*29th EPS Conference on Plasma Phys. and Contr. Fusion Montreux, 17-21 June 2002 ECA Vol. **26B**, P-4.027 (2002)*

# Negative Ions Dynamics and Attachment-induced Ionization Instability in $O_2$, $CF_4$ and $SF_6$ Low-pressure Power Modulated Capacitive RF Plasmas

A. Descoeudres, L. Sansonnens and Ch. Hollenstein

*Centre de Recherches en Physique des Plasmas, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland*

Radio-frequency discharges in electronegative gases are widely used in industrial processes, particularly for the manufacturing of semiconductor devices. Oxygen ($O_2$), sulfur hexafluoride ($SF_6$) and carbon tetrafluoride ($CF_4$) are the main electronegative gases employed for such applications. Inductive plasmas are used for most electronic devices fabrication but capacitively coupled plasmas remain the choice in large area applications such as thin film transistors for flat display.

The presence of negative ions changes considerably the physics of the plasma. Especially, several instabilities linked with the electronegativity of the gas can develop: ionization waves, attachment-induced ionization instability and instabilities attributed to the transition between inductive and capacitive modes in inductive discharges. Furthermore, it is experimentally difficult to do mass spectrometry of negative ions during the discharge. They are indeed electrically trapped within the plasma by the plasma sheath. So, modulated discharges are required to measure them during the afterglow.

Our experimental apparatus is a parallel plate capacitively coupled reactor comprising two stainless steel cylindrical electrodes 13 cm in diameter with a 2.5 or 4 cm electrode gap. The typical plasma parameters used are: gas pressure 0.1 – 0.4 mbar, gas flow of 13 sccm $SF_6$, of 20 sccm $CF_4$ and of 50 sccm $O_2$, RF power up to 100 W at 13.56 MHz. A low frequency (50 Hz – 1 kHz) square wave modulation is applied to the high frequency excitation. This modulation permits the measurements of the negative ions during the afterglow and to differentiate between transient and steady-state phenomena.

For the characterization of the plasma, we use a voltage probe connected directly to the RF electrode to measure the peak-to-peak voltage. A Scientific Systems Langmuir probe coupled to a boxcar integrator is used to obtain time resolved current-voltage characteristics. We measure the global emission intensity with a Perkin Elmer C953 photomultiplyer and quartz fiber optics. Finally, we use a Balzers PPM422 mass spectrometer combined with a EG&G Ortec multi channel scaler to obtain time resolved ions flux measurements.

As shown in Fig. 1, the negative ions dynamics are different for the three studied gases.

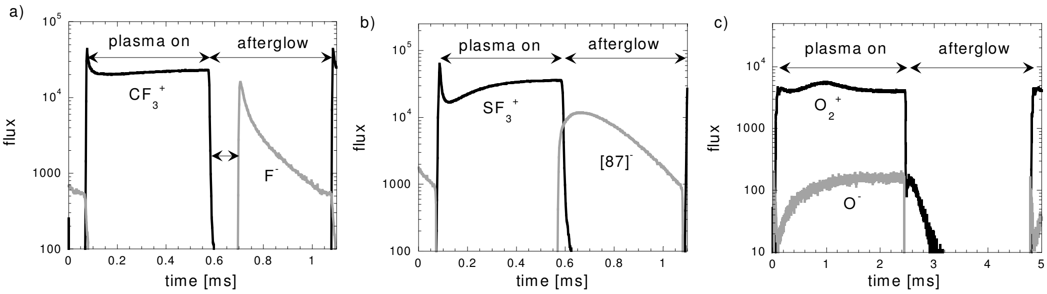


*Fig. 1 : Positive and negative ions flux in a) $CF_4$, b) $SF_6$ and c) $O_2$ plasmas*

A delay of 0.12 ms is measured before the escape of the negative ions in the $CF_4$ plasma (Fig. 1a). This corresponds to the collapse time of the sheath. In $SF_6$, a very short delay is observed (Fig. 1b): the sheath collapses almost instantly. This explains the dependence of the negative ions flux with the modulation frequency in these two plasmas (Fig. 2). The constant delay in $CF_4$ results in a cutoff frequency (4 kHz). At higher frequencies, the modulation period is shorter than the sheath collapse time, and therefore no negative ions can escape the plasma anymore. Similar results have been found in silane modulated plasmas [1]. In $SF_6$, the sheath collapse so fast that negative ions can be measured up to 100 kHz. The $O_2$ plasma, weakly electronegative, behaves completely differently. A small amount of negative ions is measured during the discharge, but no negative ions are observed during the afterglow (Fig. 1c). The attachment and ionization cross sections given in Fig. 3 are useful to understand the origin of the differences observed.

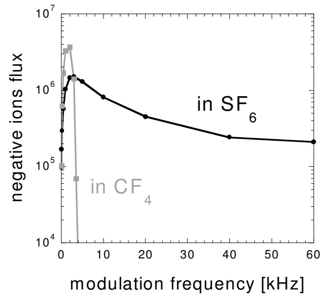


*Fig. 2 : Negative ions flux vs modulation frequency*

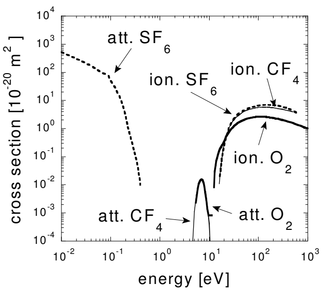


*Fig. 3 : Ionization & attachment cross sections*

The $SF_6$ stands out from the two other gases by his very efficient low energy attachment. In the beginning of the afterglow, electrons are rapidly attached to form negative ions. This is the cause of the fast collapse of the sheath. The weak luminosity and the low self bias voltage of this plasma illustrate his strong electronegativity (low electronic density). The negative ions in $CF_4$ plasma are created by high energy electron attachment, so they can be formed only during the discharge. Therefore in the afterglow the low energy electrons are lost by diffusion and not by attachment. This electrons loss process is slower and the negative ions are still trapped for about 0.1 ms by the remainig sheath. In $O_2$ discharges, detachment reactions of $O^-$ by $O_2(a^1\Delta_g)$ metastables are very effective. This is the reason why we do not measure negative ions in the afterglow. The negative ions observed during the discharge mut result from indirect formation at the mass spectrometer orifice.

An unstable phenomenon can develop in $O_2$ and $CF_4$ discharges under specific conditions of power and pressure: between 185 and 490 V in $O_2$ (resp. 220 and 550 V in $CF_4$) at 0.25 mbar, above 0.195 mbar in $O_2$ (resp. 0.1 mbar in $CF_4$) at 250 V. This instability behaves globally in the same way in these two plasmas, but $SF_6$ discharges remain stable under any conditions. The stability of this plasma will be explained further.

Oscillations in the kHz range are detected simultaneously with all our available diagnostics. Fig. 4 shows such oscillations on voltage envelope, positive ions flux, light emission and floating potential in $O_2$ plasmas.

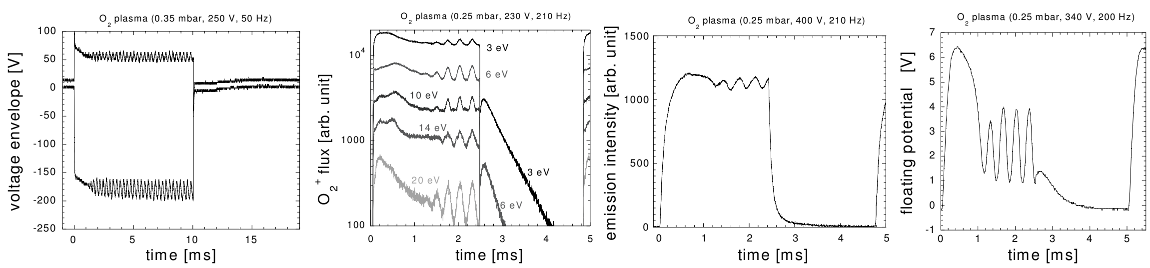


*Fig. 4 : Instability observation on voltage envelope, positive ion flux, light emission and floating potential*

Discharges in mixtures of electronegative and electropositive gases show directly the link between negative ions and the instability. The amplitude of the oscillations increases with the concentration of the electronegative gas.

These oscillations are due to the attachment-induced ionization instability described in details by Nigham and Wiegand [2]. The instability mechanism can be summarized with Fig. 5. A small initial increase in the electronic density $n_e$ is generally followed by a decrease in the electronic temperature $T_e$ due to the quasi-steady nature of the electron energy response. This diminution of $T_e$ has different consequences according to the nature of the gas. In electropositive plasmas, electrons are created by ionization and lost mainly by diffusion to the walls. Ionization is less effective if $T_e$ is diminished, so the electronic density decreases. This negative feedback stabilizes the perturbation. In electronegative plasmas, electrons can also be lost by attachment, and the efficiency of this process depends on electronic temperature. In certain cases, the attachment can become less effective than ionization if $T_e$ decreases. Consequently, the initial disturbance is reinforced by this positive feedback and the discharge becomes unstable. In this type of instability, $n_e$ and $T_e$ are the physical values that are the source of the oscillations, leading to changes on the other measurable values.

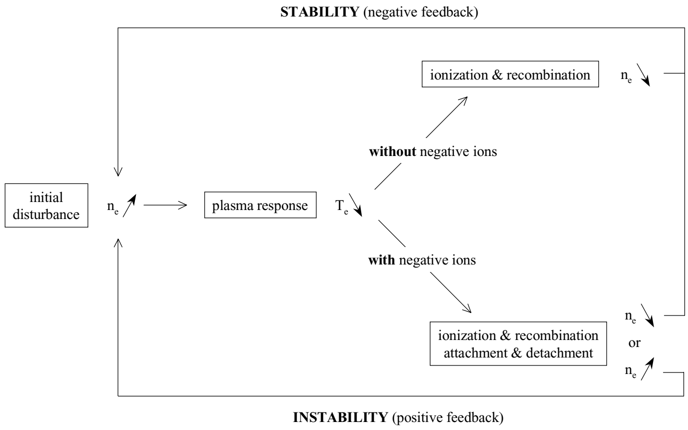


*Fig. 5 : Instability mechanism*

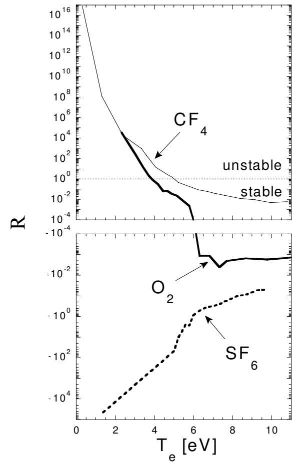


*Fig. 6 : Instability criterion*

This general description can be specified with a necessary condition for the appearance of the instability, derivated from the conservation equations of electronic and ionic densities [2]. The plasma can be unstable if

$$R = \frac{k_a \hat{k}_a}{k_i \hat{k}_i} > 1$$

where $k_j = \sqrt{\frac{2e}{m_e}} \cdot \int_0^\infty \sigma_j(E) \cdot f(E) \cdot E \cdot dE$ and $\hat{k}_j = \frac{T_e}{k_j} \cdot \frac{\partial k_j}{\partial T_e} \equiv \frac{\partial \ln k_j}{\partial \ln T_e}$

Practically, the criterion is fulfilled if the attachment rate coefficient increases with electronic temperature and if attachment and ionization rate coefficients are of a magnitude at least comparable (electronic density of the same order of magnitude than negative ions density).

Fig. 6 shows calculations of the ratio R for the three gases ( *f* calculated with Bolsig from Kinema Software [3]). The ionization cross sections and therefore the ionization rate coefficients are quite similar for the three gases. But $SF_6$ differs from $O_2$ and $CF_4$ by his attachment cross section. The calculations of R demonstrate that $O_2$ and $CF_4$ plasmas can be unstable at low electronic temperature. On the contrary, the $SF_6$ plasma always remains stable because the attachment rate coefficient decreases with $T_e$ ($R < 0$ at any electronic temperature). The peculiar attachment cross section is the source of the stability of $SF_6$ discharges.

[1] Howling A A, Sansonnens L, Dorier J-L and Hollenstein C 1994 *J. Appl. Phys.* **75** 1340

[2] Nighan W L and Wiegand W J 1974 *Phys. Rev. A* **10** 922

[3] Pitchford L C, O'Neil S V and Rumble J R 1981 *Phys. Rev A* **23** 294