Influence de la nature de la paroi sur les réactions de recombinaison des radicaux

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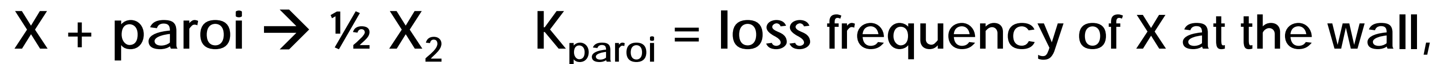
OUTLINE

- Introduction
- Kinetics of atoms in low pressure molecular plasmas
- How to determine the atom recombination frequency (γ) ?
- Example : determination of γ_O by time resolved optical emission spectroscopy (TROES)
  - influence of the nature of the wall on γ_O in pulsed oxygen ICP plasmas
  - Values of γ_O in O_2/TTIP and O_2/HMDSO plasmas
- Conclusion

Kinetics of X atoms in low pressure plasmas



$K_{paroi} = 1/\tau$, τ : characteristic loss time

Global Model :

$$[X] = 2\, K_{diss} \times n_e \times [X_2] \,/\, K_{paroi} = \tau \times K_{diss} \times n_e \times [X_2]$$

X_2 dissociation degree :

$$= \frac{[X]}{2[X_2]+[X]} = \frac{100}{1+\frac{2K_{paroi}}{K_{diss}\, n_e}}$$

Recombination probability : γ

$$\tau = \tau_{diff} + \tau_{loss}$$

$$\tau = \frac{\Lambda^2}{D} + \frac{V}{A} . \frac{2(2-\gamma)}{\overline{\mathrm{v}}.\gamma}$$

$$\frac{1}{\Lambda^2} = \left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{R}\right)^2$$

D = binary diffusion coefficient of X in X_2

V = Volume of the reactor

A = Area of the reactor

V = thermal velocity of X

Chantry et al J. Appl. Phys. 62, 1141 (1987)

Dissociation degree of Cl_2 as a function of γ_{Cl}

V.M. Donnelly, J. Guha, L. Stafford, JVSTA. 010801(2011)

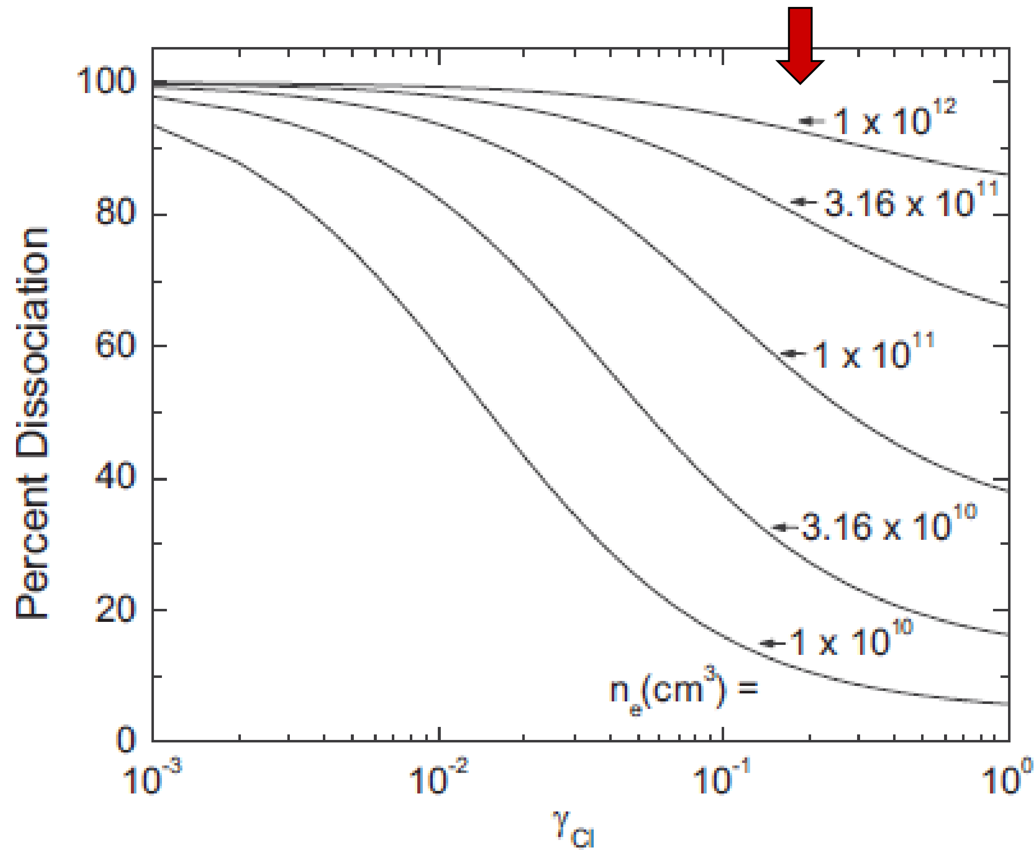
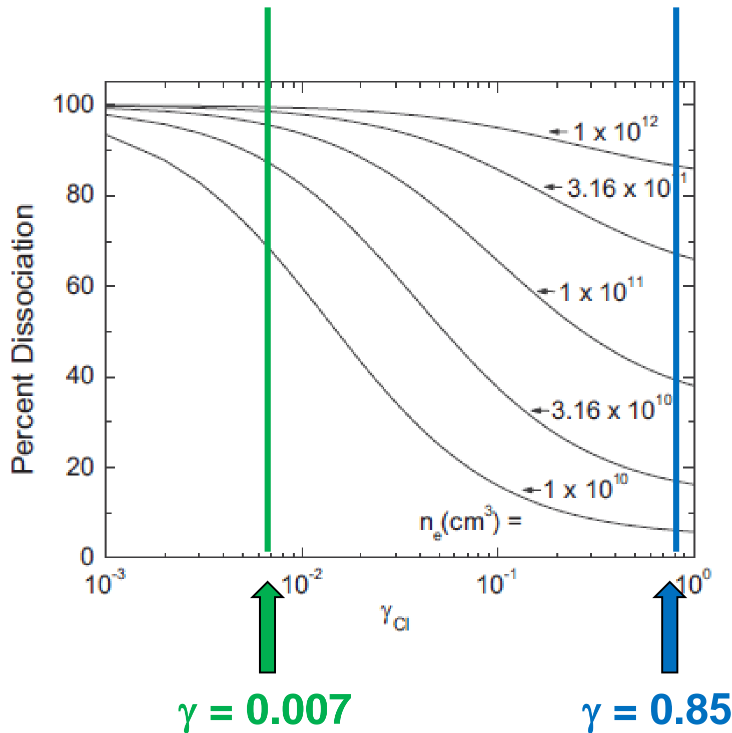


FIG. 1. Global model predictions of percent dissociation of Cl_2 in a chlorine plasma as a function of the Cl recombination coefficient for different electron densities. $R=L=20$ cm, pressure=10 mTorr, gas temperature, T_g =300 K, and $T_e=3$ eV.

Values of gamma for Cl on stainless steel (literature)

V.M. Donnelly, J. Guha, L. Stafford, JVSTA. 010801(2011)



Kota et al : value derived from a high vacuum beam experiment : γ = 0.85

Richards and Sawin : value derived from plasma measurements : γ = 0.007

γ dependent of :

- the nature of the material of the walls of the reactor
- the surface roughness (the specific area)
- the surface temperature
- the reactions at the wall : vacant sites created by ion bombardment…..

How to determine γ ?

best fit between predictions of the global model and experimental measurements in Cl_2 ICP plasmas
$\Rightarrow \gamma = 0.04$ and 0.03 in two different studies (Malyshev et al, Ullal et al)

What happens at the walls ?

stainless steel walls are rapidly covered with silicon oxide or oxichloride (SiOCl) due to etching of the dielectric quartz windows of the ICP
$\Rightarrow$ surface quite different from stainless steel

General case :

γ depends on the nature of the wall surface, which itself depends on the plasma process and species present in the plasma

$\Rightarrow$ need to measure γ in situ, in « real » deposition conditions

Some examples of diagnostics used to determine in situ the value of γ

- Absorption spectroscopy ➔ measurement of [X] and [X_2]
  (G. Cunge et al for Cl and Cl_2)

- Fluorescence spectroscopy ➔ Radial profile of [X]
  (JP Booth et al, in CF_4 based plasmas)

- Spinning wall method
  (L. Stafford and V. Donnelly, in Cl_2 plasmas)

- Time resolved optical emission spectroscopy in pulsed plasma
  (A. Bouchoule and P. Ranson, A. Rousseau et al in H_2 plasmas, A. Granier et al in O_2 and O_2/organometallic plasmas)

V.M. Donnelly, J. Guha, L. Stafford, JVSTA. 010801(2011)

Exemple of determination of γ in a low pressure ICP plasma by time resolved emission spectroscopy (TROES) in pulsed O_2, plasmas

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Low pressure RF ICP PECVD reactor

O_2/Ar 95:5

p : 3 mTorr

$P_{RF\ source}$: 400 W

CW and pulsed mode

O_2/HMDSO/TTIP plasmas

O_2

Power supply (13.56 MHz)

Match Box

Pyrex tube
ϕ = 15 cm

Helicon Antenna

Coils

Diffusion chamber

Ellipsometer

Temperature regulated lines

Mass flow

O_2

Pumping unit

substrate

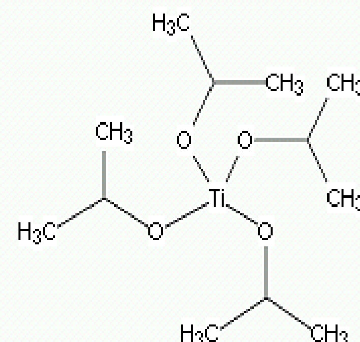
Power supply (13.56 MHz)

Match Box

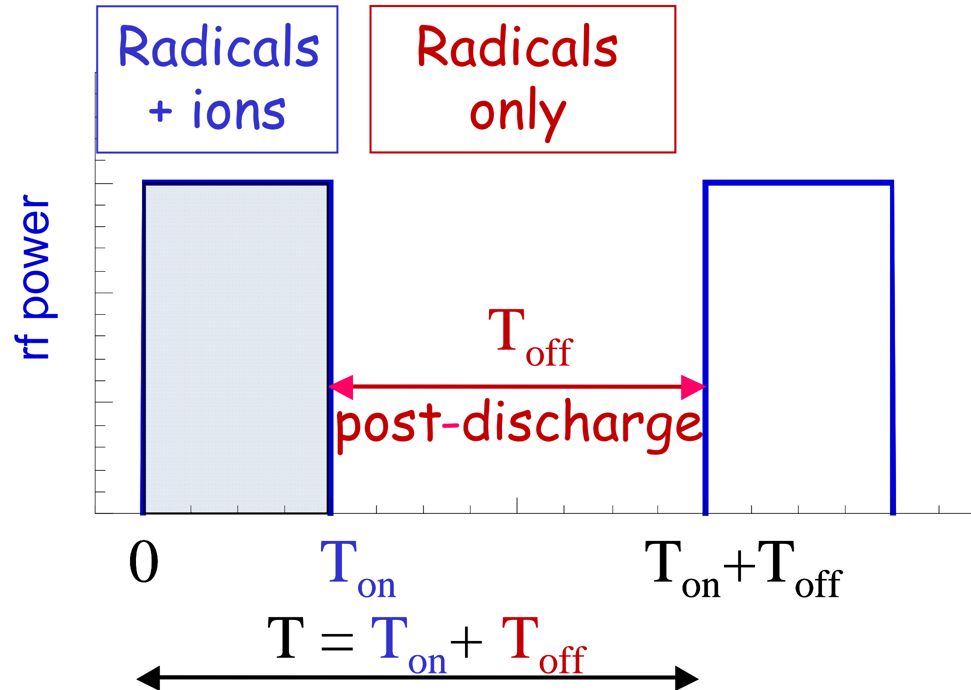
Biased substrate holder (13.56 MHz)

HMDSO or TIPT

TTIP



Characteristic times in pulsed plasmas

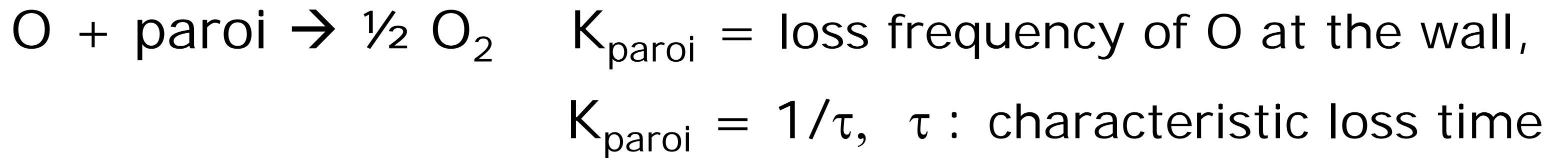


$$DC = \frac{T_{on}}{T_{on} + T_{off}}$$

- **Characteristic times in low pressure plasmas (1 mTorr < p < 1 Torr):**
- **Electron temperature rise and decay : 10-50 µs**
- **Radical lifetime : 1-10 ms**
- **Residence time of stable species : 100-1000 ms**

1 Hz - 100 kHz

O atom kinetics (O in fondamental state)



Plasma created in continuous mode (CW) :

$$[O] = 2\, K_{diss} \times n_e \times [O_2] / K_{paroi} = t \times K_{diss} \times n_e \times [O_2]$$

Plasma created in pulsed mode :

$$[X]_{ON}(t) = [X]_{max} \cdot \left[1 - \exp\left(-\frac{t}{\tau_{on}}\right)\right]$$

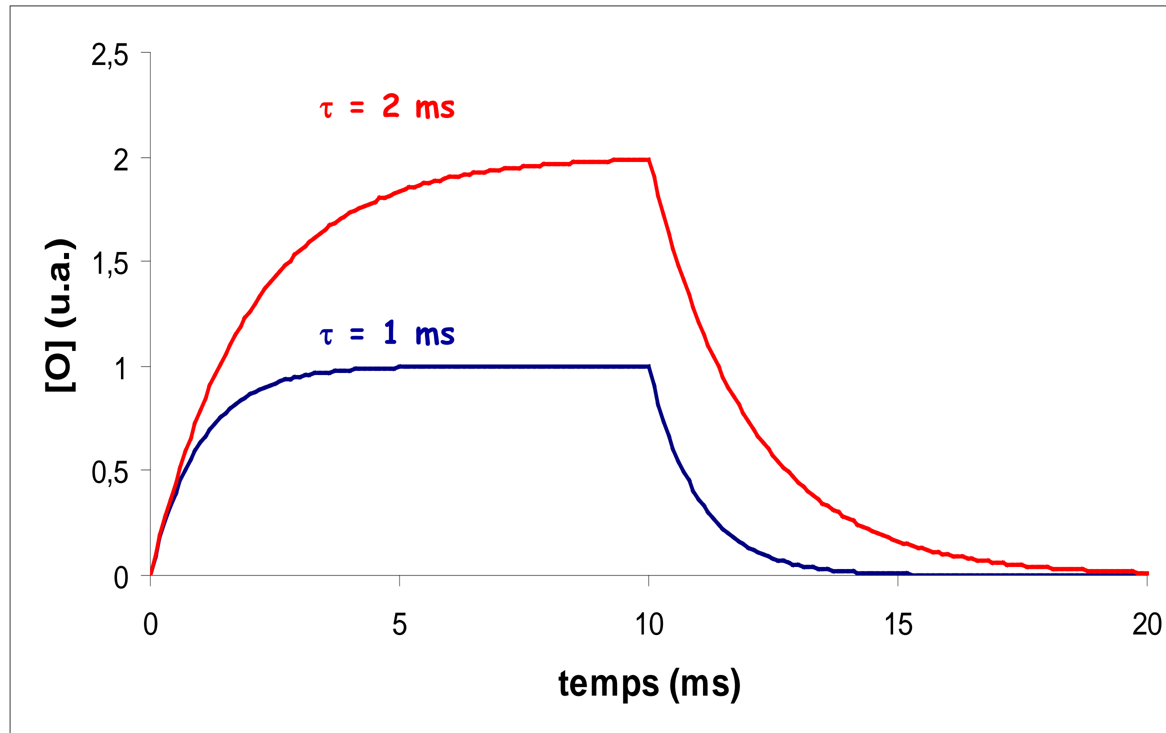
$$[X]_{off}(t) = [X]_{max} \cdot \exp\left(-\frac{t}{\tau_{off}}\right)$$

Kinetics of X atoms in fundamental state

if τ is doubled (i.e. K_{paroi} divided by 2)

→ creation of X 2 times more slowly

→ density of X at the stationnary state multiplied by 2



Determination of [O] from I_O/I_{Ar}

O_2 (+ 5% Ar) - O line at 844.6 nm and Ar line at 750.4 nm

hypotheses :

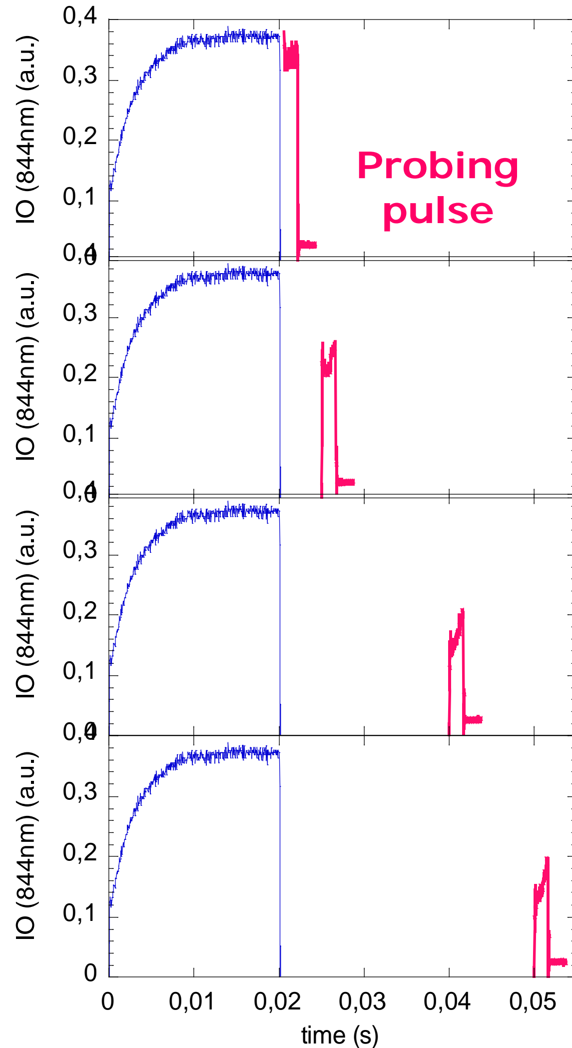
- maxwellian EEDF, T_e measured in O2 plasma (T_e = 3.5 eV)
- O + e → O* + e et O_2 + e → O* + O + e (*Walkup et al, 1986*)
- Ar + e → Ar* + e (*Lawrence, 1976*)
- O* and Ar* lost by radiative deexcitation
- C(λ) response of the optical system (measured)

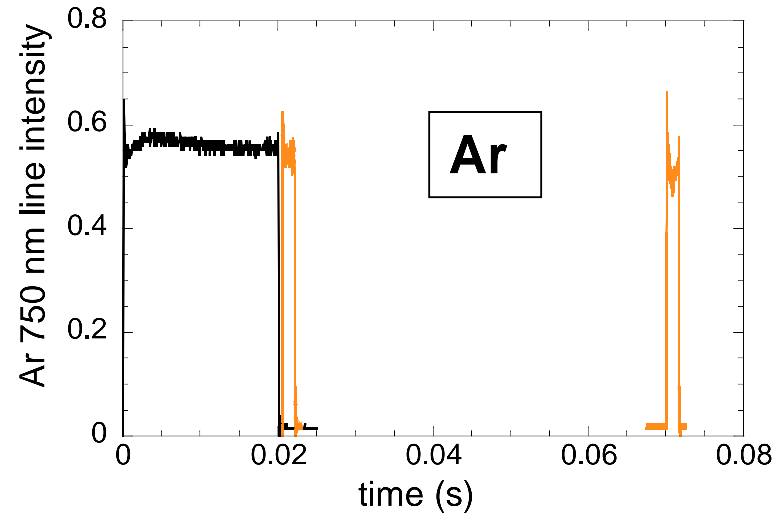
$$\frac{I_O}{I_{Ar}} = \frac{C(\lambda_O)}{C(\lambda_{Ar})} \times \frac{\nu_O}{\nu_{Ar}} \times \frac{k_{exc}^{O}[O] + k_{diss}^{O_2}[O_2]}{k_{exc}^{Ar}[Ar]}$$

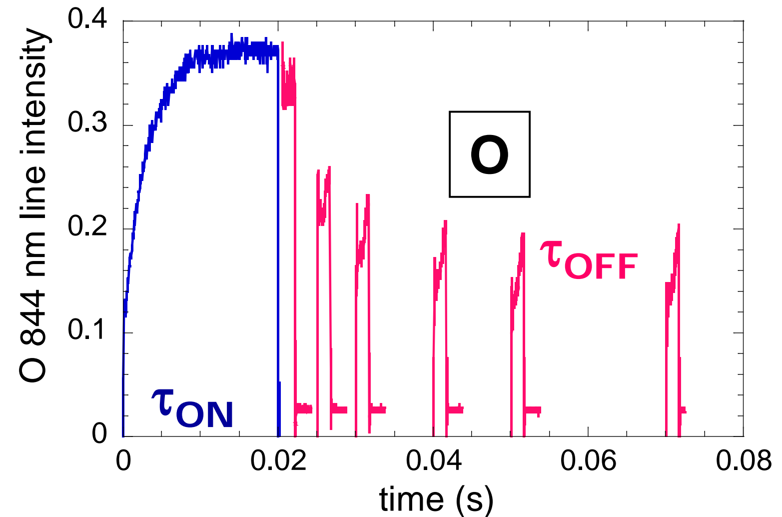
A. Granier et al , J. Appl. Phys 75, 101 (1994)

A. Granier et al, Plasma Sources Sci. Technol. 97, 147 (1997)

Time Resolved Optical Emission Spectroscopy

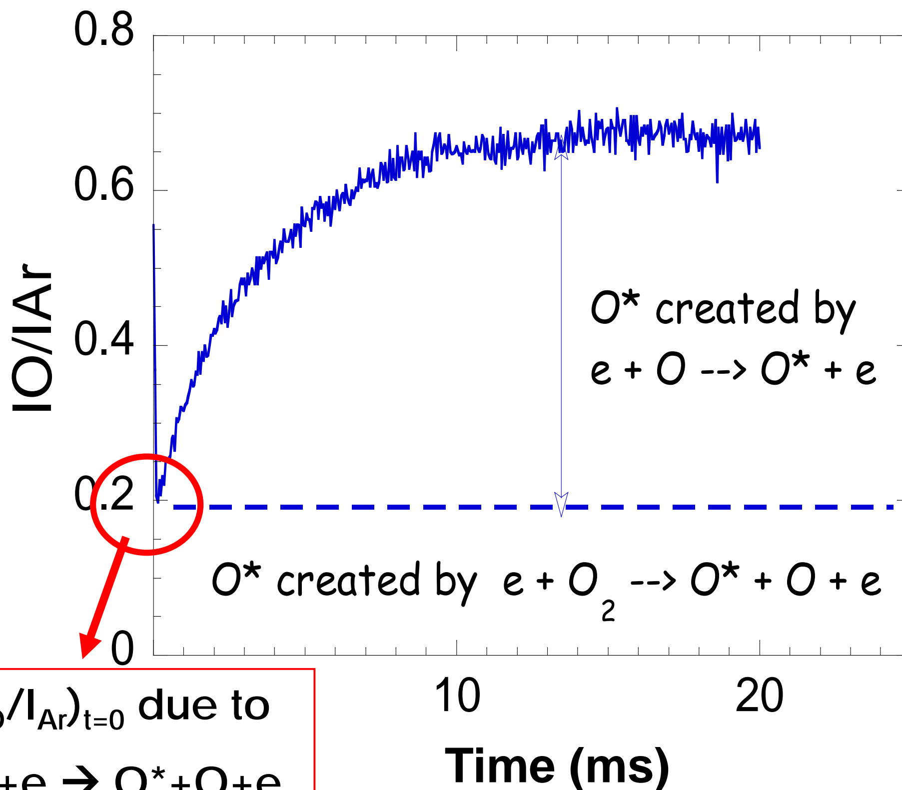




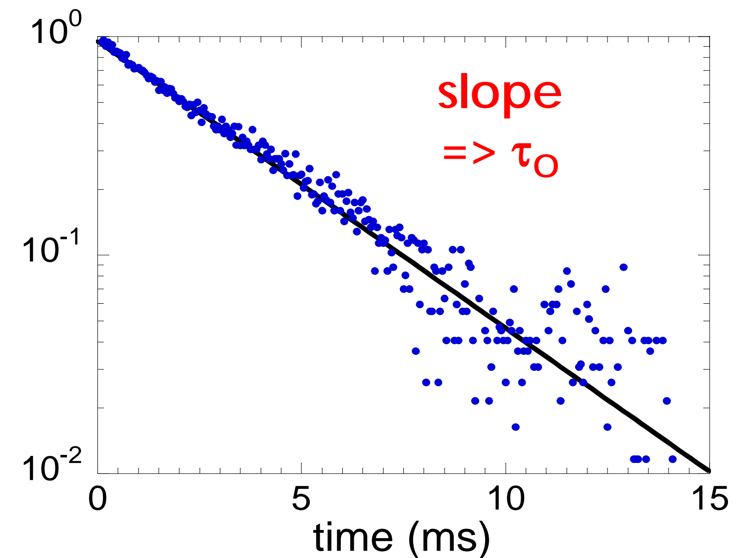


A. Bouchoule, P. Ranson – J. Vac. Sci. Technol. A 9(2) (1991) 317.

Determination of γ_O from $I_{O\ 844nm}/I_{Ar\ 750\ nm}$ (T_{on})



$(I_O/I_{Ar})_{t=0}$ due to
O_2+e → O*+O+e



$$\frac{I_O}{I_{Ar}} = \frac{C(\lambda_O)}{C(\lambda_{Ar})} \times \frac{\nu_O}{\nu_{Ar}} \times \frac{k_{exc}^{O}[O] + k_{diss}^{O_2}[O_2]}{k_{exc}^{Ar}[Ar]}$$

$$\tau_{on} = \tau_{diff} + \tau_{loss}$$

$$\tau_{on} = \frac{\Lambda_0^2}{D} + \frac{V}{A} \cdot \frac{2(2-\gamma_{on})}{\bar{v}.\gamma_{on}}$$

Chantry et al J. Appl. Phys. 62, 1141 (1987)

→ γ_O

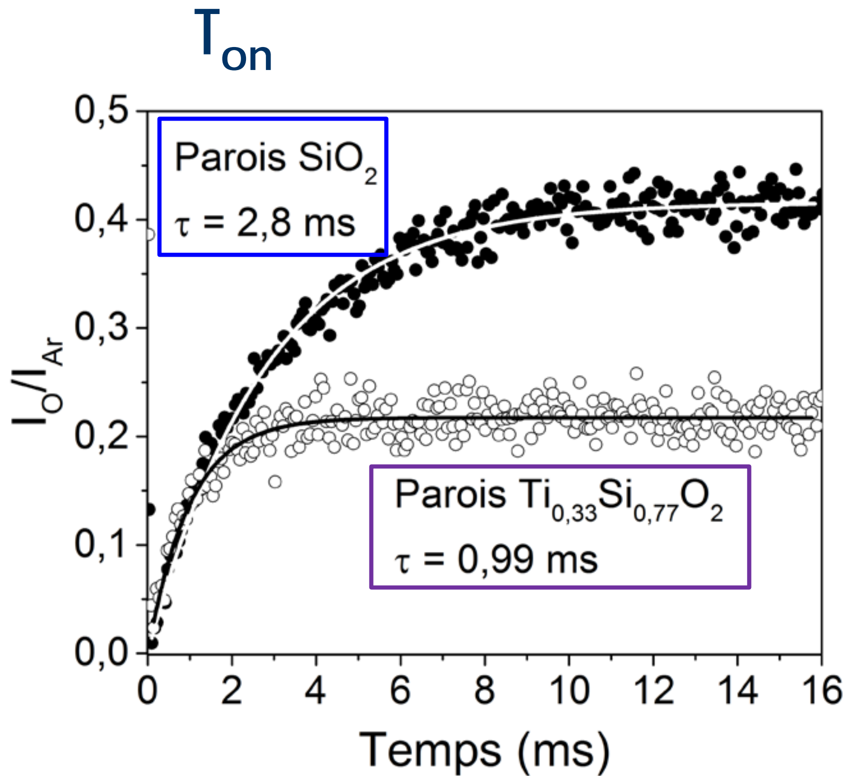
Oxygen plasma created under the same conditions (pressure, power) with the walls covered with different materials:

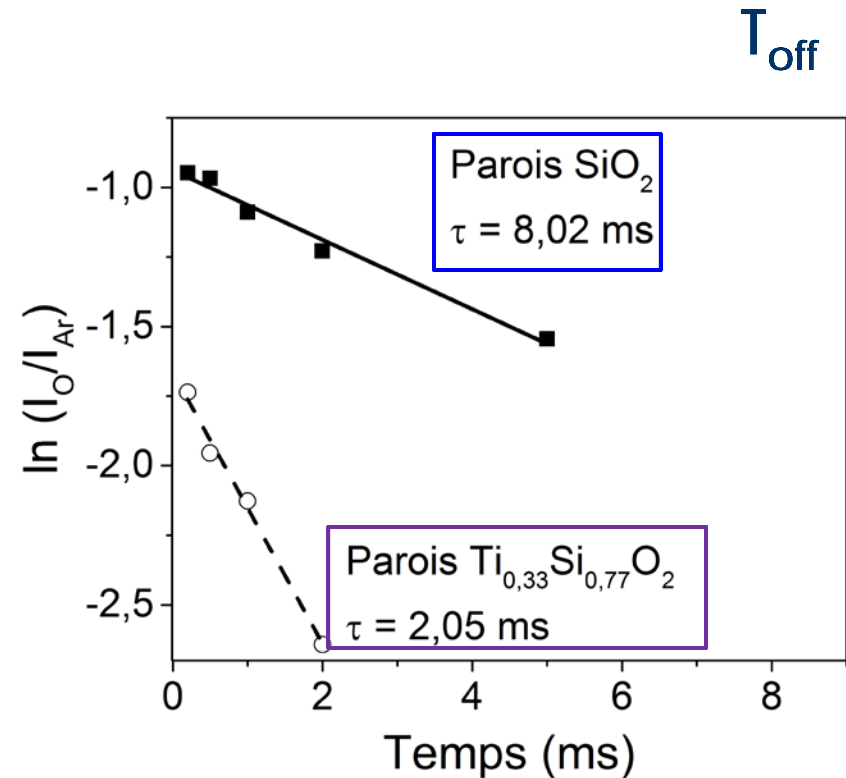
- SiO_2 (deposited in O_2/HMDSO plasmas)
- **TiO_2 (deposited in O_2/TTIP plasmas)**
- **$Ti_xSi_{1-x}O_2$ (deposited) in O_2/HMDSO/TTIP plasmas**

Influence of the wall nature on O kinetics in O_2 plasmas (T_{on})

5 Hz, T_{on} = 20 ms, T_{off} = 180 ms

T_{on} T_{off}





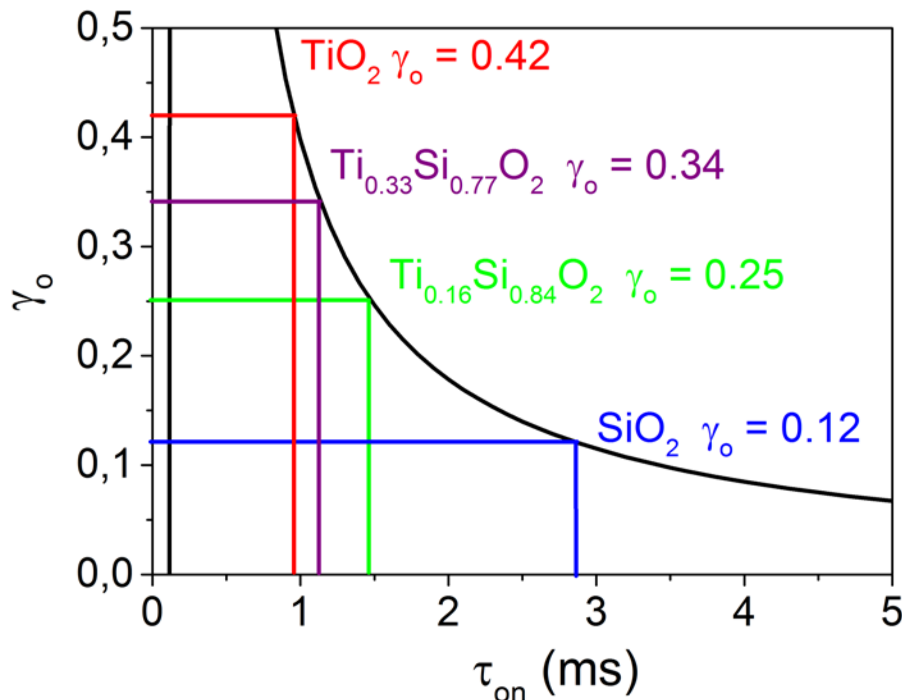
Thèse A. Bousquet (2005), Thèse de S. Elisabeth (2015)

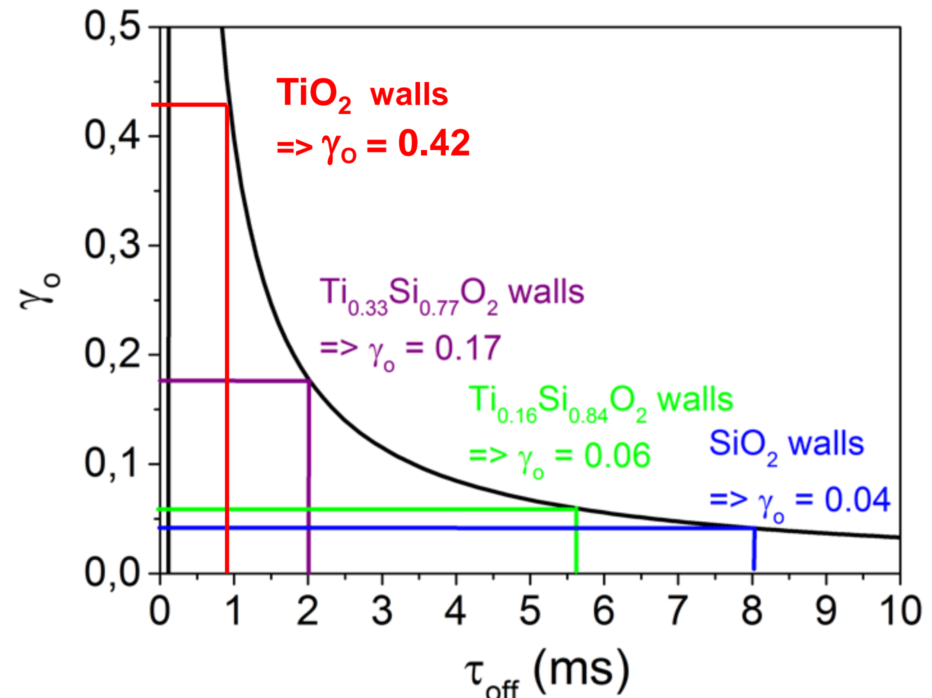
A. Bousquet, A. Goullet, A. Granier dans "Plasmas Froids. Interactions Plasma-Surface : Modèles, Diagnostics et Procédés». Collection : Intégrations, Vol 7 – Ed. G Lelièvre, MRCT CNRS 2011 ISBN 978-2-918701-05-7 (2011), pp 211-234.

Influence of the wall nature on γ_O in O_2 plasmas (T_{on} & T_{off})

Chantry et al J. Appl. Phys. 62, 1141 (1987)

$$\tau = \tau_{diff} + \tau_{loss} = \frac{\Lambda_0^2}{D} + \frac{V}{A} \cdot \frac{2(2-\gamma)}{\bar{v}.\gamma}$$





Thèse de S. Elisabeth (2015)

A. Bousquet, G. Cartry, A. Granier, Plasma Sources Science and Technology 16, 597-605 (2007)

Influence of the wall nature on γ_O in O_2 plasmas (T_{off})

wall material	γ_O (T_{on})	γ_O (T_{off})
TiO_2	0.42 ± 0.2	0.42 ± 0.2
$Ti_{0.33}Si_{0.67}O_2$	0.34 ± 0.1	0.17 ± 0.05
$Ti_{0.16}Si_{0.84}O_2$	0.25 ± 0.1	-
SiO_2	0.12 ± 0.02	0.04 ± 0.01

- γ_O (T_{on}) decreases as Si added to TiO_2, from 0.42 on TiO_2 to 0.12 on SiO_2
- TiO_2 : same (high) value of γ_O during T_{on} and T_{off}
- SiO_2 : γ_O reduced by a factor 3 in the post-discharge

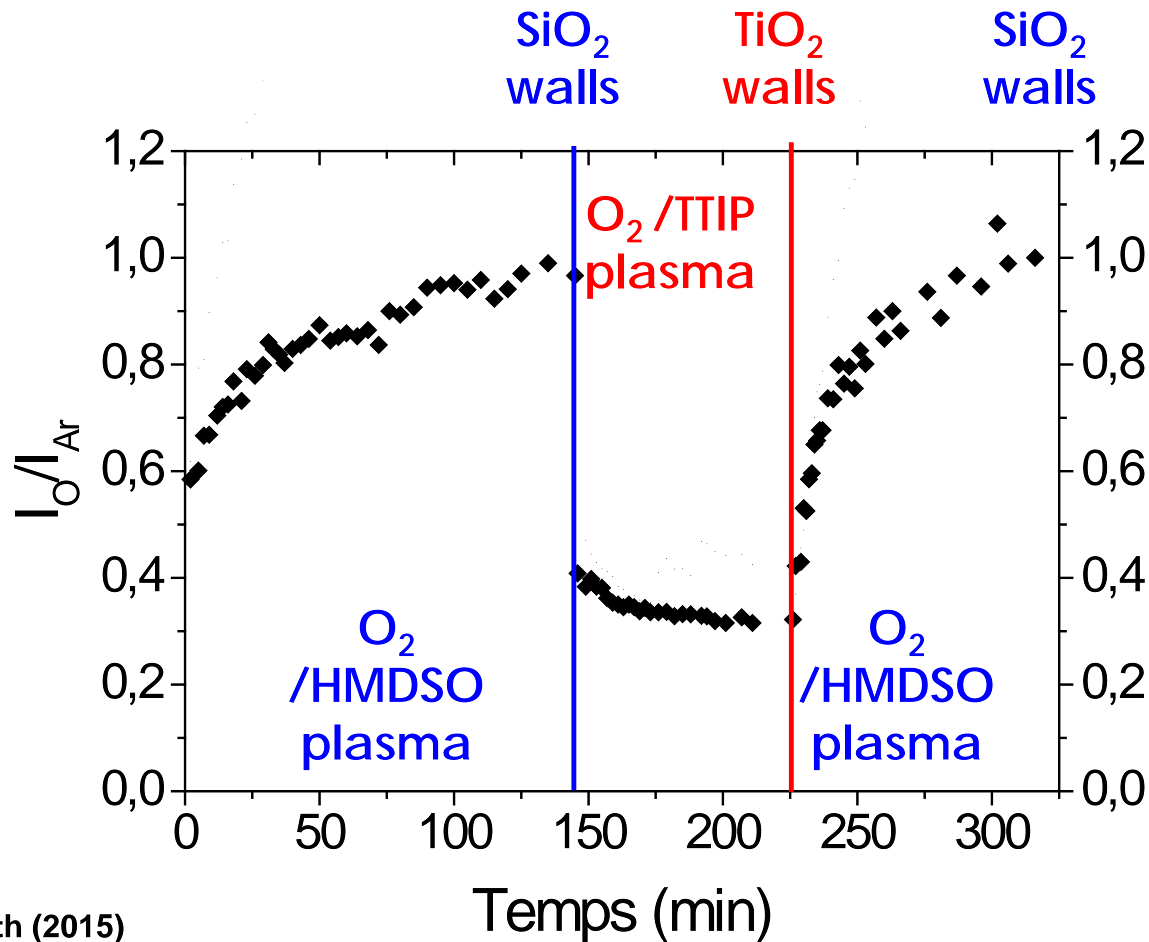
consistent with the literature and attributed to ion induced recombination and absence of ion bombardment during the post-discharge

Thèse A. Bousquet (2005), Thèse de S. Elisabeth (2015)

O atom kinetics studied by TROES in pulsed O_2/TIPT and O_2/HMDSO plasmas

In situ demonstration of the strong effect of the nature of the oxide covering the wall by OES : O atoms

I_O/I_{Ar} monitored during successive cycles of O_2/HMDSO and O_2/TTIP plasmas



Thèse de S. Elisabeth (2015)

O atom kinetics in O_2/TTIP and O_2/HMDSO plasmas

PECVD plasma	γ_O (T_{on})	O_2 plasma on	γ_O (T_{on})
O_2/TTIP 98.5 : 1.5	0.42 ± 0.2	TiO_2	0.42 ± 0.2
O_2/HMDSO 99.5 : 0.5	0.065 ± 0.01	SiO_2	0.12 ± 0.02

- TiO_2 walls : same value of γ_O in O_2/TTIP plasmas and O_2 plasma
- SiO_2 walls : **γ_O in O_2/TTIP plasmas = 0.5 x γ_O in O_2 plasma**

attributed to OH reactivity on reactive sites which limits O recombination in O_2/HMDSO plasma (consistent with results obtained in O_2/HMDSO 85:15 plasmas, where the effect was stronger due to higher OH contents)

Does it mean that O is more reactive than OH on TiO_2 surfaces while OH more reactive than O on SiO_2 surfaces ?

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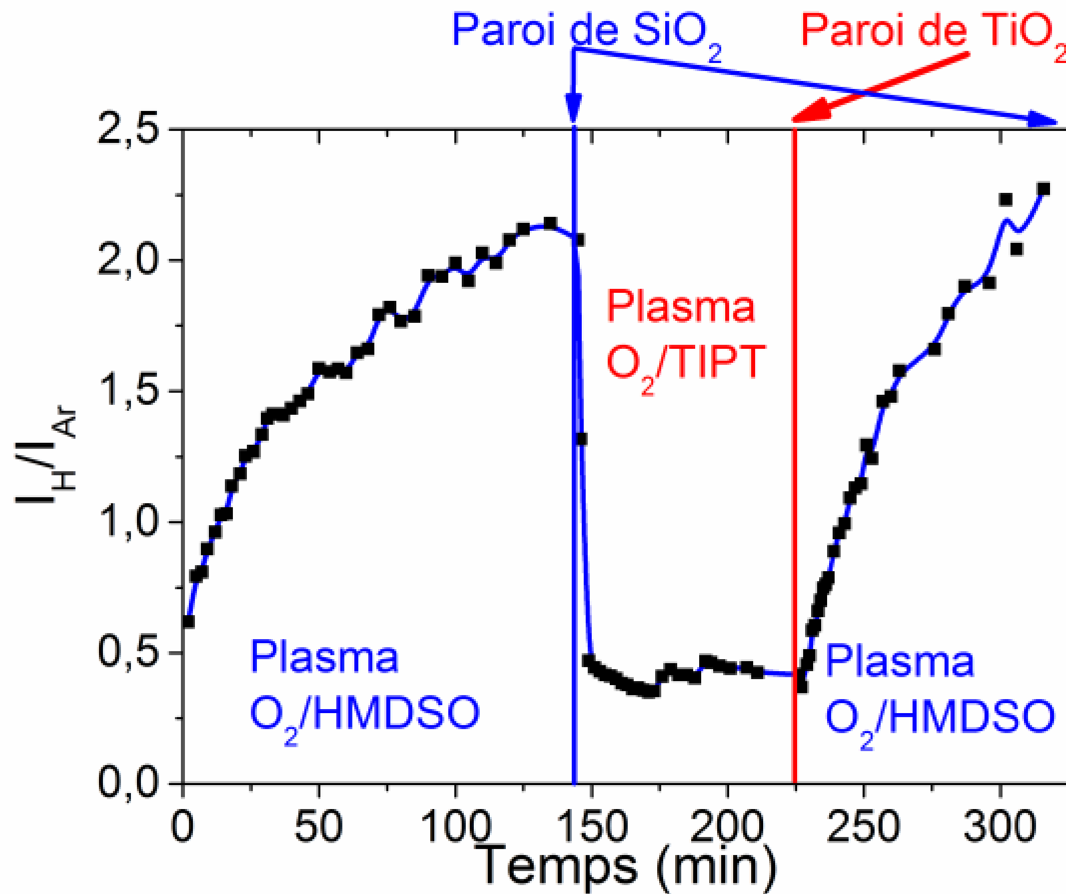
In situ demonstration of the strong effect of the nature of the oxide covering the wall by OES : H atoms

I_H/I_{Ar} monitored during successive cycles of O_2/HMDSO and O_2/TTIP plasmas



Thèse de S. Elisabeth (2015)

H atom kinetics in O_2/TTIP and O_2/HMDSO plasmas

PECVD plasma	γ_H (T_{on})
O_2/TTIP 98.5 : 1.5	0.065 ± 0.2
O_2/HMDSO 99.5 : 0.5	0.01 ± 0.002

γ_H in O_2/TTIP plasmas (TiO_2 walls) = 6 x γ_H in O_2 /HMDSO plasma (SiO_2 walls)

Conclusion

Real difficulty to predict values of recombination frequencies

Atom densities can vary on very large scales according to the nature of the walls for the same discharge parameters (power, pressure…), typically from 1% to several ten percent

Pulsed plasma : for the same « walls » γ values most often different in discharge and post-discharge times

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