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Kinetics of O and H atoms in pulsed O_2/HMDSO low pressure PECVD plasmas

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The O and H atom kinetics in a low pressure inductively coupled radiofrequency O_2/Hexamethyldisiloxane and water vapour pulsed plasma is investigated by Time-Resolved Optical Emission Spectroscopy. The O and H-atom loss coefficients in the post-discharge of O_2/HMDSO pulsed plasmas were measured to be 210^{-3} and 3.10^{-4} respectively. Such low recombination coefficients, as compared to the ones measured in oxygen plasmas ($\approx 10^{-2}$), are attributed to the adsorption of OH and H_2O at the reactor walls which limits the O and H atom recombination. O and H atoms are likely to be responsible for HMDSO dissociation and subsequent film deposition during the post-discharge.

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1. Introduction

New applications of low-pressure plasmas for thin film deposition often demand precise control of the film structure and properties. This can be reached by using pulsed plasmas which allow an additional control of the active neutral and charged species fluxes [1-3]. In the case of SiO_2-like thin film deposited in low pressure inductively coupled plasma in O_2/hexamethyldisiloxane (HMDSO) mixtures, it was shown that the pulse parameters significantly affect the structure as well as the optical and mechanical properties of the film [4-5]. In addition it was shown that deposition occurs in the post-discharge on times as long as a few ten ms. In order to interpret such a surprising result the O and H atom kinetics was investigated in low pressure pulsed O_2/HMDSO plasma by Time-Resolved Optical Emission Spectroscopy (TROES).

2. Experiment

The experiments were carried out in a helicon reactor using a O_2/HMDSO 85:15 mixture at a pressure of 0.65 Pa. In pulsed mode, the 300 W radio frequency (13.56 MHz) power was 100% rectangular-wave modulated at 1Hz with a duty cycle of 23 % corresponding to a discharge time T_{on}=230 ms and a post-discharge time T_{off}=770 ms. In these pressure and power conditions, the plasma is inductively coupled. The O-atom was investigated using the O(844nm) and Ar(750nm) lines time resolved emission (5% argon added to the mixture). These lines were chosen since they were previously shown to be the most favorable for the measurement of the O-atom density by actinometry [6,7]. The H_γ (434nm), H_β (486nm) and H_α (656nm) Balmer lines were used to investigate H-atom kinetics In order to monitor O and H during the post-discharge, the short pulse excitation technique proposed by Bouchoule et al was used [8]. During the post-discharge, a second shorter probing pulse of rf power was applied after the main one (with the same power level) in order to create electrons which excite remaining long lived species. The light emitted during this probing pulse was recorded for different delay times Δt between the main and the probing pulse in order to scan all the time in post-discharge. To overcome problems related to the emission peak at the plasma ignition, the probing pulse length was fixed at 1.5ms. The signal at t=0 was extrapolated from the time evolution of the signal after the plasma ignition, as proposed by Rousseau et al [9].

3. Results

In order to validate the TROES technique, measurements were first carried out in a pure oxygen plasma created at the same pressure, RF power and pulse frequency. Results obtained in O_2 and O_2/HMDSO plasmas are successively presented and discussed.

3.1. O_2 plasma

The time variations of O(844nm) and Ar(750nm) lines were recorded in the discharge and the post-discharge.

First, the decay time of the Ar* 750 nm line emission, when the plasma is switched off, was

measured to be less than 50 µs. Time-resolved measurements by Langmuir probe carried out in the pulsed oxygen plasma, which are displayed in Fig. 1, indicate that this time corresponds to the electron temperature decay time in the post-discharge.

Figs. 2a and 2b display the O* to Ar* line intensity ratio measured during the discharge and the post-discharge of a pulsed O_2 plasma (300 W) operating at 0.27 and 0.67 Pa.

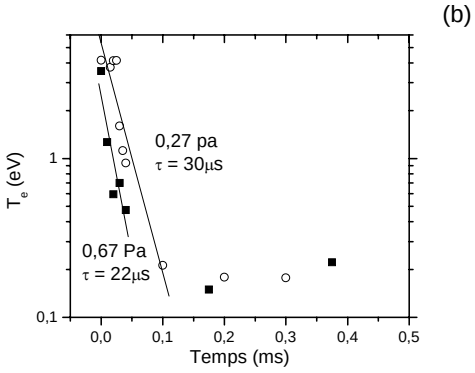

Fig.1. Decay of the electron temperature in the post-discharge of a pulsed oxygen plasma at 0.27 and 0.67 Pa, 300W).

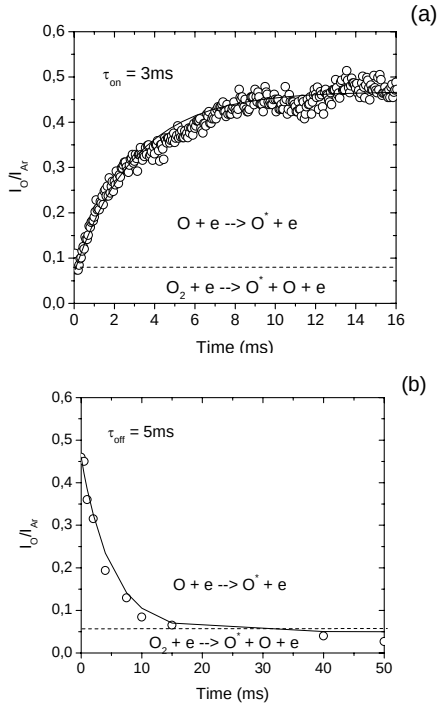

Fig. 2. time variations of O to Ar line intensity ratio in the discharge (a) and post-discharge (b) of the O_2 plasma (300W, 0.67 Pa).

Since the post-discharge time (=770 ms) is longer than the residence time (≈300 ms), all transient species created during the discharge, even stable ones, are lost during the post-discharge. At the beginning of the discharge (at t=0), since only O_2 molecules are present, the signal comes from dissociative excitation of O_2. Then, as this plasma only contains O atoms and O_2 molecules, the upper part of the signal can be attributed to the direct excitation of O-atoms. Hence TROES allows to discriminate the O_2 and O contributions to the 844 nm line emission.

Since the O_2 dissociation rate is expected to be less than 5% [10], the molecular oxygen density can be assumed to be constant during all the period. Hence, the contribution of O_2 dissociative excitation to I_O/I_{Ar} is assumed to be constant and equal to the value measured at t=0 and is subtracted to the measured I_O/I_{Ar} value. Finally, $I_O/I_{Ar}(t)$- $I_O/I_{Ar}(t=0)$ exponentially increases during the discharge and exponentially decreases during the post-discharge. The corresponding time constants, denoted τ_{on} and τ_{off}, are deduced from the measured time variations of I_O/I_{Ar}.

Then, using the Chantry formalism [11], the O atom loss coefficient by recombination at the walls (γ_{on} during the discharge and γ_{off} during the post-discharge) can be derived as follows (the i subscript denotes on or off):

$$\tau_i = \frac{1}{k_i} = \tau_{diff} + \tau_{loss} = \frac{\Lambda_0^2}{D} + \frac{V}{A}.\frac{2(2-\gamma_i)}{\overline{v}.\gamma_i}$$

where D is the atom diffusion coefficient, A is the recombination area, V is the chamber volume, $\overline{v}$ is the atom thermal velocity and Λ_0 is the diffusion length determined by the reactor geometry and dimensions.

Within the precision of the measurements, γ_{on} and γ_{off} are equal to 0.09 ± 0.03, which is in pretty good agreement with values reported in the literature for O-atom recombination on silica under similar plasma conditions [12]. From these measurements it is concluded that direct O-atom excitation by electron impact is the dominant mechanism and that actinometry can be used to monitor O atom kinetics in O_2 plasmas.

3.2. O_2/HMDSO (85:15) plasma

The time behavior of O^*(844 nm), H Balmer lines and Ar^* (750 nm) emission lines were recorded in pulsed O_2/HMDSO 85:15 plasma (300 W, 0.67 Pa).

3.2.1. O-atom kinetics

Figs. 3a and 3b display the time variations of the O to Ar line intensity ratio in the discharge and post-discharge. Before deducing the O-atom recombination constant from these variations, it is worth studying whether O* atoms may be significantly created by dissociative excitation of the stable molecules formed in O_2/HMDSO plasmas, namely O_2, CO, CO_2 H_2 and H_2O molecules. TROES measurements carried out in pure CO_2 and H_2O plasmas (under similar pressure and

power conditions) have previously shown that O* creation by dissociative excitation of CO, CO_2 and H_2O was negligible, so that only O_2 dissociative excitation has to be considered and subtracted from the measured signal (more detail can be found in [13]).

Finally, from the exponential variations of I_O/I_{Ar} the O-atom apparent loss times constants during the discharge (τ_{on}) and the post-discharge (τ_{off}) are found to be equal to 10 ms and 160 ms, respectively, which corresponds to γ_{on}=3 10^{-2} and γ_{off}= 2 10^{-3}.

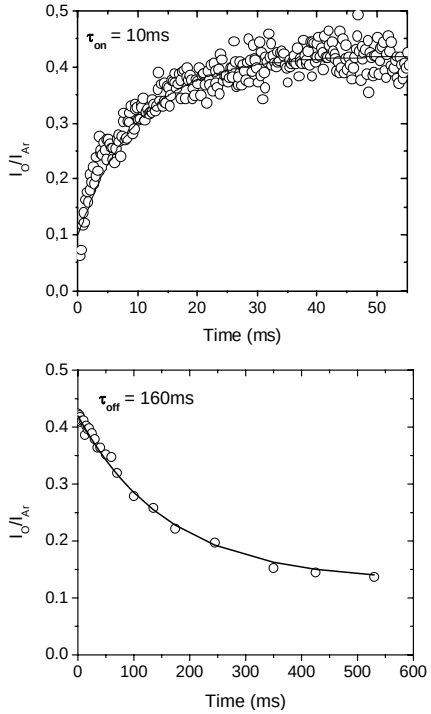

Fig. 3. time variations of O to Ar line intensity ratio in the discharge (a) and post-discharge (b) of the O_2/HMDSO (85:15) plasma (300W, 0.67 Pa).

Table 2. O-atom time constants and loss coefficients determined during the discharge and the post-discharge of pulsed plasmas in different gases (0.67 Pa, 300 W).

Plasmas	Time constants (ms)		Loss coefficients	
	Discharge	Post-discharge	Discharge	Post-discharge
O_2	3	5	0.09 ± 0.03	
CO_2	12	16	0.024 ± 0.002	
H_2O	24	63	0.014 ± 0.002	0.0050 ± 0.0007
O_2/HMDSO 85:15	10	160	0.034 ± 0.002	0.0020 ± 0.0001

The O-atom time constants and loss coefficients determined during the discharge and the post-discharge of pulsed plasmas in different O_2, CO_2, H_2O (for more detail see [13]) and O_2/HMDSO (0.67 Pa, 300 W) are given in Table 2.

3.2.2. H-atom kinetics

The H-atom emission was first investigated in O_2/HMDSO (85:15) plasma. The three Balmer lines were recorded and were shown to follow very similar time variations. The variations of the H_β to Ar line intensity ratio in the discharge and post discharge are displayed in Figure 4. The initial value of I_H/I_{Ar} is almost null which indicates that H* creation by dissociative excitation of HMDSO can be neglected. Assuming that H* is created by direct excitation of ground state atoms, the following values of H-atom recombination coefficient can be deduced : γ_{on}=10^{-3} and γ_{off}=4 10^{-4}.

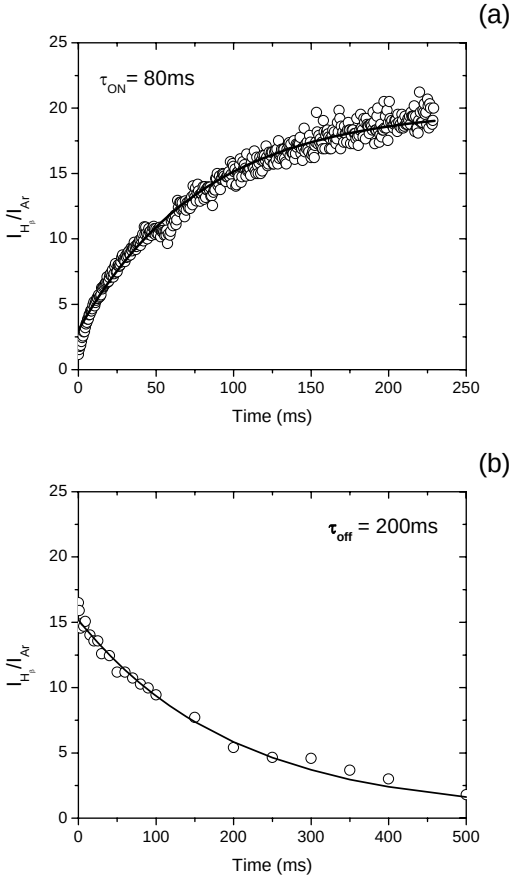

Fig. 4. time variations of H to Ar line intensity ratio in the discharge (a) and post-discharge (b) of the O_2/HMDSO (85:15) plasma (300W, 0.67 Pa).

To get better insight in H* creation mechanisms in O_2/HMDSO, further measurements were carried out in water vapor plasmas. These latter (see Fig.5) show that the creation of H* by dissociative excitation of H_2O has to be taken into account. The H atom recombination

coefficient in water vapor plasma is found to be equal to $2\ 10^{-3}$ in the discharge and 10^{-3} in the post-discharge.

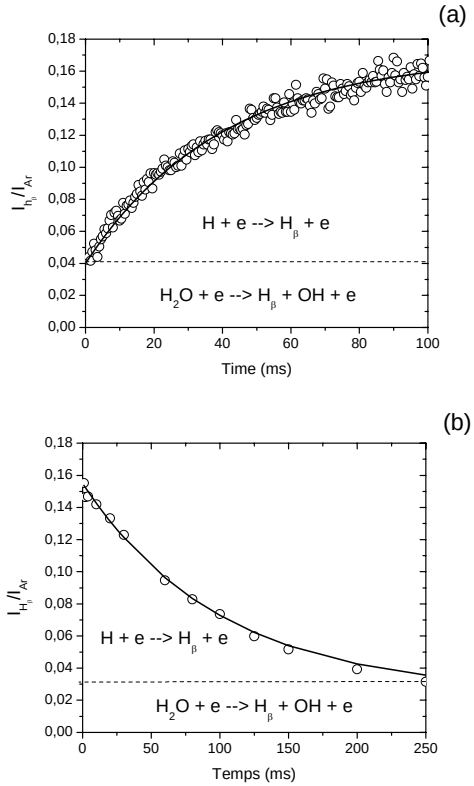

Fig. 5. time variations of H to Ar line intensity ratio in the discharge (a) and post-discharge (b) of the water vapor plasma (300W, 0.67 Pa).

4. Discussion and conclusion

If we look at the O and H-atom kinetics in O_2/HMDSO plasma, it appears that the value of γ is very low during the post-discharge (γ_{off} = 2.10^{-3} for O and 4.10^{-4} for H) compared to the one measured during the discharge (γ_{on} = 3.10^{-2} for O and 10^{-3} for H). Although slightly smaller, these values are very close to the ones measured in pulsed H_2O plasma both in the post-discharge (equal to 5.10^{-3} and 10^{-3}, respectively) and the discharge (equal to $1.5.10^{-2}$ and 2.10^{-3}, respectively.

The H_2O and/or OH molecules created during the O_2/HMDSO discharge are likely to play the same role as in pure water vapor plasma: they are absorbed at the walls, which limits the number of sites available for atomic oxygen and hydrogen recombination and thus reduces the O and H-atom loss coefficient.

During the discharge, this effect is reduced due to ion bombardment upon the reactor walls, which facilitates OH and H_2O desorption [14]. Hence, the surprising long O and H-atom lifetimes in post-discharge are attributed to the wall adsorption of H_2O or OH molecules formed in O_2/HMDSO plasma.

Furthermore, the long lifetime of oxygen atoms, which are able to dissociate HMDSO [13], could explain that the deposition proceeds for several tens of milliseconds after the power switch-off. Using the cross section measured by Kudrle et al [15] and considering a pressure of 0.67 Pa and a density of O-atoms equal to 20% of the neutral density, the frequency for O-atom loss by homogeneous reaction with HMDSO (equal to $[O].k_{O/HMDSO}$) is estimated at 0.7 s^{-1}. Since this value is very low compared to the O-atom surface loss frequency during both the discharge and the post-discharge (around 100 and 6 s^{-1}, respectively), the homogeneous reaction between O atoms and HMDSO molecules during the post-discharge allows HMDSO dissociation during times as long as several tens of milliseconds, without significant depletion of the O-atoms. Similarly, long lived H atoms may also contribute to HMDSO dissociation in the post-discharge.

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