Investigation of plasma surface interactions in pulsed O_2/TTIP low pressure ICP plasma by time resolved optical emission spectroscopy

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Pulsed O_2 and O_2/TTIP (tetraispopropoxide) plasmas created in a low pressure inductively coupled RF plasma were analysed by time resolved optical emission spectroscopy (TROES). Using TROES, O, H, OH species creation and loss kinetics were investigated. The O atom recombination probability is estimated at 0.5 ± 0.2 in oxygen plasmas and 0.25 ± 0.1 in 99:1 O_2/TTIP plasma while the H atom recombination probability is found to be equal to 0.014 ± 0.005. Results obtained in O_2/TTIP discharges are compared to those previously obtained in O_2/HMDSO pulsed plasmas created in the same reactor and similar plasma conditions. It is shown that O and H creation and loss characteristic times are much shorter in O_2/TTIP plasmas than in O_2/organosilicon plasmas.

Titanium dioxide films (TiO_2) have been extensively studied for a large range of applications including photocatalysis, photovoltaic cells, optical coatings and waveguides. TiOx films can be prepared by reactive magnetron sputtering or plasma enhanced chemical vapour deposition (PECVD) using oxygen/titanium tetraisopropoxide (TTIP - $Ti[OCH(CH_3)_2]_4$) mixtures. TiO_2 film deposition by magnetron sputtering has been largely investigated in the literature and is known to allow the deposition of dense polycrystalline films, in anatase and/or rutile phase as well as porous films integrated in dye solar cell for instance. The literature related to PECVD deposition is less important and most studies concern the deposition in capacitively coupled RF plasma. PECVD is known to be a versatile process allowing to prepare films with tunable properties (for instance tunable refractive index). More recently, low pressure high density plasmas, such as microwave electron cyclotron resonance (ECR) plasmas [1] and inductively coupled RF (ICP) plasma sources [2] have been shown to allow deposition of amorphous and partially crystallized (anatase and/or rutile phases) films at temperature less than 100°C. On the other hand, very few studies deal with the analysis of TTIP based plasmas and relations between the film structure and the composition of the plasma.

In this study we investigate an inductively coupled RF (ICP) O_2/TTIP plasma operated at 4 mTorr with an RF power coupled to the ICP source of 400 W. TTIP is heated at 60°C and its vapor can be introduced in the diffusion chamber (via a line heated at 62°C), either pure (for very low TTIP fractions) or using oxygen as a bubbling gas. The pulsed O_2 and O_2/TTIP plasmas were analysed by time resolved optical emission spectroscopy (TROES), carried out in the diffusion plasma. In order to probe the post-discharge, a second pulse was applied to monitor the active species decay in the post-discharge using the method proposed by A.Bouchoule et al [3] and previously developed in pulsed O_2/HMDSO plasmas [4-5].

TROES measurements were carried out in pulsed discharges created in pure oxygen (more exactly O_2/Ar 95:5) and different O_2/TTIP mixtures (99:1 and 95:5). The plasma on time (denoted T_{on}) was varied from 10 to 50 ms at a frequency f equal to 5 Hz. O, H, OH species creation (in the discharge) and loss (in the post-discharge) kinetics were investigated.

The time variations of the intensities of the following lines (denotes I_X) were recorded : Ar line at 750.4 nm; O line at 844.6 nm, Hα line at 656 nm and OH emission at 310 nm. The time variations of I_O/I_{Ar} and I_H/I_{Ar} during the discharge are plotted in figure 1. From these curves, which exhibit exponential variations; on can derive characteristic creation times of 0.8 ms for O in the oxygen plasma and characteristic times of 1.5 ms for O and 4.5 ms for H in the 99:1 O_2/TTIP plasma. Recombination probabilities of O and H on the amorphous TiO_2 walls of the reactor can be deduced from theses characteristic times, assuming the Chantry formalism. The O atom recombination

probability (γ_O) is estimated at 0.5 ± 0.2 in oxygen plasmas and 0.25 ± 0.1 in 99:1 O_2/TTIP plasma while the H atom recombination probability (γ_H) is found to be equal to 0.014 ± 0.005.

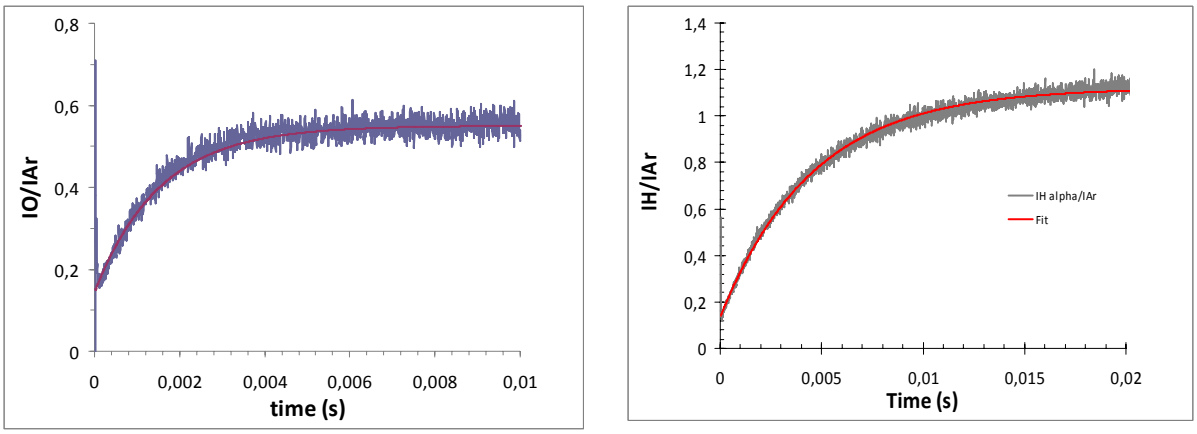

Fig. 1: Time variations of the O and H line emissions (normalized to the Ar line intensity) during the discharge Ton = 30 ms, T_{off} = 170 ms, f = 5 Hz

Results obtained in O_2/TTIP discharges are finally compared to those previously obtained in O_2/HMDSO and O_2/TEOS pulsed plasmas created in the same reactor and similar plasma conditions, but in a reactor covered with a SiO_2-like film. It is shown that O and H creation and loss characteristic times are much shorter in O_2/TTIP plasmas than in O_2/organosilicon plasmas [4-5].

In pure oxygen plasma, γ_O varies from 0.5 in the case of the reactor covered with amorphous TiO_2 to 0.09 for the reactor covered with SiO_2.

In O_2/TTIP plasma, the difference is amplified as far as γ_O varies from 0.25 onTiO_2 walls to 0.03 on SiO_2 walls, which means that O atom recombination probability is ten times higher on amorphousTiO_2 than SiO_2. On the other hand, γ_H varies from 0.015 on TiO_2 walls to 0.001 on SiO_2 walls, which again corresponds to a H atom recombination probability which is 15 times higher on amorphous TiO_2 than SiO_2.

To conclude, Time resoved optical emission spectroscopy measurements carried in low pressure O_2 and O_2/TTIP plasmas has allowed to determine recombination probabilities of O and H on TiO_2 amorphous walls. Up to our knowledge, while the literature devoted to O and H recombination on SiO_2 and glass walls is very rich, these measurements are likely to be the first ones for O and H recombination probabilities on TiO_2 walls.

References

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