# Pulsed ICP plasmas processing : 0D Model vs. Experiments

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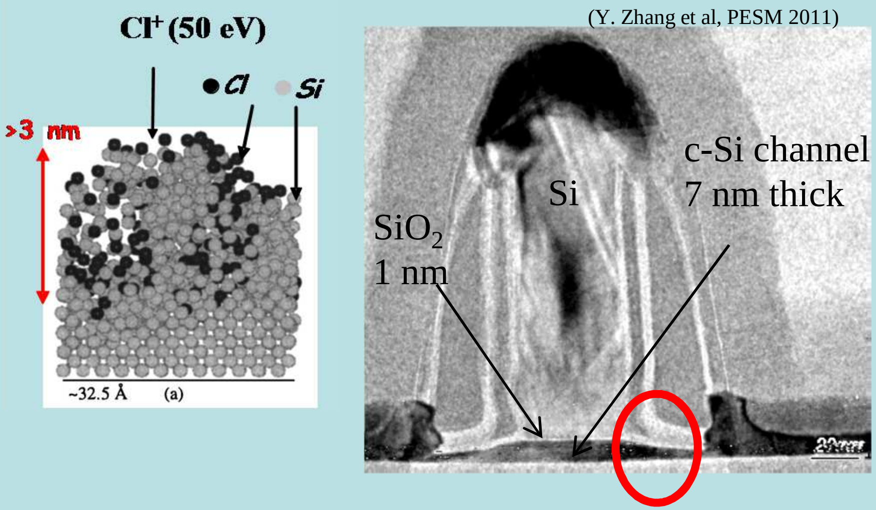
# Limitations of classical CW plasmas

Miniaturization of IC circuits : how to **etch complicated stacks of ultrathin films** without damaging the active layers of nanoelectronic devices ?

## Ion/Plasma Induced Damage

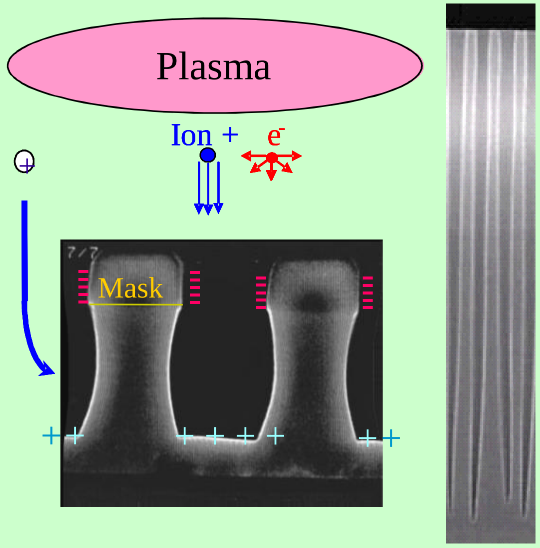


(Y. Zhang et al, PESM 2011)

**Ion energy > 15 eV + high dissociation rates**

⇒ Issue to etch stacks of ultrathin layer

## Charging effects



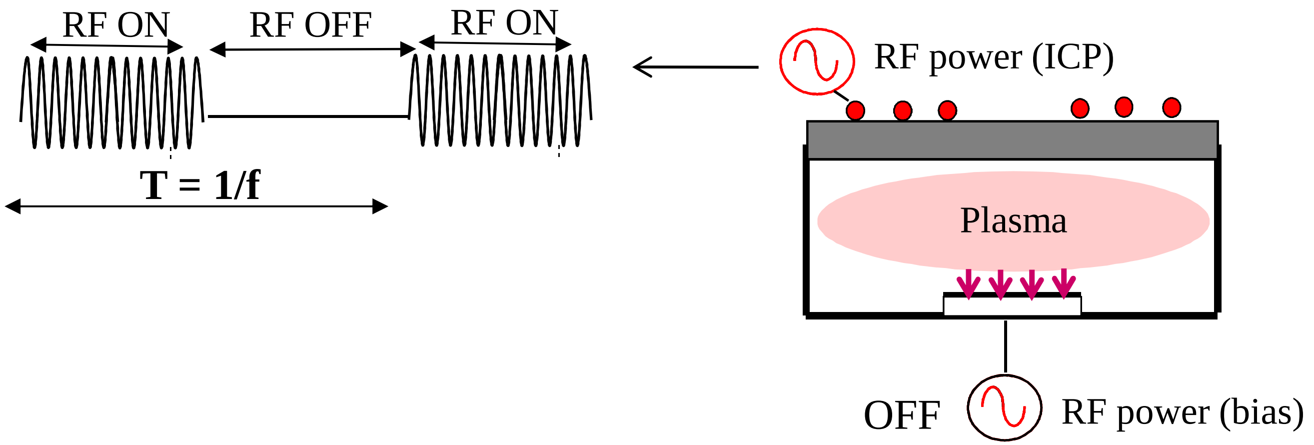
⇒ Profile control issue

⇒ classical **CW plasmas cannot address** etching challenges of advanced nanodevices

⇒ need **more control knobs** to tune the plasma chemistry, ion flux and ion energy

# Pulsed plasmas : What would we like to know about them ?

RF power t-modulated periodically ⇒ impact on **plasma characteristics** (IEDF & chemical composition)



- 2 new knobs to tune an etching process : **Pulsing frequency f** and **duty cycle DC**

⊕ selectivity, ⊖ PID in ultrathin Si layers*, ⊕ pattern transfer ( ⊖ charging)

<u>but reasons for these improvements remain somehow unclear</u>

- Impact of these new knobs on … ? **Dissociation rate** and **radical fluxes**
  **Ion fluxes**
  Ion energy

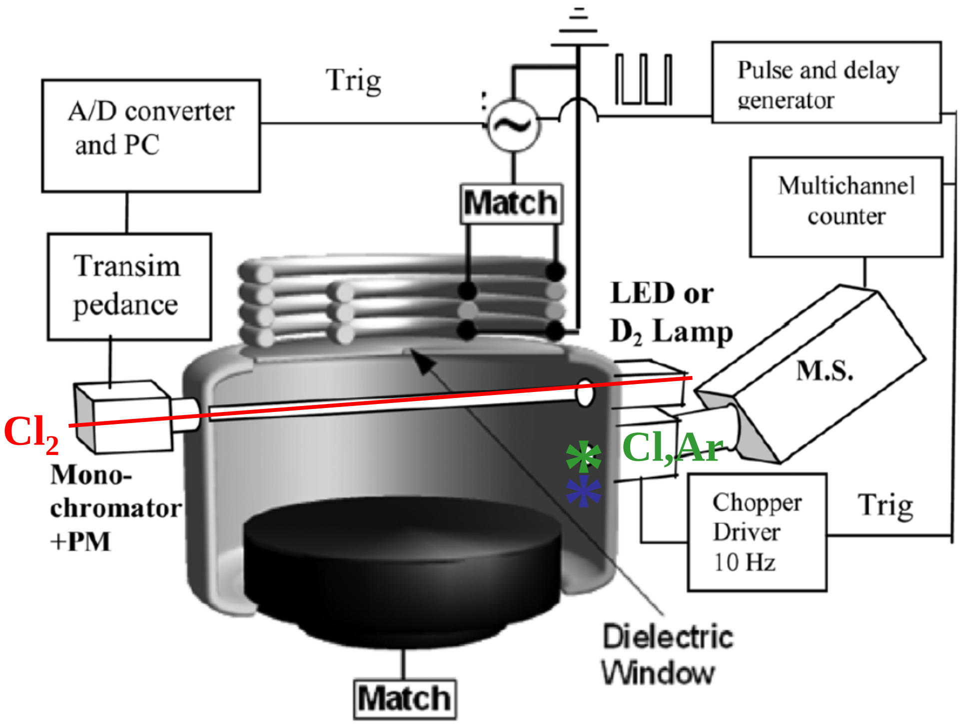
**⇒ experiments/time-resolved diagnostics + 0D model (need for benchmark)**

****Petit Etienne et al, JVSTB 28, 926 (2010)***

# Experimental setup and t-resolved diagnostics

All experiments carried out in a **DPS ICP reactor from AMAT (300 mm wafer)** modified to host plasma and surface diagnostics

***<u>Pulsed RF generators ; 1-20 kHz ; 5-50mT ; 500-1500W</u>***



- **$Cl_2$ density** by BroadBand Absorption Spectrocopy (BBAS)
- **Cl or Ar density** by modulated beam Mass Spectrometry (MBMS)
- **Ion fluxes** with a capacitive planar probe

*Bodart, Brihoum, Cunge et al., JAP 110, 113302 (2011)*

*Brihoum, Cunge, Darnon et al., JVST A 31, 020604 (2013)*

# Global model of the $Cl_2$/Ar pulsed discharge

- discharge = cylinder of radius **R = 0.25m** and length **L = 0.17m**
- ⊕ / ⊖ ions fill all the volume except the sheaths
- All densities taken to be uniform within the bulk plasma (0D)
- e- & negative ions in **Boltzmann equilibrium** at temperatures **Te** and **Ti**
- **t-varying quantities**

$$\boxed{n_e \,/\, n_{Ar} \,/\, n_{Ar+} \,/\, n_{Cl2} \,/\, n_{Cl} \,/\, n_{Cl+} \,/\, n_{Cl2+} \,/\, n_{Cl-} \,/\, Te}$$

⇒ set of **coupled non-linear** equations **- 1 power balance and 7 particle balance equations (+ quasineutrality) -** solved simultaneously with MATLAB

*Despiau-Pujo and Chabert, PSST 18, 045028 (2009)*

# Global model : Equations

**Particle balance equations for each species X in the plasma (+ quasineutrality)**

rate coefficient in $m^3s^{-1}$

$$\frac{dn^X}{dt} = \sum_k R^X_{\text{Creation},k} - \sum_k R^X_{\text{Loss},k} \quad \text{with} \quad R = K \times \prod_k n_{r,k}$$

reaction rate for e/n or n/n bulk collisions, neutral recombination, ion neutralization at walls...

**What about the loss rate for positive ions, electrons and negative ions at walls ?**

$$\left.\begin{aligned}
\Gamma_+ &= \frac{h_L A_L + h_R A_R}{A_L + A_R}\left(\sum n_{i+} u_{B,i+}\right) \text{ with } u_{B,i+} = \left(\frac{eT_e}{m_{i+}}\right)^{1/2} \\
\Gamma_e &= \frac{1}{4}\left(\frac{8eT_e}{\pi m_e}\right)^{1/2} \underbrace{\frac{h_L A_L + h_R A_R}{A_L + A_R}\,\frac{1}{1+\alpha_s}\left(\sum n_{i+}\right)}_{n_{se}} \exp\left(\frac{\Phi}{T_e}\right) \\
\Gamma_- &= \frac{1}{4}\left(\frac{8eT_i}{\pi m_{Cl-}}\right)^{1/2} \underbrace{\frac{h_L A_L + h_R A_R}{A_L + A_R}\,\frac{\alpha_s}{1+\alpha_s}\left(\sum n_{i+}\right)}_{n_{s-}} \exp\left(\frac{\Phi}{T-}\right)
\end{aligned}\right\}$$

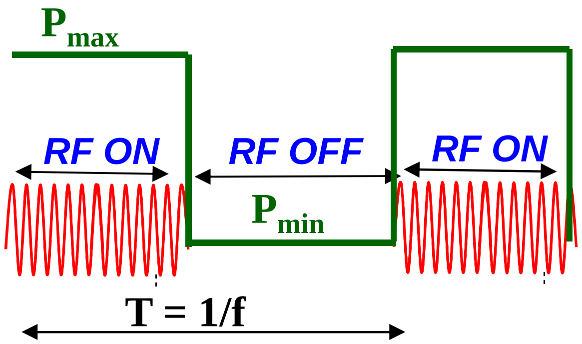
**Sheath voltage Φ** obtained at each t from

$$\Gamma_+ = \Gamma_e + \Gamma_-$$

# Global model : Equations

**Power balance equation for the electron temperature Te :**

$$V\frac{d}{dt}\left(\frac{3}{2}en_eT_e\right) = P_{abs} - P_{loss}$$



with $P_{abs}(t) = \begin{cases} P_{max} & 0 \le t \le DC/f \\ P_{min} & DC/f \le t \le 1/f \end{cases}$

and $P_{loss} = eVn_e\sum_X n^{(X)}\varepsilon_C^{(X)}k_{iz}^{(X)} + A\left\{e\left(\Phi_s + \frac{T_e}{2}\right)\Gamma_+ + 2eT_e\Gamma_e + 2eT_i\Gamma_-\right\}$

collisional energy loss per e/i pair created (ionization, excitation, elastic scattering...) for Ar, Cl, $Cl_2$

kinetic energy loss to the walls for positive ions, electrons and negative ions

# Global model : Chemistry and Reactions rates

| Reaction |
|---|
| (R1) $e + Cl_2 \rightarrow Cl_2^+ + 2e$ |
| (R2) $e + Cl_2 \rightarrow Cl^+ + Cl + 2e$ |
| (R3) $e + Cl \rightarrow Cl^+ + 2e$ |
| (R4) $e + Cl_2 \rightarrow Cl- + Cl$ |
| (R5) $e + Cl_2 \rightarrow 2Cl + e$ |
| (R6) $e + Cl_2 \rightarrow Cl^+ + Cl- + e$ |
| (R7) $e + Cl- \rightarrow Cl + 2e$ |
| (R8) $Cl_2^+ + Cl- \rightarrow 3Cl$ |
| (R9) $Cl^+ + Cl- \rightarrow Cl + Cl$ |
| (R10) $e + Ar \rightarrow Ar^+ + 2e$ |
| (R11) $Cl- + Ar^+ \rightarrow Cl + Ar$ |
| (R12) $Cl_2 + Ar^+ \rightarrow Cl + Cl^+ + Ar$ |
| (R13) $Cl + Ar^+ \rightarrow Cl^+ + Ar$ |
| (R14) $Cl_2 + Ar^+ \rightarrow Cl_2^+ + Ar$ |

+ excitation reactions to metastable or resonant states in energy loss channel

- **Volume reactions**

⇒ rates from cross section data (Maxwellian EEDF) and fitted to analytical forms over the range **0.01< Te <10eV**

- **Surface reactions**

- ion **neutralization** (ion flux = Bohm flux)

$$\Gamma_{i+} = \frac{h_L A_L + h_R A_R}{A_L + A_R} n_{i+} u_{B,i+} \quad \text{with} \quad u_{B,i+} = \left(\frac{eT_e}{m_{i+}}\right)^{1/2}$$

- radical **recombination** $Cl + Cl + \text{wall} \rightarrow Cl_2$

$$K_{Cl,wall} = \left[\frac{\Lambda_{Cl}^2}{D_{Cl}} + \frac{2V(2-\gamma)}{A v_{Cl} \gamma}\right]^{-1} \quad \text{with} \quad \Lambda_{Cl} = \left[\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2\right]^{-1/2}$$

diffusion coef

effective diffusion length

wall recombination coef

# Global model: Neutral gas injection/pumping and heating

- **Gas injection/pumping**

flow of species X in sccm

$$[\mathrm{Source}] \xrightarrow{R} \{\mathrm{Cl}_2, \mathrm{Ar}\} \text{ with } R = 4.48 \times 10^{17}\, Q_{\{\mathrm{Cl}_2,\mathrm{Ar}\}}/V$$

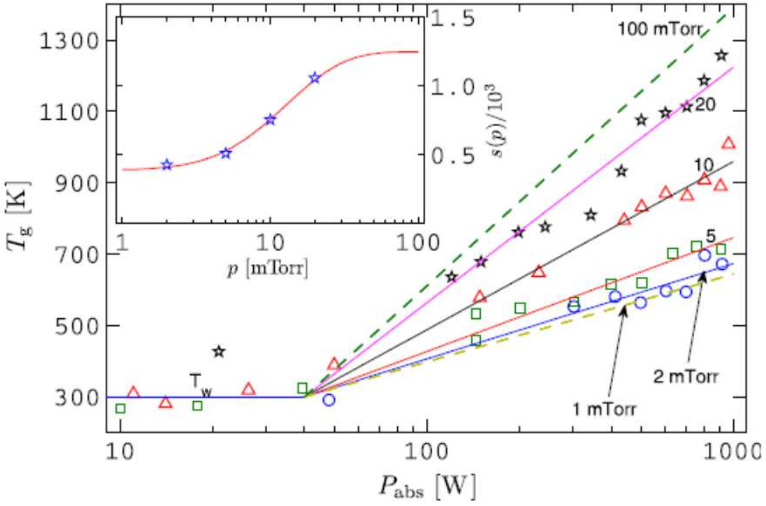
$$\{\mathrm{Cl}_2, \mathrm{Cl}, \mathrm{Ar}, \mathrm{Cl}_2^+, \mathrm{Cl}^+, \mathrm{Ar}^+\} \xrightarrow{K_{po}} [\mathrm{Drain}] \text{ with } K_{po} = 1.27 \times 10^{-5} \frac{Q_{\mathrm{Cl}_2} + Q_{\mathrm{Ar}}}{p_o V}$$

outlet flow pressure (Torr) calibrated until a particular discharge p is reached

- **Gas heating**

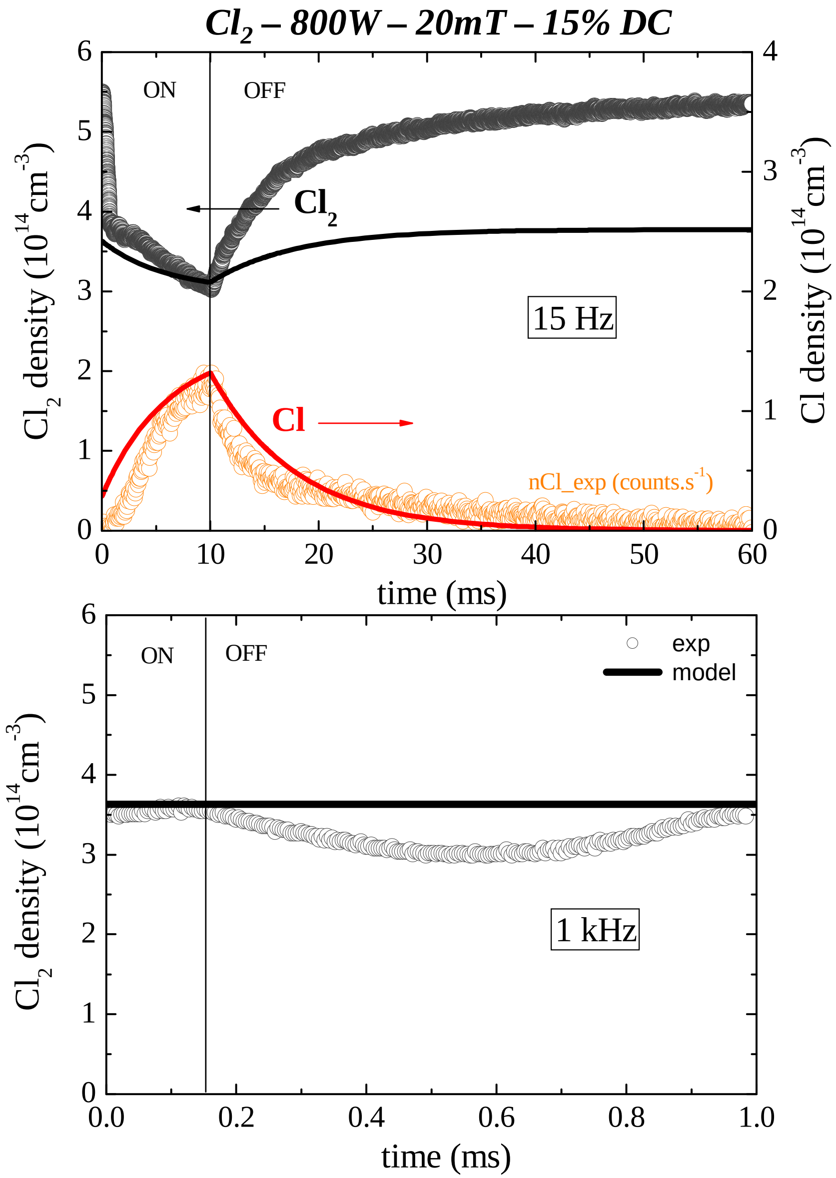
$$T_g(\overline{P_{abs}}, p) = 300 + s(p) \frac{\log_{10}(\overline{P_{abs}}/40)}{\log_{10}(40)}$$

$$s(p) = 1250 * (1 - e^{-0.091p}) + 400e^{-0.337p}$$



*Thorsteinsson and Gudmundsson, J Phys D 43 (2010)*

# Frequency influence on radicals



- Reactive radicals Cl are :

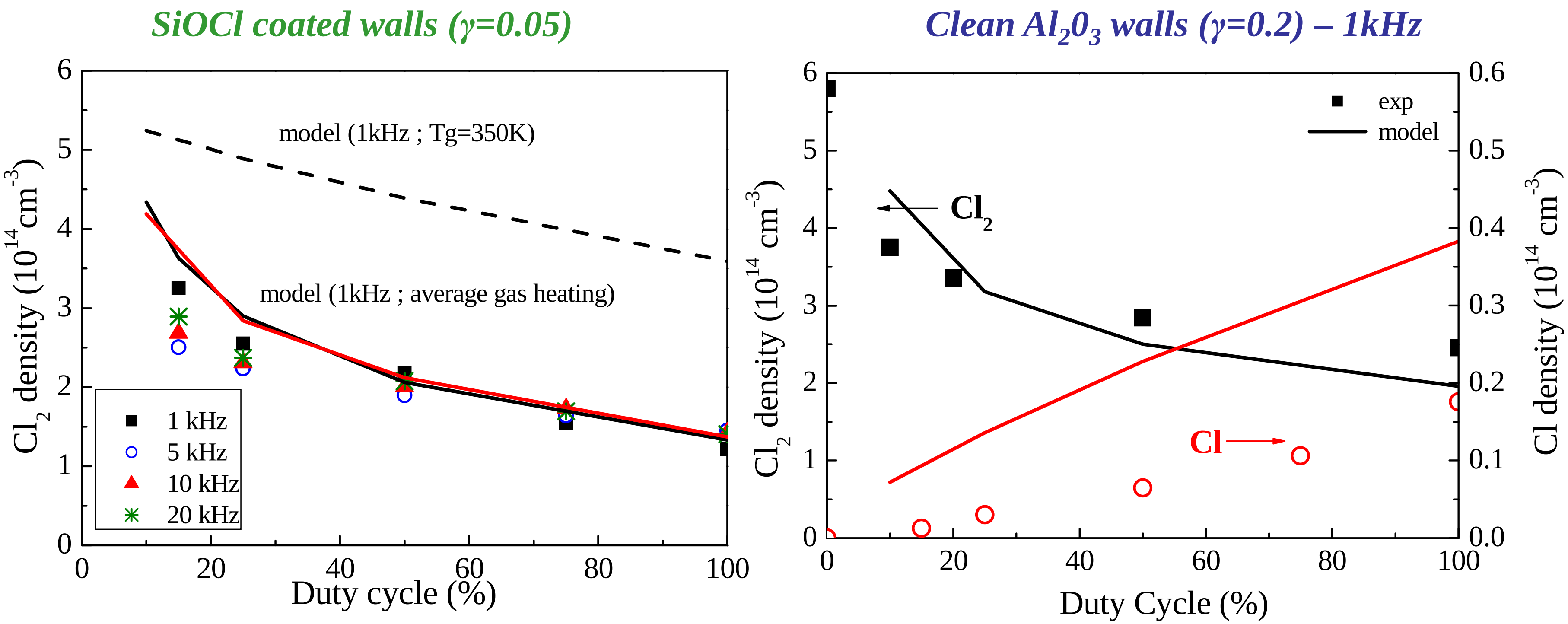
- produced only in **ON-time** [e- + $Cl_2$ → 2Cl + e-]
- lost **continuously** at walls [Cl + wall → $Cl_2$]

- T-scale for significant radical density variations (dissociation/recombination) ~ **several ms**

**For pulsing frequencies > 1 kHz (T<1 ms) the radical density is not anymore modulated during the pulse**

⇒ Only **time-averaged** values will be considered in the following

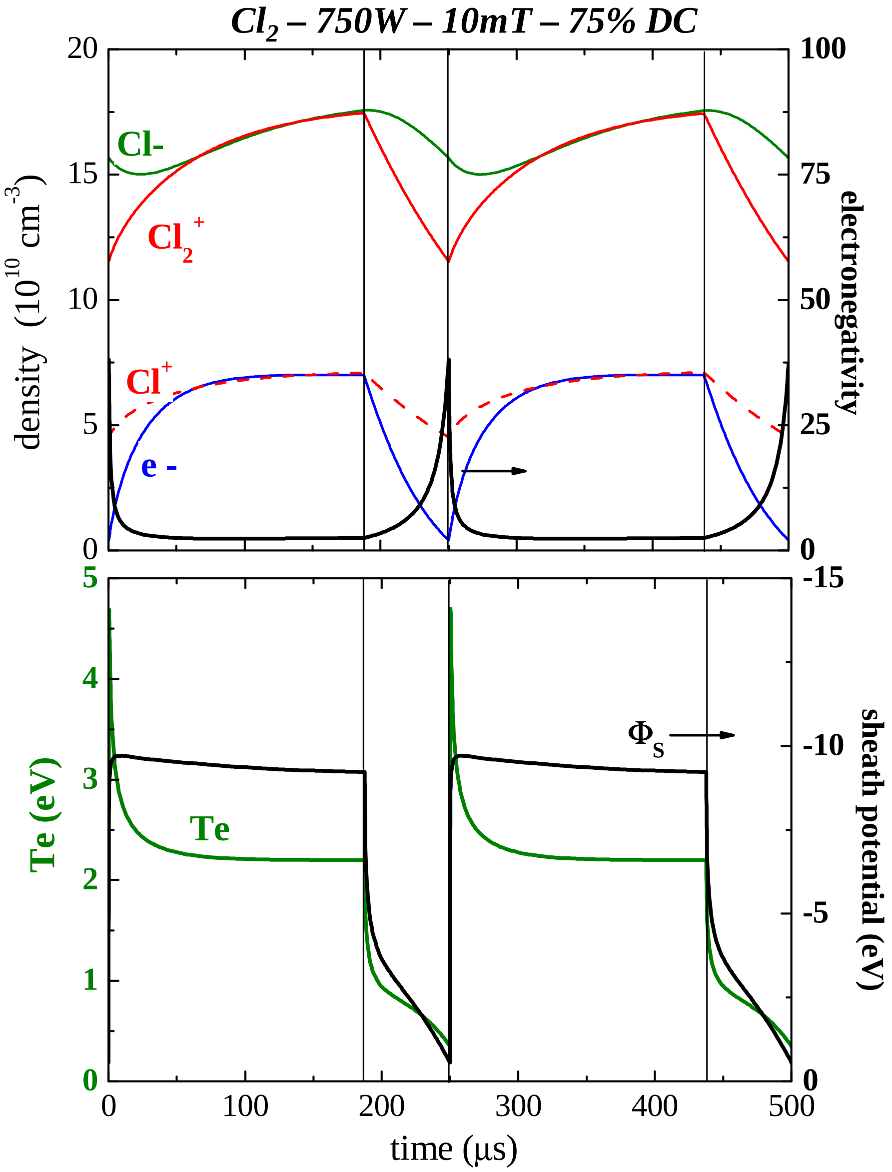
# Duty Cycle influence on radicals



- Strong impact of **duty-cycle :** DC increases ⇒ longer ON period ⇒ higher nCl
- No effect of **pulsing frequency :** f increases ⇒ total ON time (avg) unchanged ⇒ same nCl

**Low modulation of neutral species with frequency for f >1kHz**
**Atomic to molecular densities ratio (Cl/$Cl_2$) controlled by the duty cycle**

# Modulation of charged species at high frequency (4kHz)



- T-scale for charged species density variations (e- heating/ambipolar diffusion)
  ~ **tens of µs**

**⇒ high modulation of charged species densities between 1kHz and 100kHz**

- Sharp **overshoot** of $T_e$ at 1st stage of ON period -> steady state after ~ 30 µs

- In the afterglow :
  *ne drops rapidly

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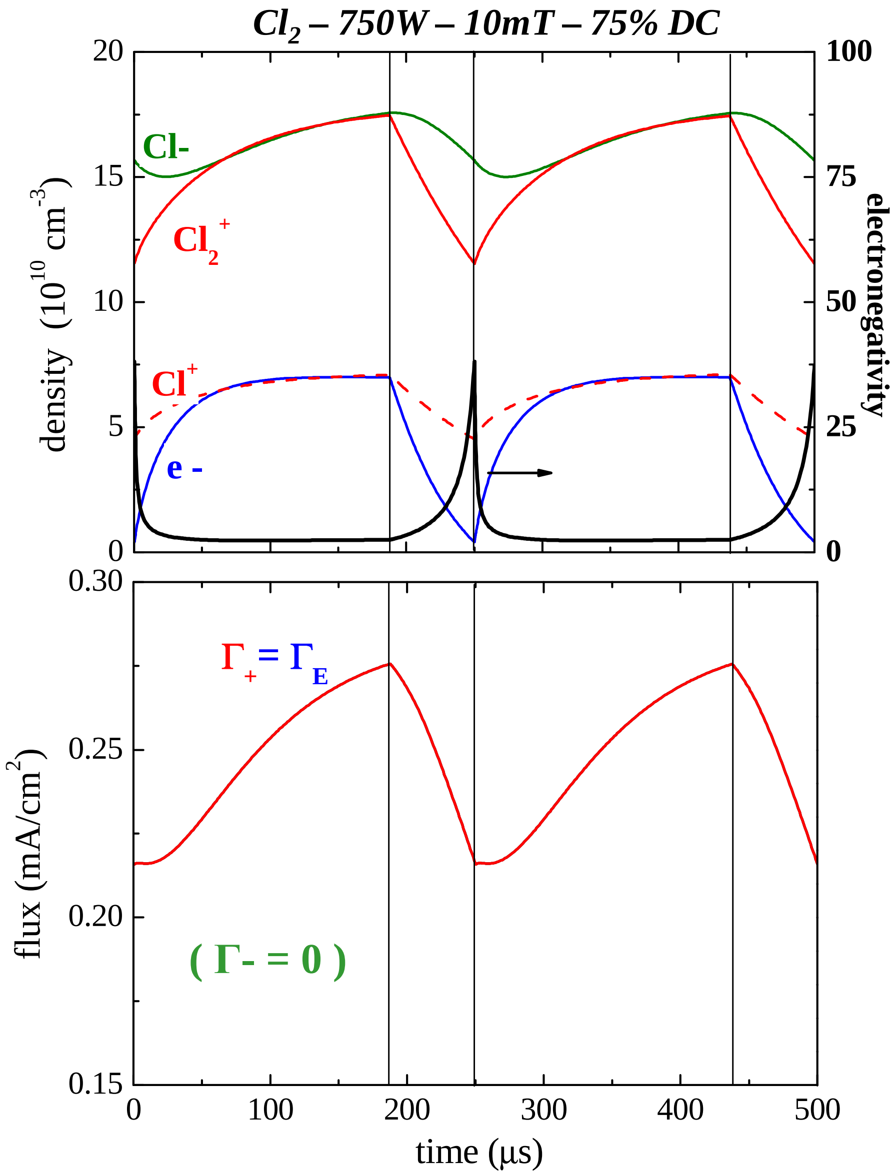

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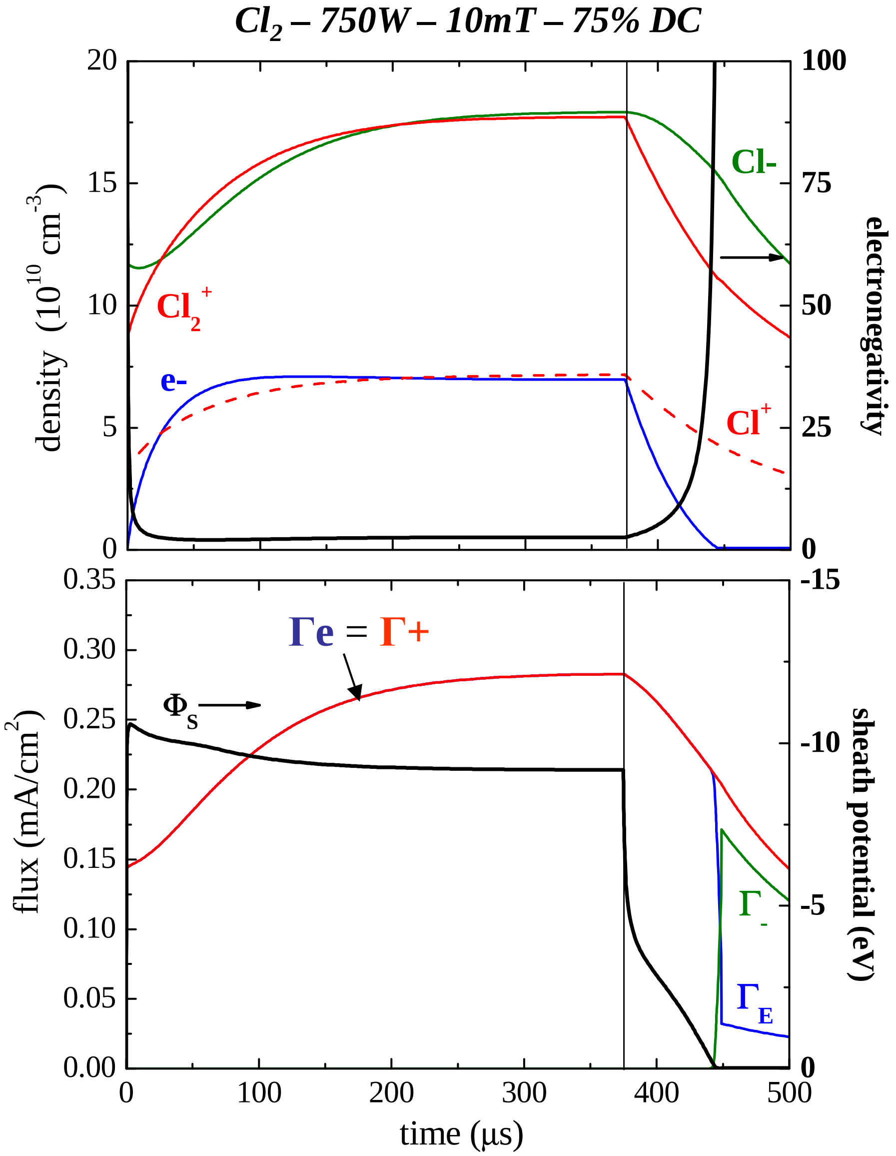
- In the afterglow :
  ***** ne drops rapidly
  *** ion flux decay** is due to Te drop ($U_{Bohm}$ ↓) and ambipolar losses (ni ↓)

# Modulation of charged species at high frequency (2kHz)



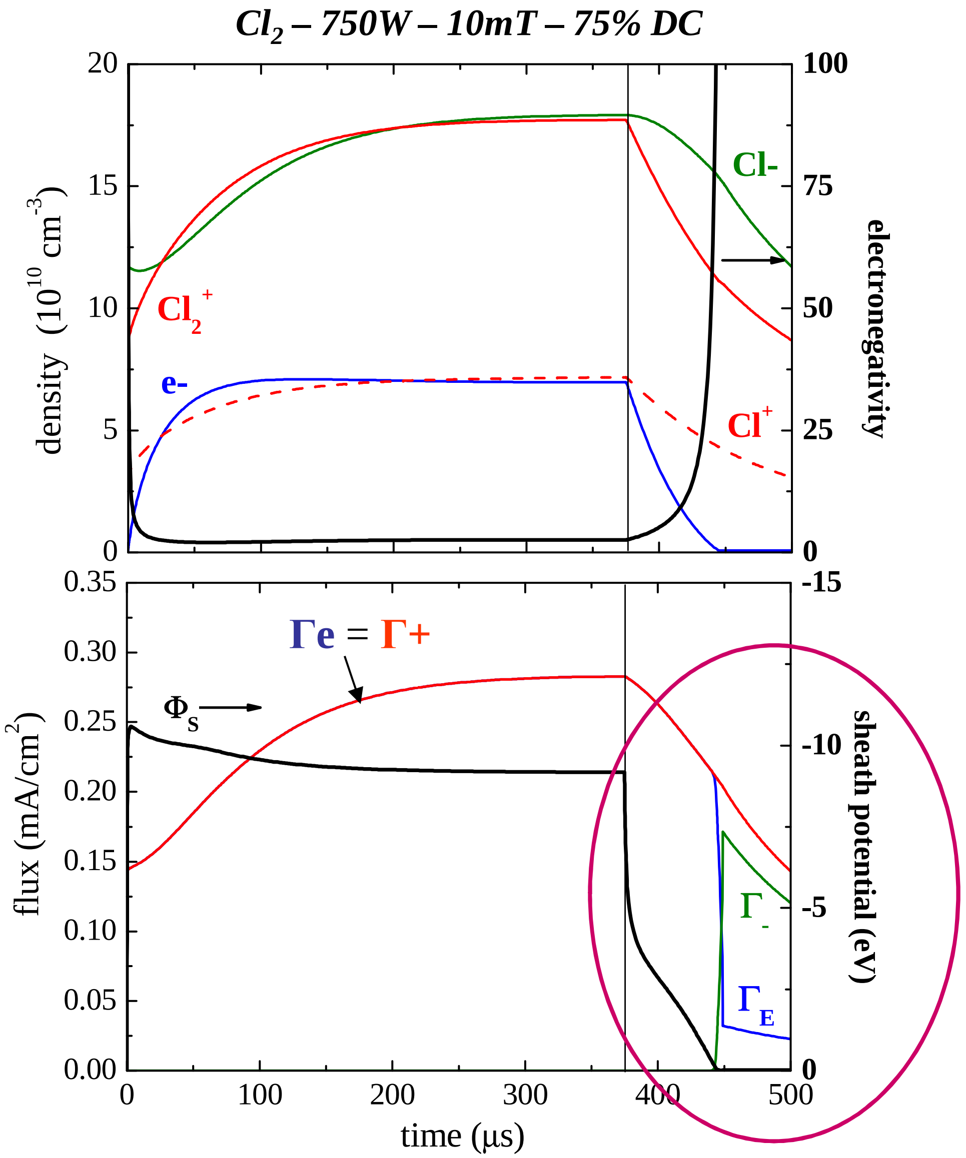
- At lower frequency, ne << n- at the end of the afterglow

⇒ **ion-ion plasma** formation

⇒ sheath collapses

⇒ **negative ions flow out** of the plasma

# Modulation of charged species at high frequency (2kHz)



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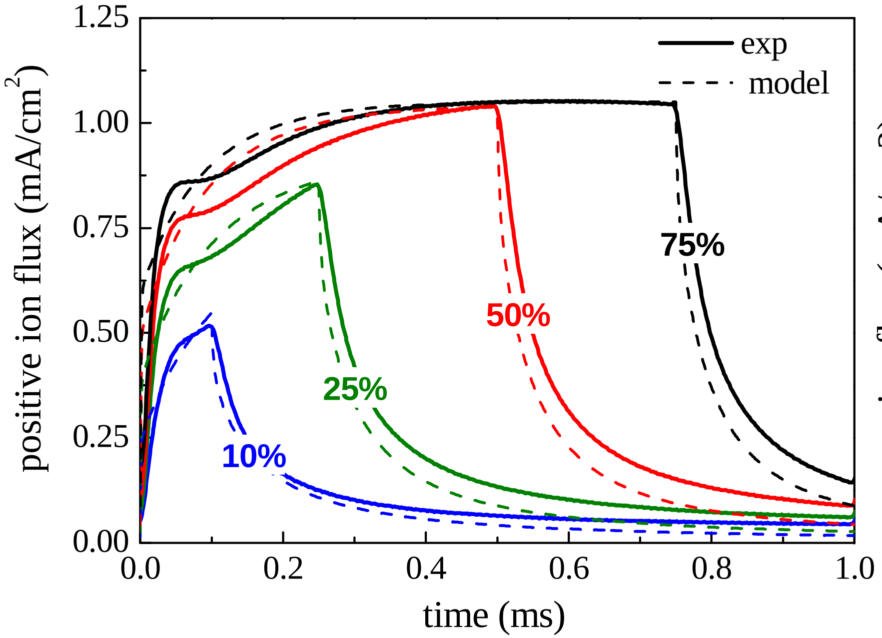
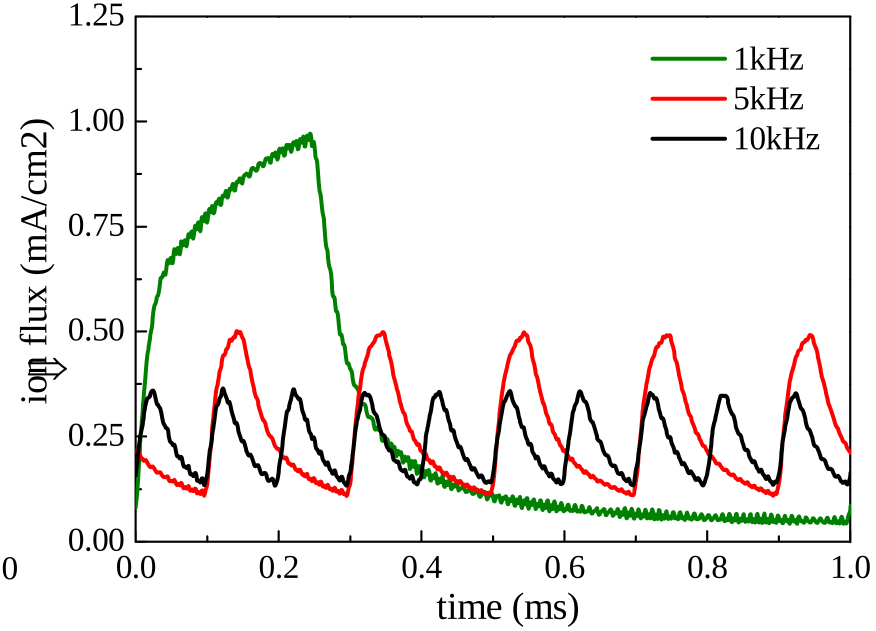
# DC and f influence on ion flux (EP plasma)

***Ar plasma / 10 mTorr / 750 W / 1kHz***



***Ar plasma / 10 mTorr / 750 W / 25%DC***



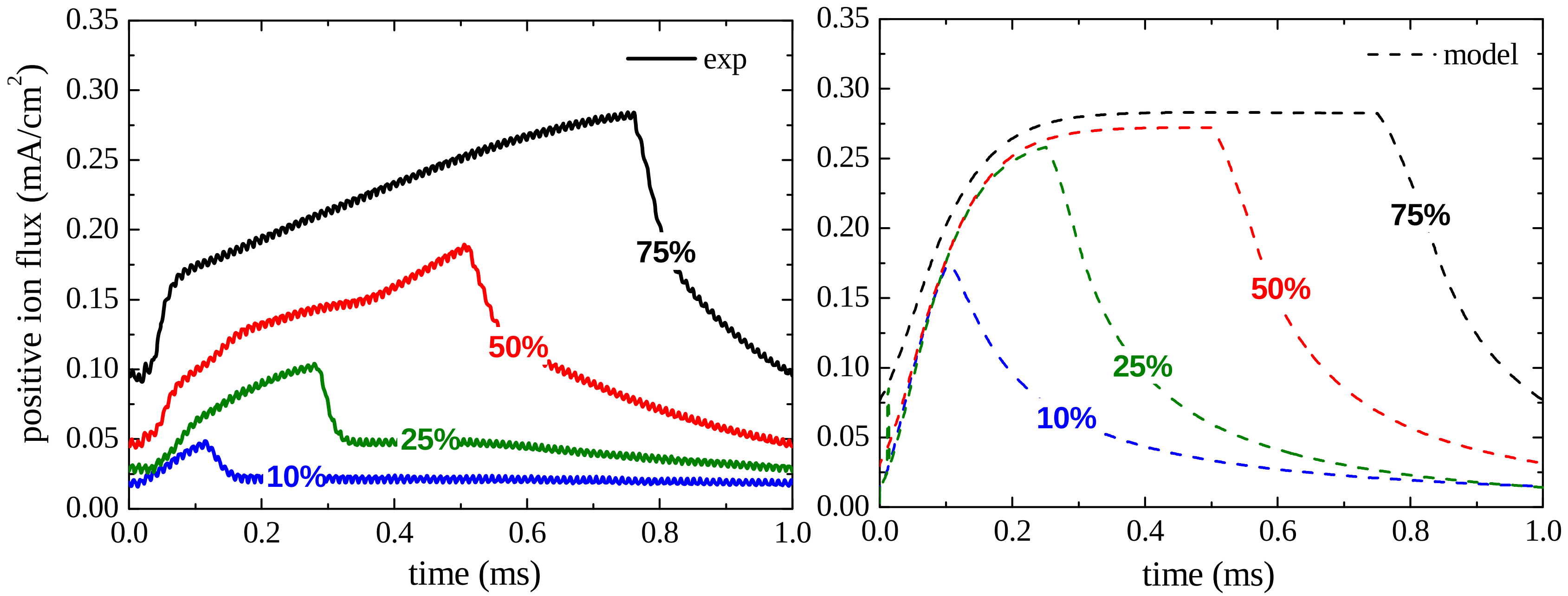
- In the afterglow, ion flux decay is due to $T_e$ drop ($U_{Bohm}$ ↓) and ambipolar losses ($n_i$ ↓)
  ⇒ rise and fall times of ion flux ≈ 50-100 µs << pulsing period (1000 µs)

- Ion flux decreases with increasing frequency

**In ON-time, ion flux ≈ reaches steady state and is high even at 10% DC**

# DC influence on ion flux (EN plasma)

***$Cl_2$ plasma / 10 mTorr / 750 W / 1kHz***

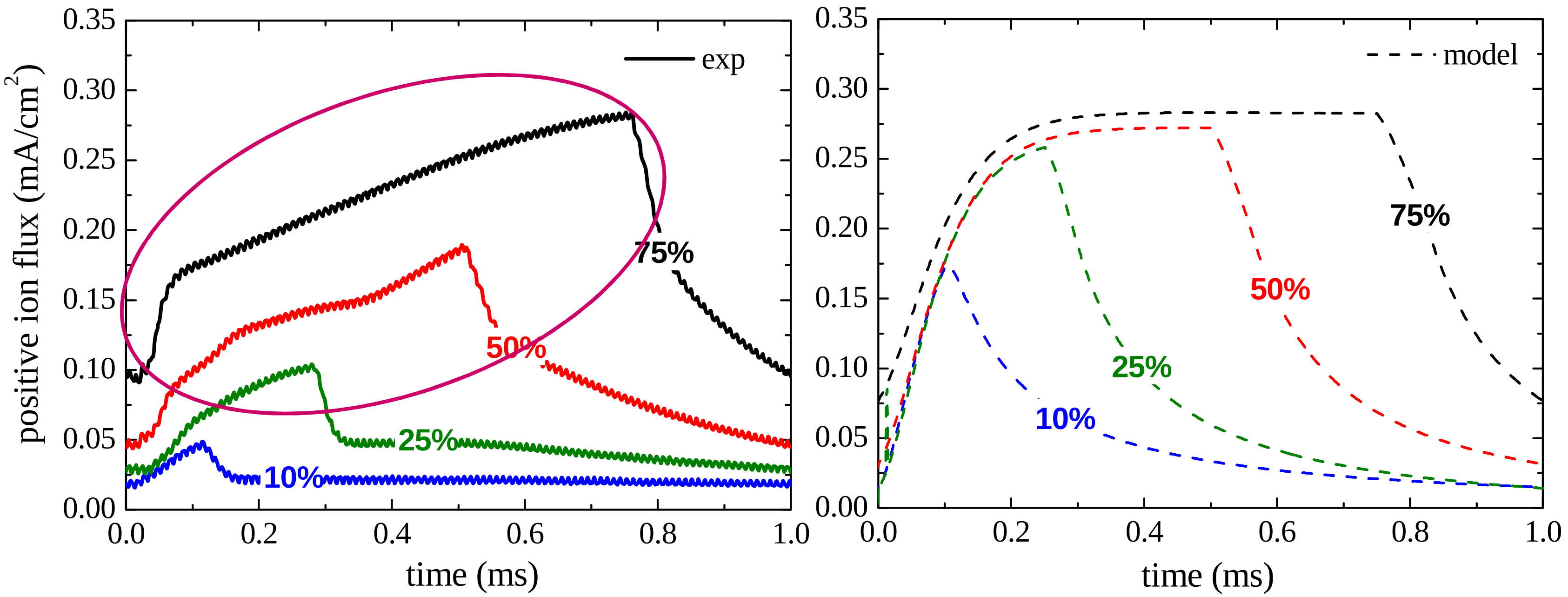


- Ion flux much smaller than in Ar (mod/exp in quantitative agreement)
- Rise/decay time of ion flux longer than in Ar

**In ON-time, ion flux strongly depends on DC & remains small below 25 % DC**

# DC influence on ion flux (EN plasma)

***$Cl_2$ plasma / 10 mTorr / 750 W / 1kHz***



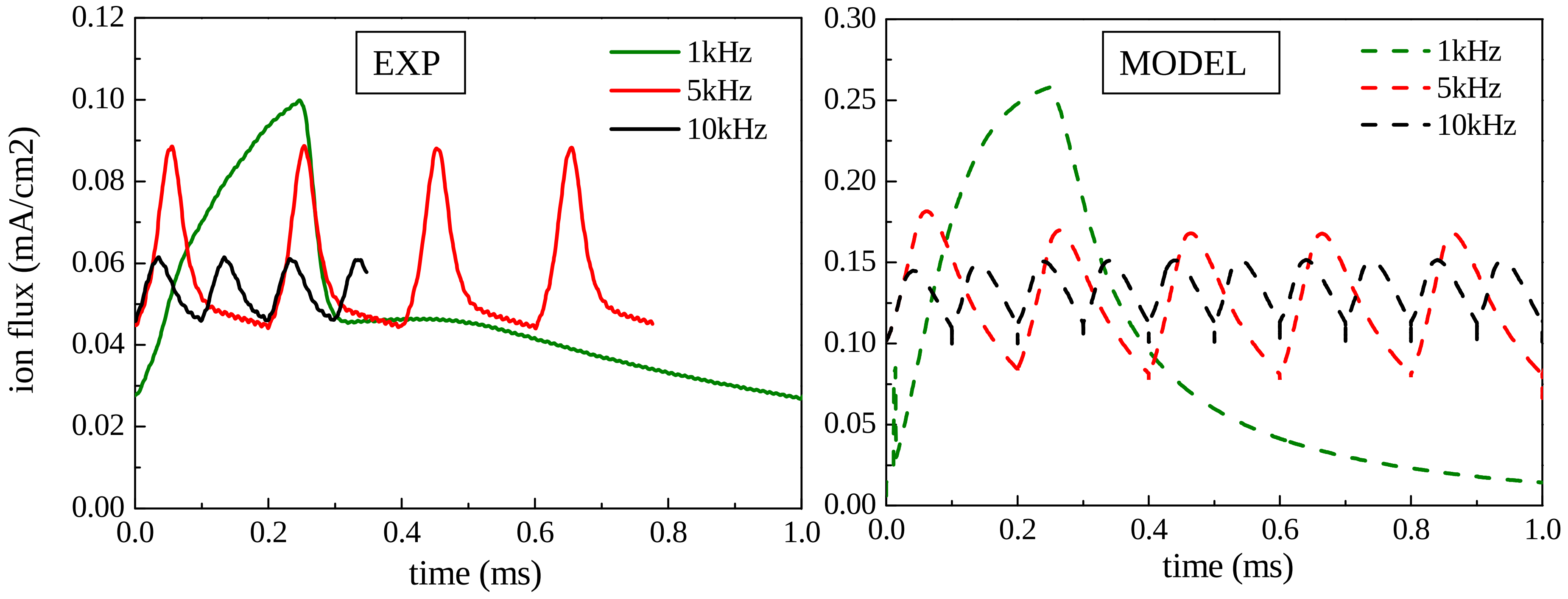
- Ion flux much smaller than in Ar (mod/exp in quantitative agreement)
- Rise/decay time of ion flux longer than in Ar

  ⇒ **but exp and model differ in ON-time : acoustic waves ??**

**In ON-time, ion flux strongly depends on DC & remains small below 25 % DC**

# Frequency influence on ion flux (EN plasma)

***$Cl_2$ plasma / 10 mTorr / 750 W / DC=25%***



**In the ON period the ion flux depends on the pulsing frequency and remains smaller at high frequency (10kHz)**

# Conclusions and perspectives

- **Neutral composition :**

- for f >1 kHz (T<1 ms) : **radical densities** no more t-modulated
- ratio **$Cl/Cl_2$** can be controlled by duty cycle

- **Charged species densities and fluxes :**

- **high t-modulation** between 1kHz and 100kHz
- for afterglow > 100µs, ne << n- ⇒ sheath collapses ⇒ **negative ions flow out**
- EP plasma (ion flux **independent** of DC) ≠ EN plasma (ion flux **depends on both** DC & f)

# Conclusions and perspectives

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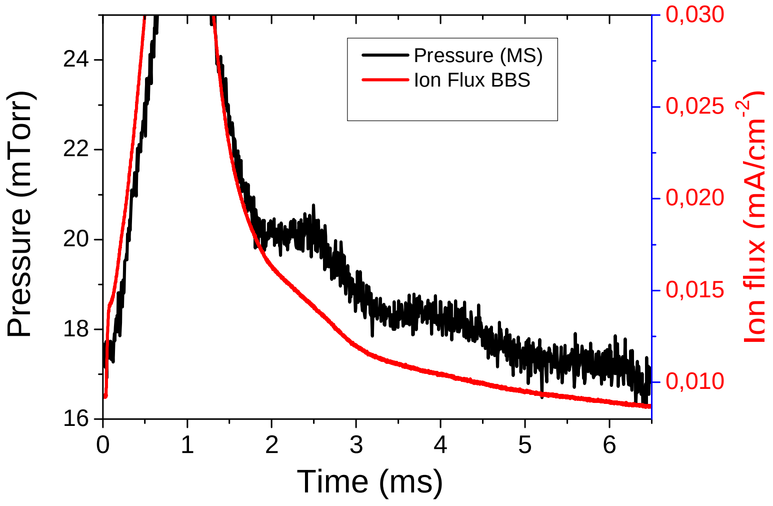
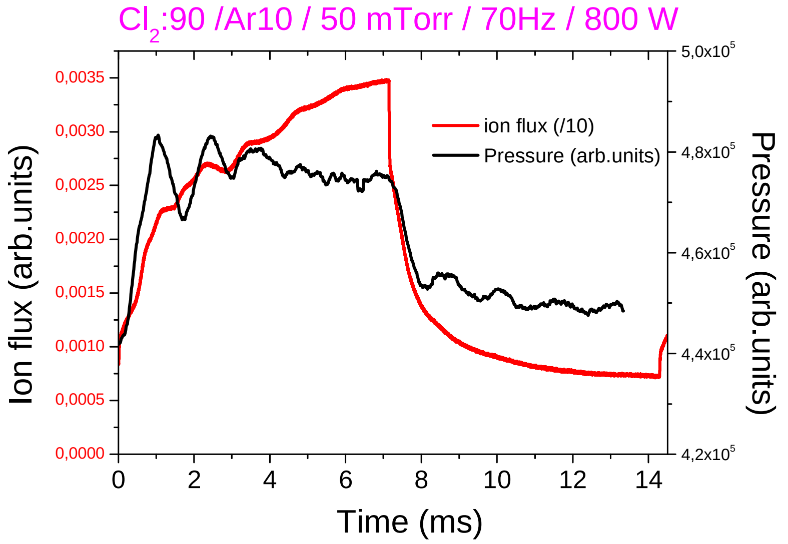
## ▪ Perspectives [see Gilles Cunge talk]

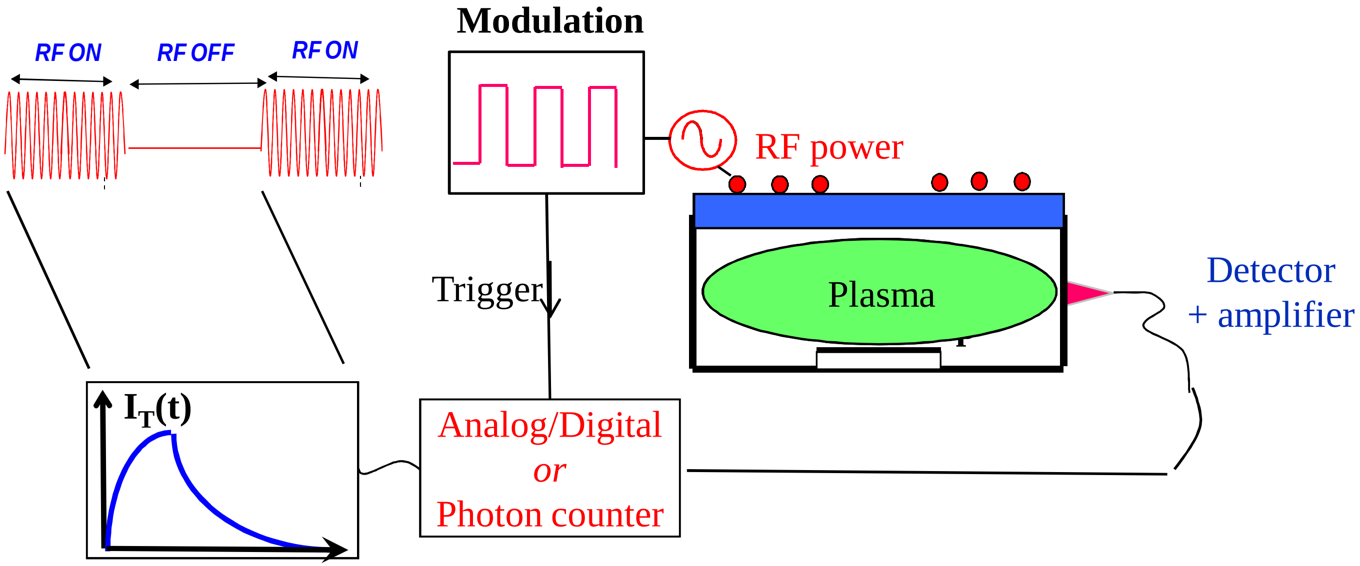
**oscillations** of ion flux at walls and gas density during plasma ignition/afterglow ⇒ add plasma equations (ne, n-, n+) in **2D fluid model** to study it





# Time-resolved measurements in pulsed plasmas

Plasma diagnostics provide a signal (typically a current).
Goal: capture signal variations during one pulsing period (100 µs at 10 kHz)



**→ Fast acquisition systems synchronized with plasma pulses**

A/D converter
(16 bit, 1 Ms/s)

**CW signal**

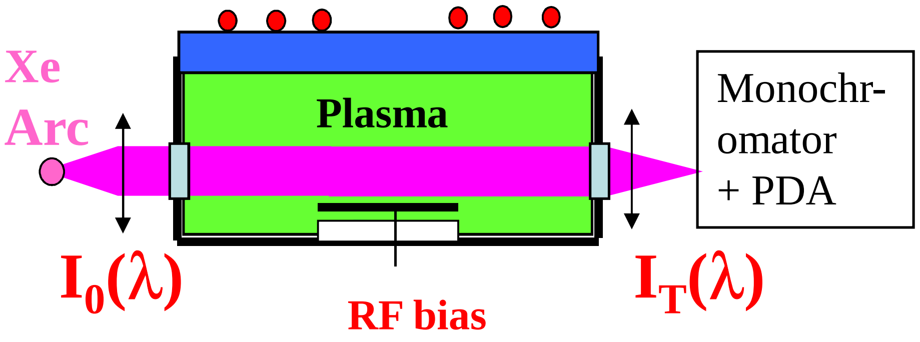
(photodiode,
Langmuir
probes….etc)

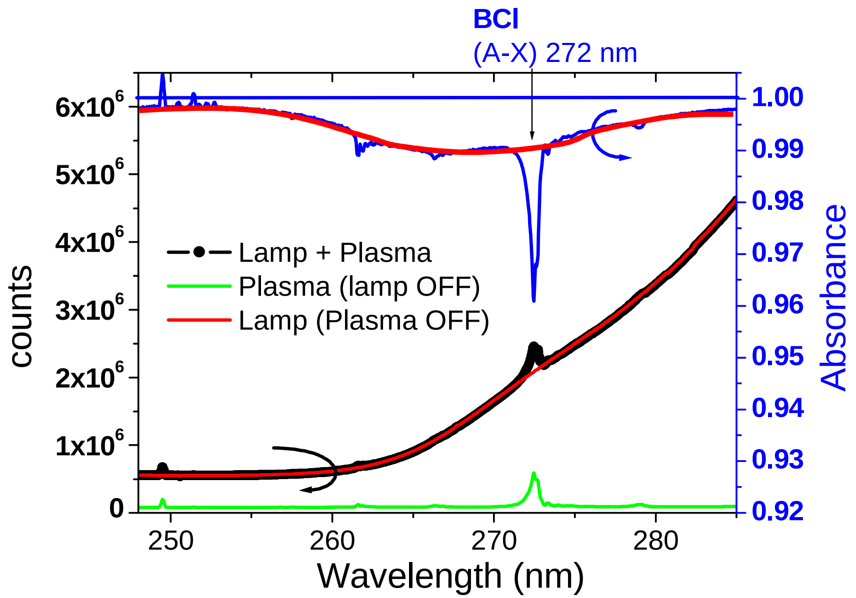
**Pulses**

(Mass spec,
PMT…etc)

Multichannel
analyzer

# $Cl_2$ density : BBUV Absorption Spectroscopy





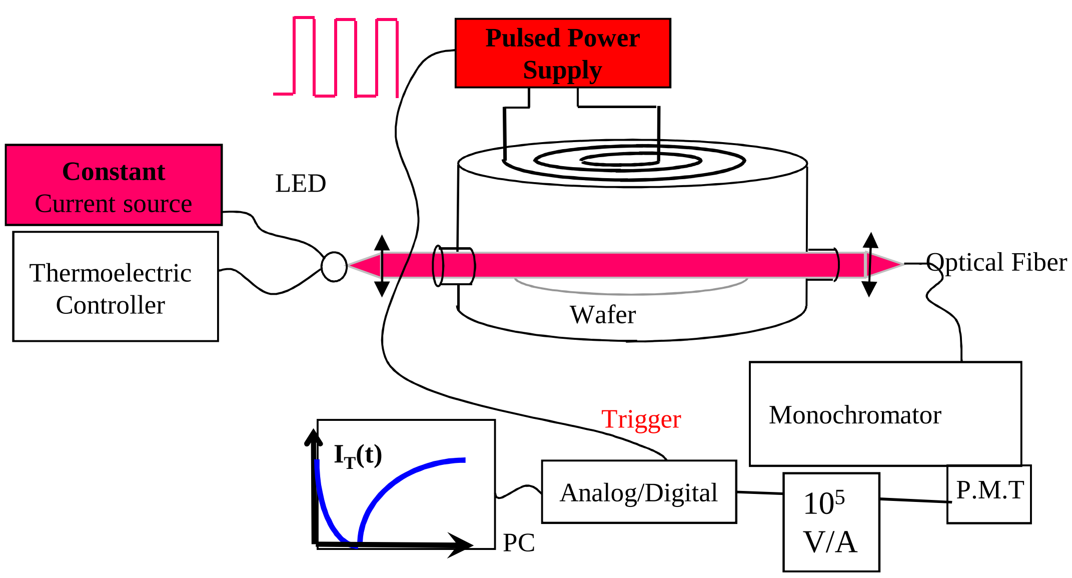
Beer-Lambert law: $\mathbf{I_T(\lambda) = I_o(\lambda)\, e^{-N\,L\,\alpha(\lambda)}}$

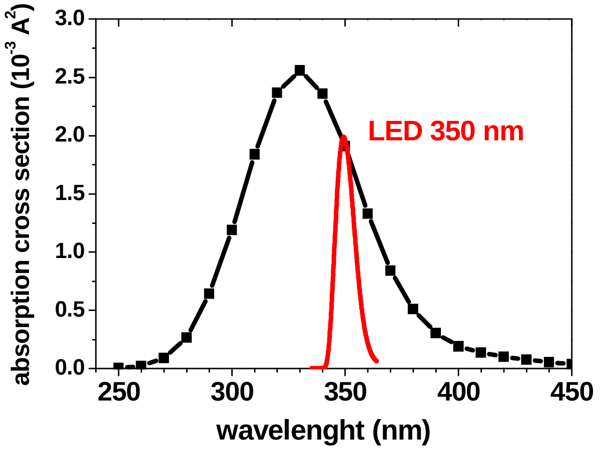
$$\frac{I_T}{I_o} = \frac{(L_P - P)}{I_o} \qquad \Rightarrow \qquad N = \frac{1}{\alpha L}\ln\left(\frac{I_o}{I_T}\right)$$

**absorbance ≈ $10^{-3}$ ⇒ high sensitivity required ⇒ introduction of UV LEDs**

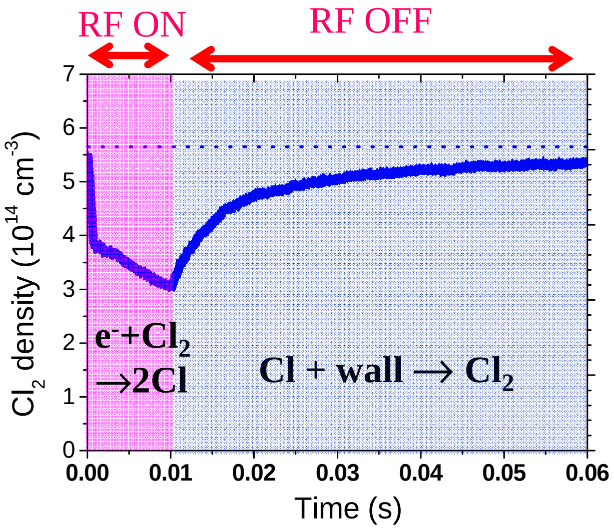
# $Cl_2$ density : BBUVAS with UV LED

**Issue:** time resolution <100 µs is required ⇔ signal accumulation over many cycles
This can be done with a **LED** because $I_0(t)$ is very stable





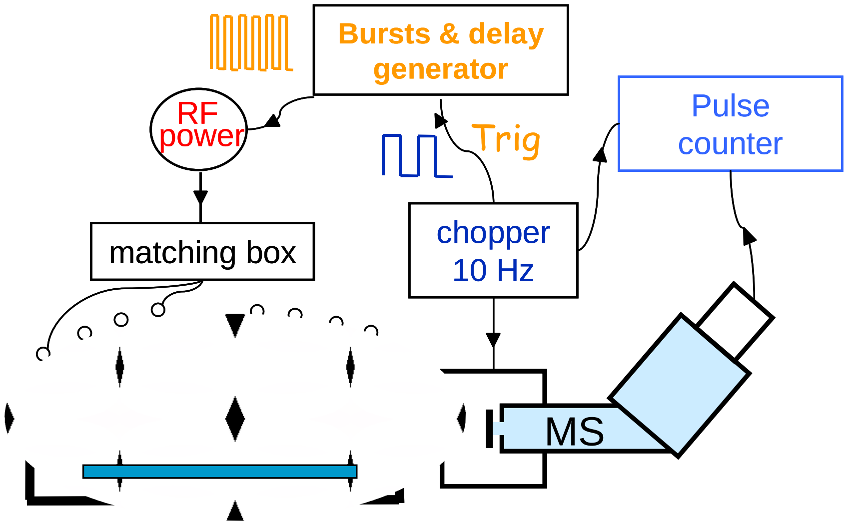
⇒ **acquisition is synchronized with the plasma** pulses thus measuring $I_T(t)$ over each pulsing period

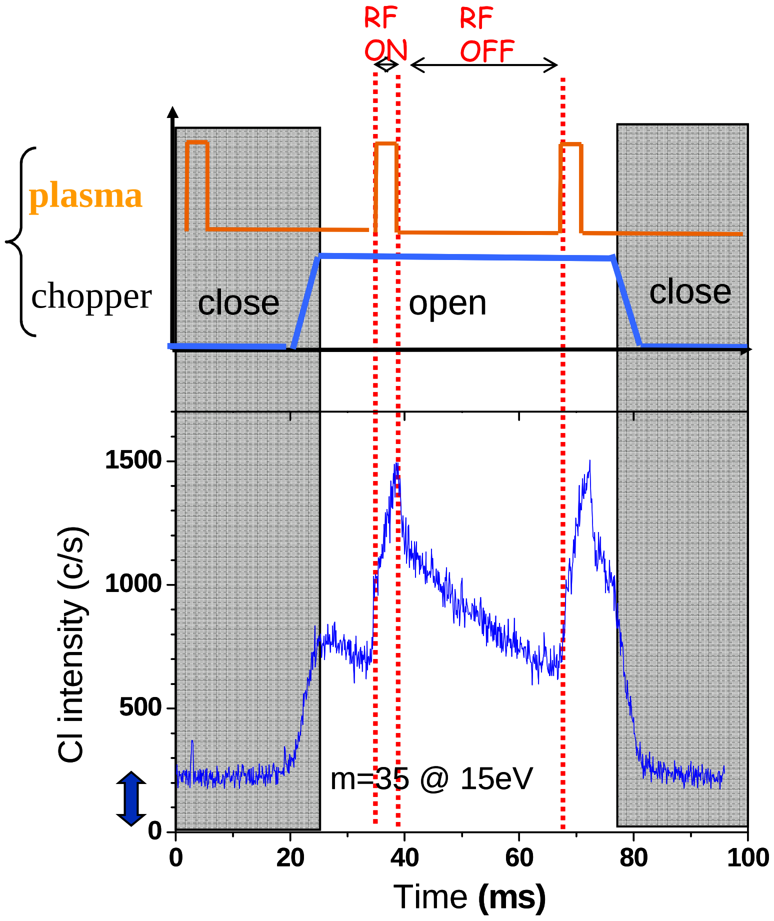


# Cl and Ar densities : Modulated Beam Mass Spectrometry

Plasma pulses must be synchronized with chopper (cf. background removal) oscillations

⇒ **plasma pulsing frequency > chopper frequency**





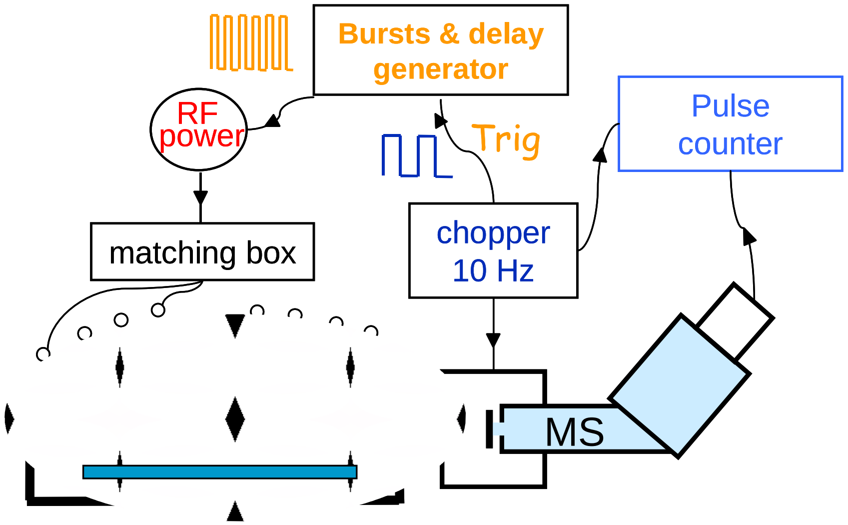
- chopper signal at 10 Hz used to trigger a **burst generator** that produces pulses at N x 10 Hz to pulse the plasma

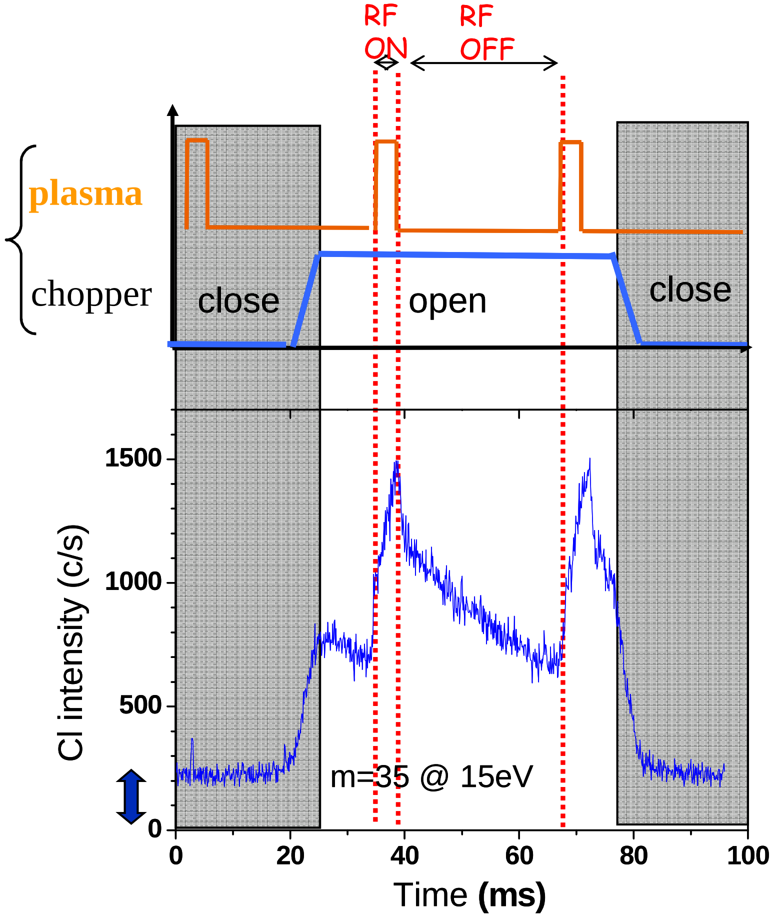
- **multichannel pulse counter** capture the signal during the entire chopping period

# Cl and Ar densities : Modulated Beam Mass Spectrometry

Plasma pulses must be synchronized with chopper (cf. background removal) oscillations

$\Rightarrow$ **plasma pulsing frequency > chopper frequency**





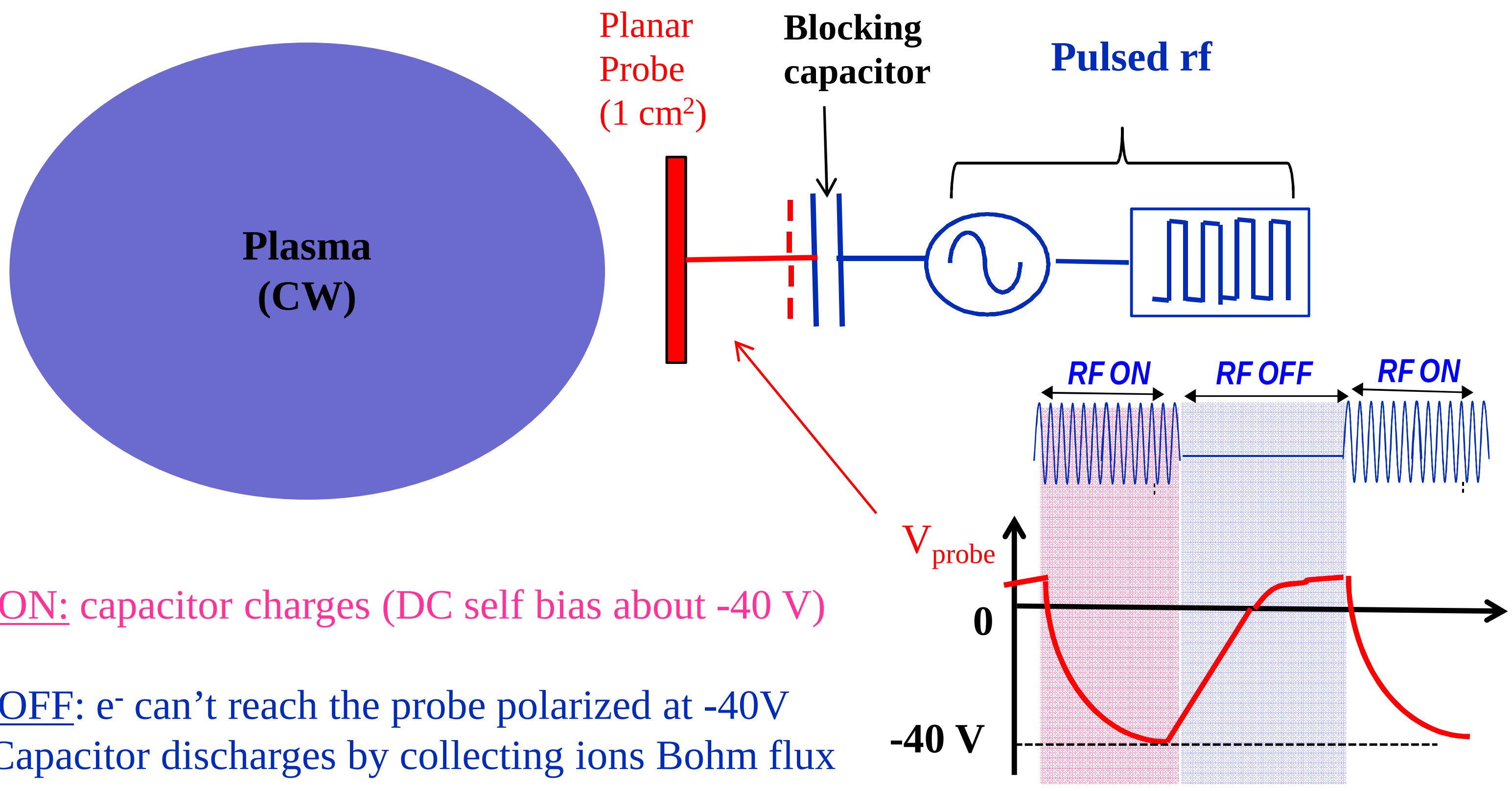
- **calibration** on absolute density by comparison with Ar signal :

$$\frac{Cl(cm^{-3})}{Cl(c.s^{-1})} = \frac{Ar(cm^{-3})}{Ar(c.s^{-1})}\frac{\sigma_{Ar}}{\sigma_{Cl}}$$

# Ion flux (current) measurement : Capacitive probe

Well known technique introduced by Braithwaite *et al* in 1996

**Principle**: fed a planar probe by RF bursts through a blocking capacitor



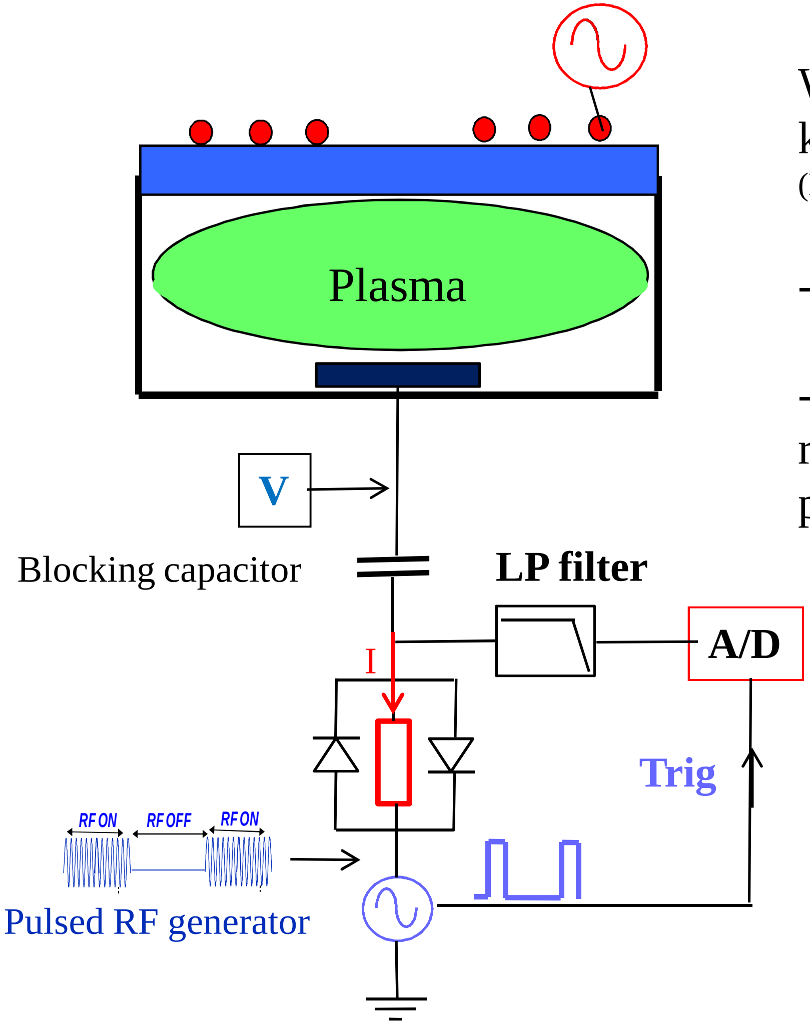
RF ON: capacitor charges (DC self bias about -40 V)

RF OFF: e$^-$ can't reach the probe polarized at -40V

→ Capacitor discharges by collecting ions Bohm flux

**Measurement of the capacitor discharge's current in OFF period → ion flux**

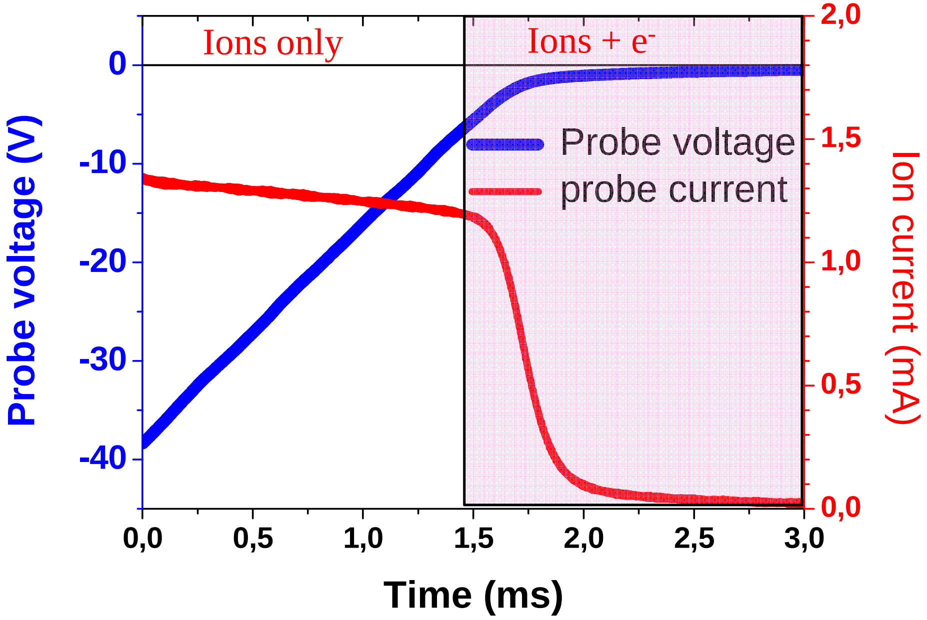
# Ion flux (current) measurement in CW plasmas



We use a direct current measurement system through a 1 kΩ serial resistor
(Booth et al, Rev. Sci. Instrum. 71, 2722)

- **RF ON**: RF signal propagates through diodes

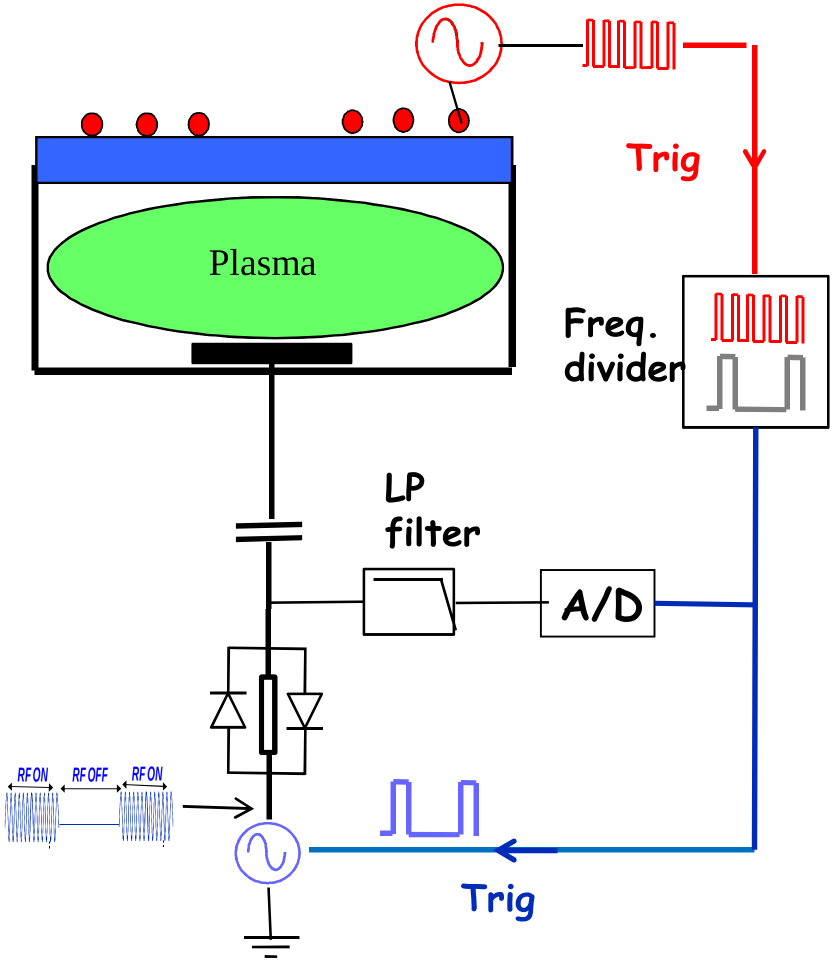
- **RF OFF**: capacitor discharge’s current flow through resistor and is measured by the A/D (triggered by probe pulses)



# Ion flux (current) measurement in <u>Pulsed</u> plasmas

**Issue**: several plasma pulses are needed to charge blocking capacitor to - 40 V

⇒ **Probe pulsing frequency < Plasma pulsing frequency** (but synchronized)

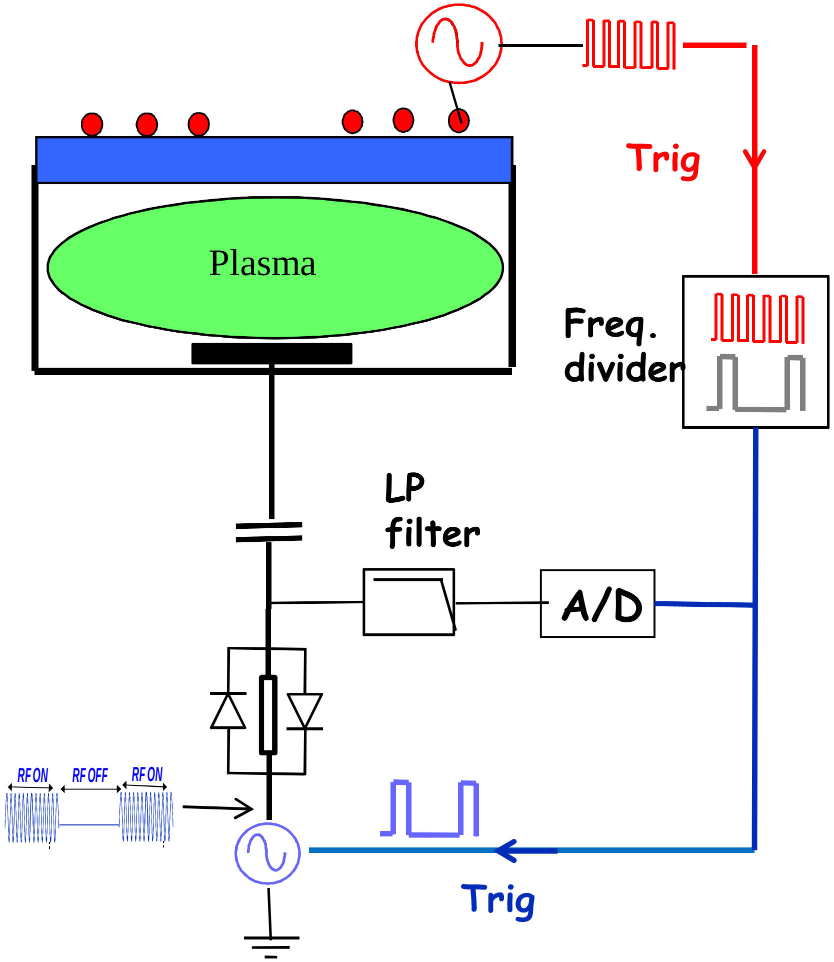


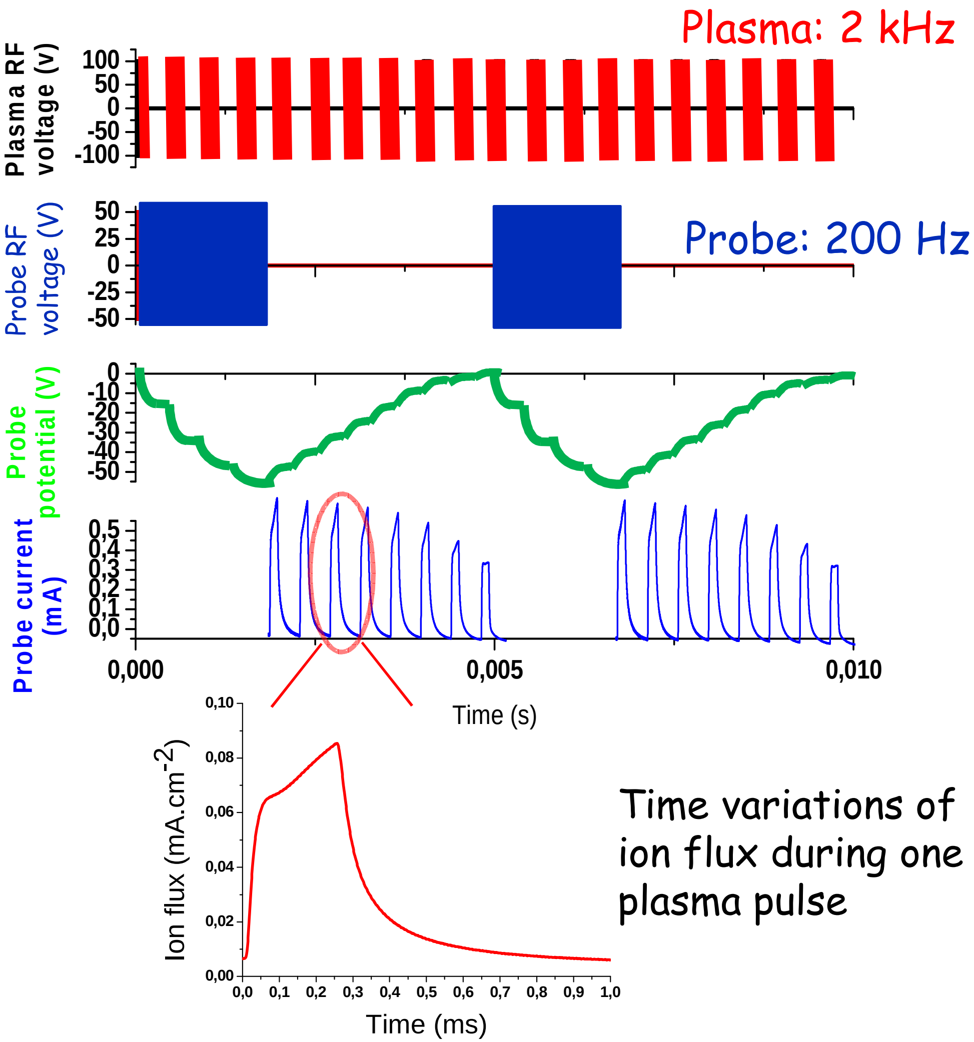
→ Use a frequency divider triggered by the plasma pulses to trigger probe pulses at f/10

# Ion flux (current) measurement in Pulsed plasmas

**Issue**: several plasma pulses are needed to charge blocking capacitor to - 40 V

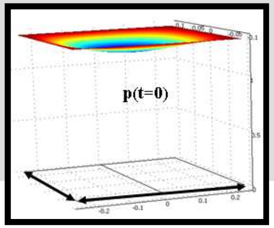
⇒ **Probe pulsing frequency < Plasma pulsing frequency** (but synchronized)

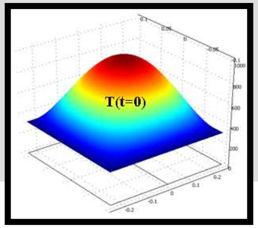




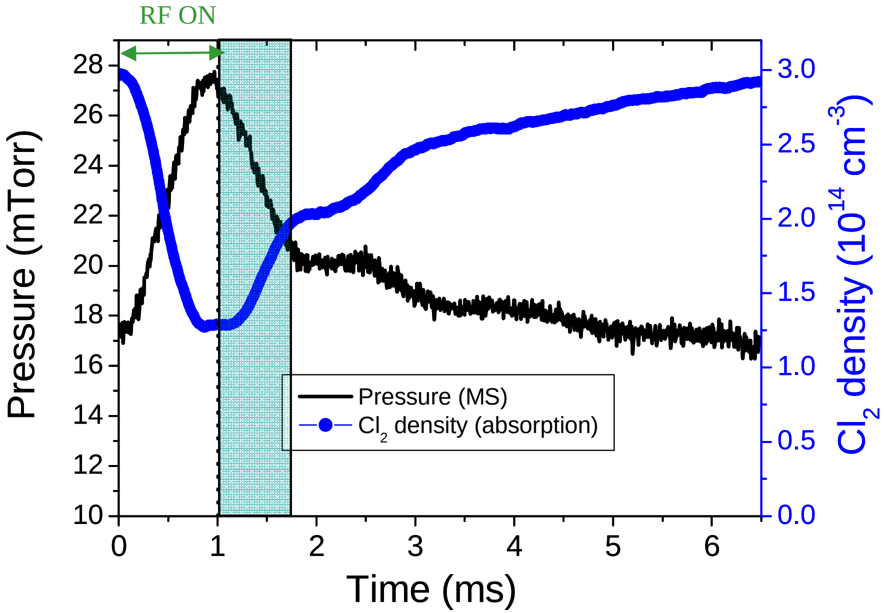
Time variations of ion flux during one plasma pulse

# Afterglow model: $P_n$ depleted + gas heating

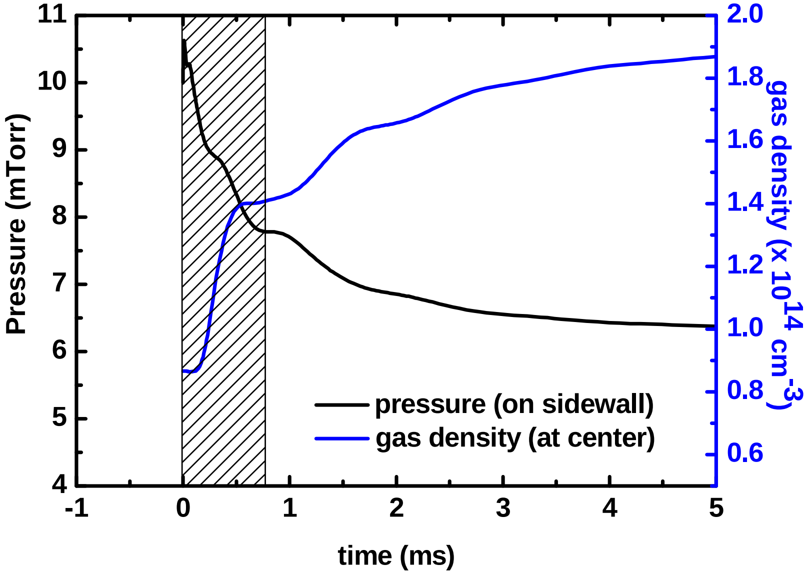




**EXP**



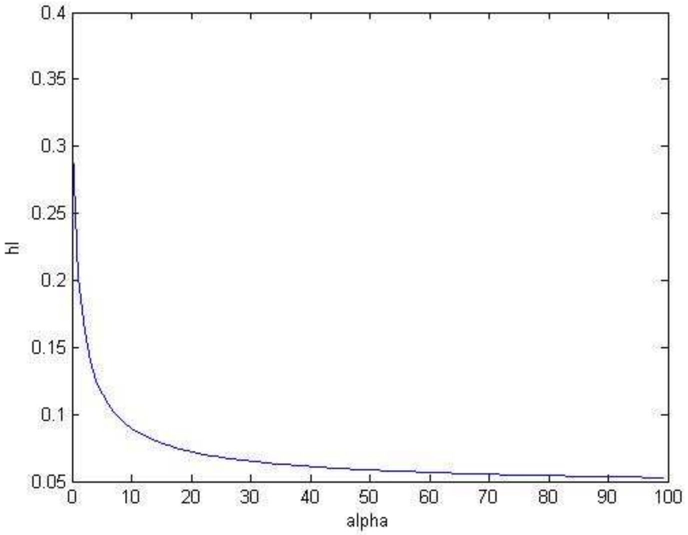
**MODEL**

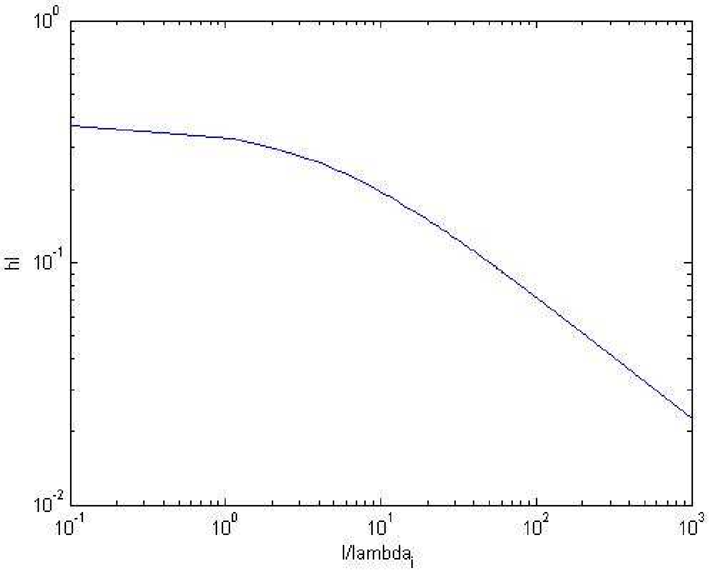


- Gaz density increases in the reactor center while pressure decreases close to the walls

⇒ relatively **good agreement between model and experiment**

# hl and hr factors in the model





$$h_L = \left[ \left( \frac{1}{1+\alpha_0} \frac{0.86}{(3+\eta L/2\lambda_i)^{1/2}} \right)^2 + h_c{}^2 \right]^{1/2} \qquad (8a)$$

$$h_R = \left[ \left( \frac{1}{1+\alpha_0} \frac{0.8}{(4+\eta R/\lambda_i)^{1/2}} \right)^2 + h_c{}^2 \right]^{1/2} \qquad (8b)$$

$$h_c = (\gamma_-^{1/2} + \gamma_+^{1/2} n_*^{1/2} n_+ n_-^{-3/2})^{-1} \qquad (9)$$