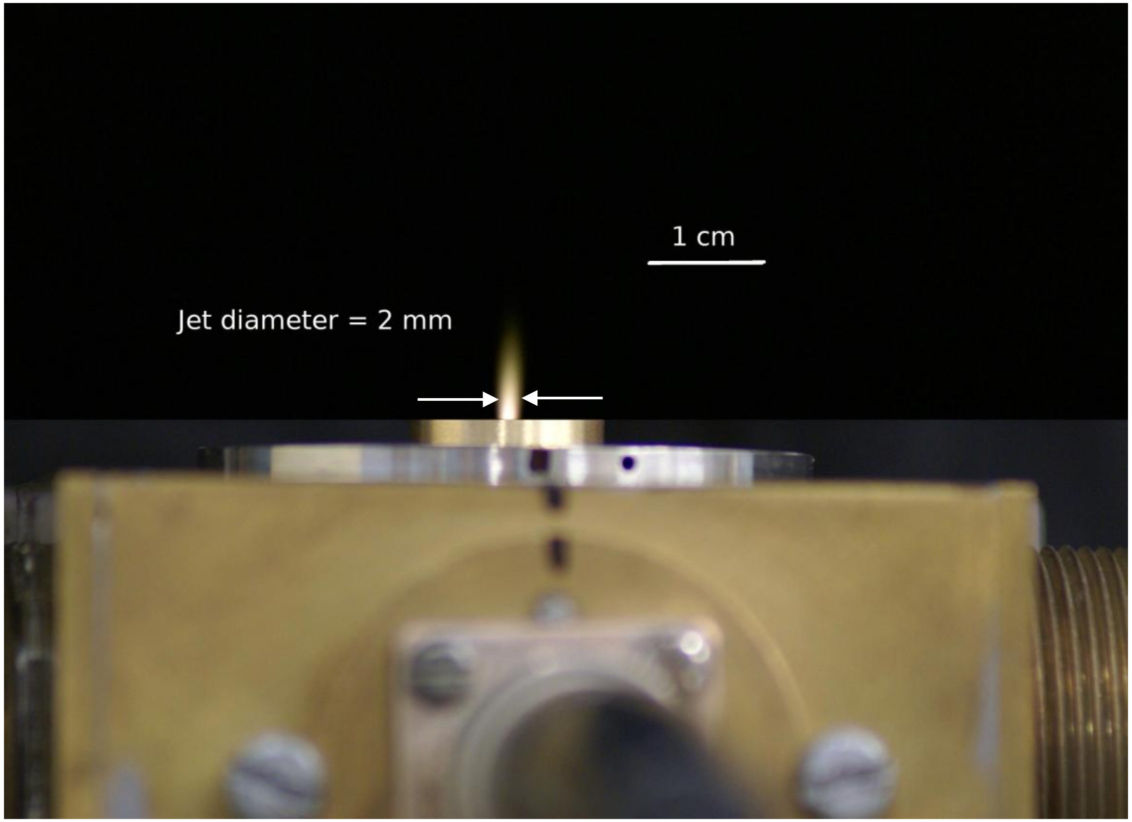
- Nevertheless, there is a lot to do in the field of plasma modeling and characterization to get a clear understanding of the main phenomena involved in the atmospheric pressure plasmas

- Concerning the applications of this discharges, despite the growing number of works in this domain, many possibilities are yet unexplored

- In the case of microwave plasmas, multiplication of sources is a mandatory way for homogeneous surface treatments, especially for large surfaces

- On the other hand, some applications can demand small discharges.

Mini-torch (new application studied in our department)



Perspectives

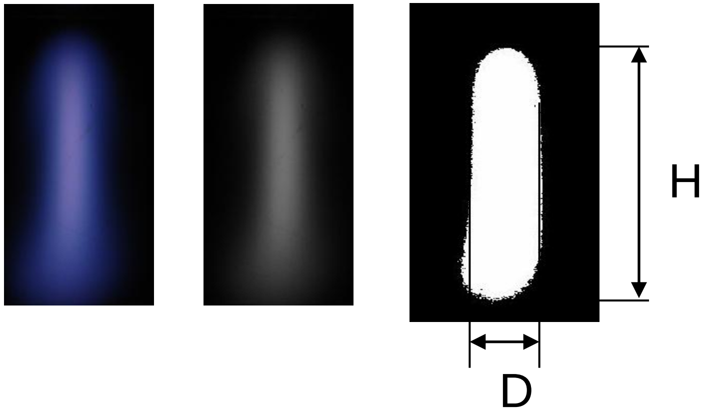
Application for cleaning and PECVD

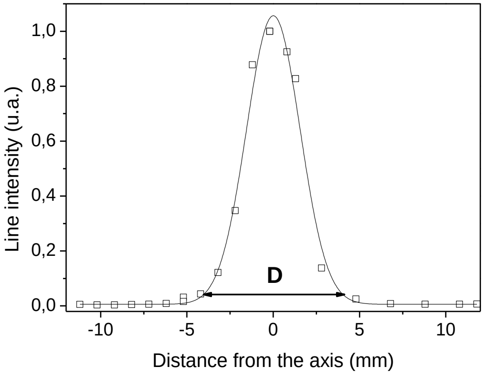
Thank you for your attention !

Plasma dimensions (contraction)

- ✓ The plasma volume is a very important parameter for plasma diagnostics like emission and absorption spectroscopy and for electromagnetic modeling
- ✓ Problem:
  - ✓Plasma limits are not easily defined
  - ✓We defined the plasma dimensions with respect to the plasma emission

Image analysis





- ✓ The image is converted in gray scale and binarized
- ✓ Thresholding is based on the radial emission profile of He(3^3D-2^3P-587.6 nm) spectral line

Plasma dimensions (contraction)

Origin of contraction: compression of the plasma into a filament located at the discharge axis. Two possible explanations relying on the ionization coefficient (α)

✓ e-e collisions

When $n_e \sim 10^{14}$ cm^{-3}, maxwellization of the eedf
n_e ↘ when r ↗ → change in the eedf (depletion of fast electrons)
As a result α decreases

G M Petrov and C M Ferreira PRE 59 (1999) 3571
Yu B Golubovskii, H Lange, V A Maiorov, I A Porokhova and V P Sushkov J. Phys. D: Appl. Phys. 36 (2003) 694

✓ Radial non-uniform gas heating

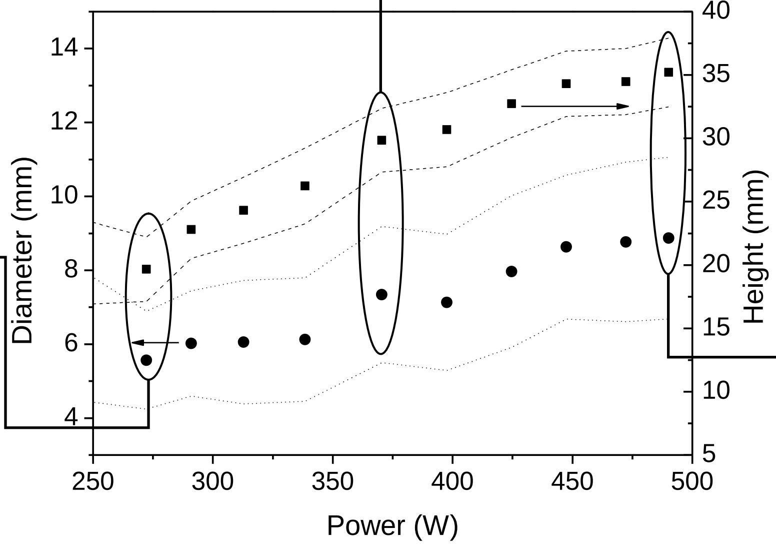
Non-uniform gas heating → *E/N* ↗ in the centre of the discharge
consequently α increases

Y Kabouzi D B Graves E Castaños-Martínez and M Moisan PRE 75 (2007) 016402

In case of helium, the second explanation is more reliable since the electron density is lower than10^{14} cm^{-3}

Plasma dimensions

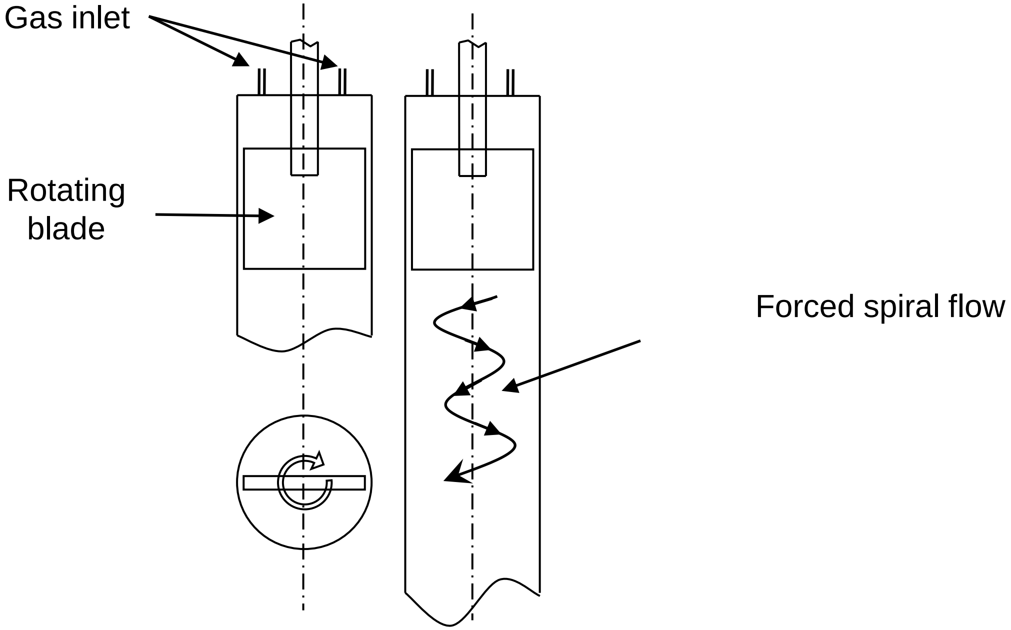
Variation of plasma dimensions as a function of power



- ✓ The plasma volume grows with power, it acts simultaneously on the plasma diameter and height
- ✓ The plasma height and diameter vary by a factor of 2 and 4 respectively

Gas injection system

The fluid dynamics is a very important feature for the discharge stability



- The blade speed will control the Reynolds’ number of the fluid flow
- The spiral flow helps to stabilize and center the discharge
- The usual injection system requires high fluid flow to obtain a spiral flow, in our system the spiral flow and the axial flow can be controlled independently

Thin film processing

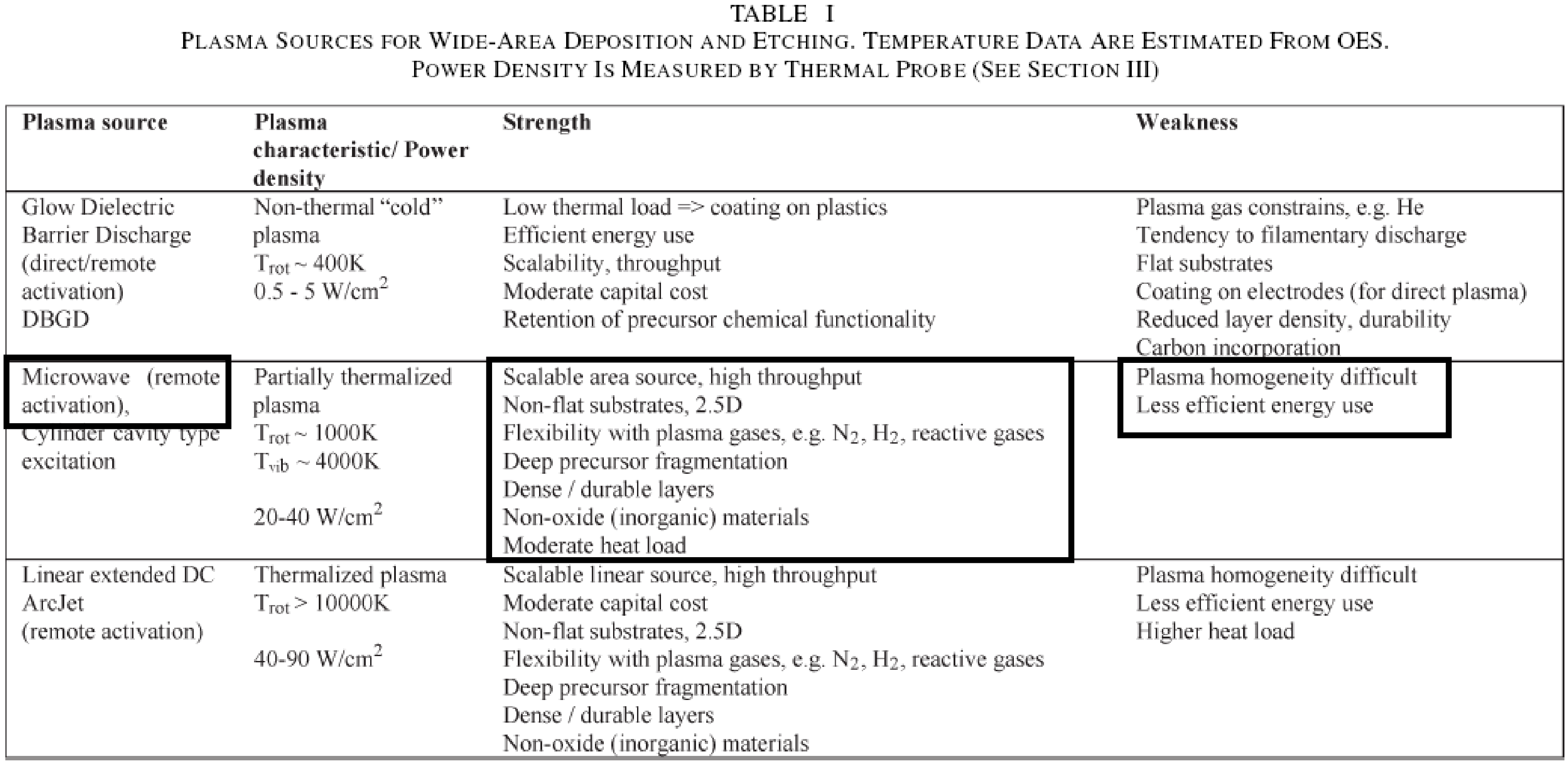


TABLE I

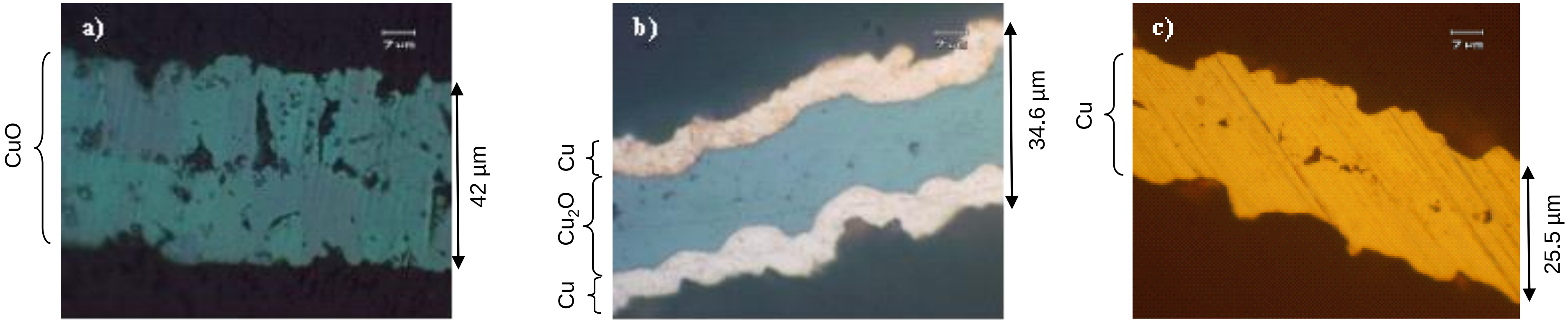
PLASMA SOURCES FOR WIDE-AREA DEPOSITION AND ETCHING. TEMPERATURE DATA ARE ESTIMATED FROM OES. POWER DENSITY IS MEASURED BY THERMAL PROBE (SEE SECTION III)

Plasma source	**Plasma characteristic/ Power density**	**Strength**	**Weakness**
Glow Dielectric Barrier Discharge (direct/remote activation) DBGD	Non-thermal “cold” plasma T_{rot} ~ 400K 0.5 - 5 W/cm^2	Low thermal load => coating on plastics Efficient energy use Scalability, throughput Moderate capital cost Retention of precursor chemical functionality	Plasma gas constrains, e.g. He Tendency to filamentary discharge Flat substrates Coating on electrodes (for direct plasma) Reduced layer density, durability Carbon incorporation
Microwave (remote activation), Cylinder cavity type excitation	Partially thermalized plasma T_{rot} ~ 1000K T_{vib} ~ 4000K 20-40 W/cm^2	Scalable area source, high throughput Non-flat substrates, 2.5D Flexibility with plasma gases, e.g. N_2, H_2, reactive gases Deep precursor fragmentation Dense / durable layers Non-oxide (inorganic) materials Moderate heat load	Plasma homogeneity difficult Less efficient energy use
Linear extended DC ArcJet (remote activation)	Thermalized plasma T_{rot} > 10000K 40-90 W/cm^2	Scalable linear source, high throughput Moderate capital cost Non-flat substrates, 2.5D Flexibility with plasma gases, e.g. N_2, H_2, reactive gases Deep precursor fragmentation Dense / durable layers Non-oxide (inorganic) materials	Plasma homogeneity difficult Less efficient energy use Higher heat load

V. Hopfe et al., IEEE Trans. Plasma Sci., 35 (2007) 204

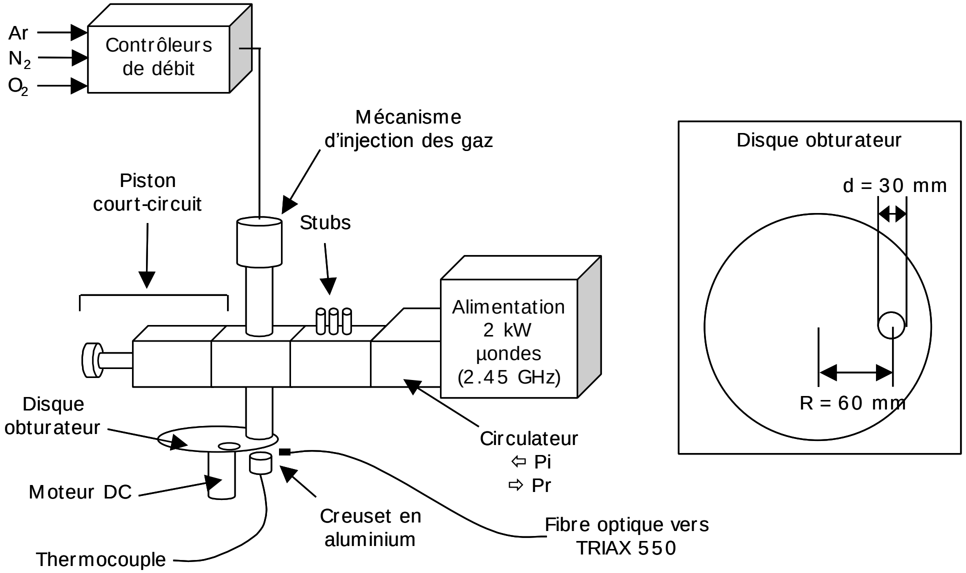
Oxide Reduction

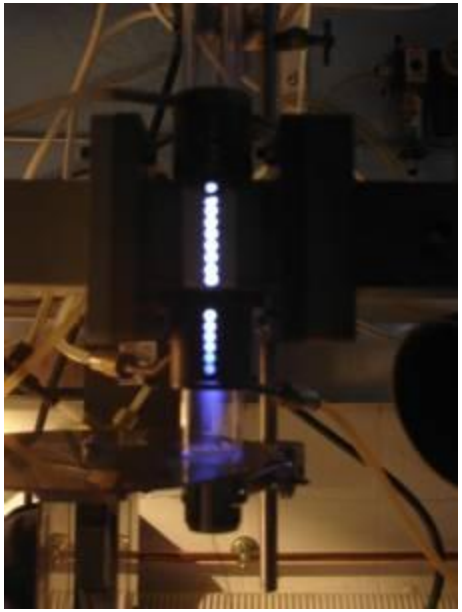
Reduction of oxides. Example of copper (helium hydrogen discharge)



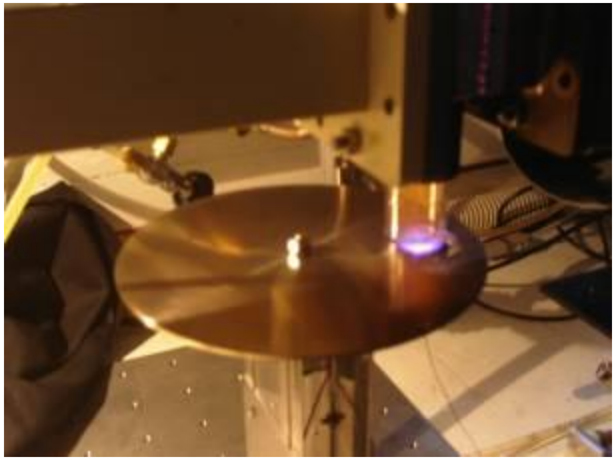
Optical micrographs
a) CuO foil obtained after Cu air oxidation at 900°C
b) CuO foil treated at 345°C during 4 min
c) CuO foil treated at 345°C during 10 min – Cu layer has been completely recovered.

Surface cleaning





Remote Ar/O_2 plasma treatment

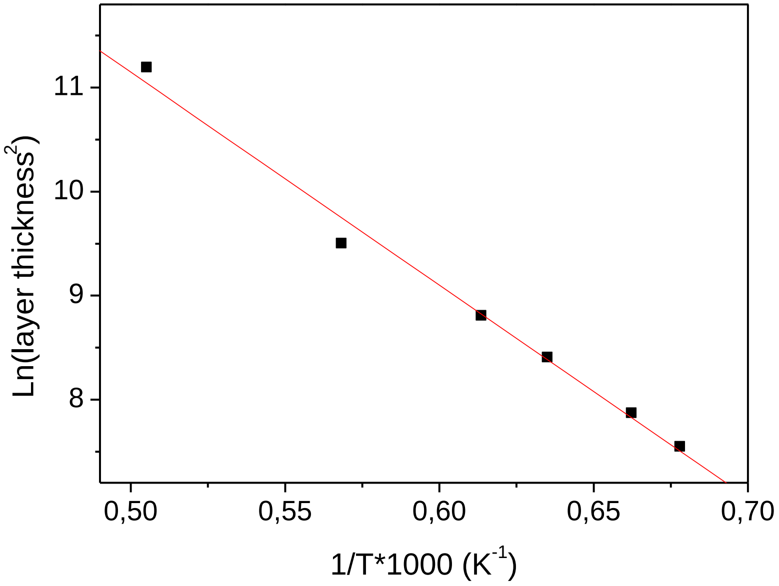


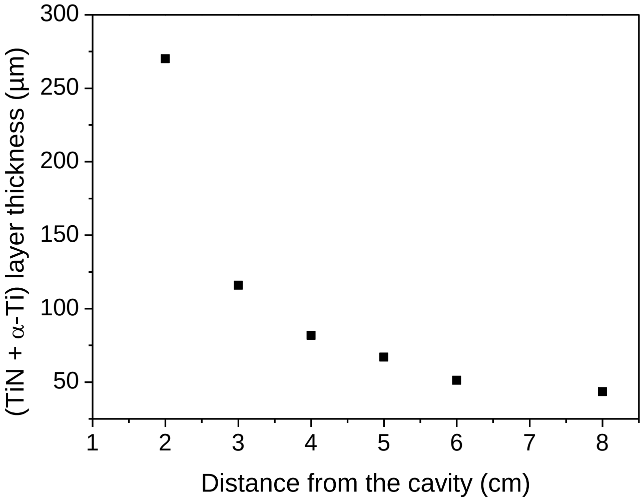
Remote Ar/N_2 plasma treatment

Discharge parameters :

  - P = 500 W
  - Ar flow = 10 slm
  - N_2 or O_2 flow = 1 slm
- Static treatment is not possible (High temperature)

Arrhenius plot (Treatment kinetics)





- **ΔE = 170 KJ/mol (N diffusion in α-Ti)**