Oxygen atom kinetics in pulsed Radiofrequency Capacitively-coupled plasmas at intermediate pressures

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Radiofrequency capacitively-coupled plasmas (RF-CCP) operating at intermediate gas pressures (1-10 Torr) are significant for many applications, notably thin film deposition (PECVD), but have been much less studied than lower pressure RF-CCPs because common diagnostic techniques (such as Langmuir probes) cannot be used. Modelling of RF plasmas in this pressure range is also difficult, because Particle-in-cell simulations become prohibitively slow, whereas fluid models are unable to correctly describe the electron kinetics due to non-local and time dependent effects. We are studying a highly-symmetric CCP reactor (aluminium, 50 cm diameter with a 2.5 cm gap), excited at 13.56 MHz in pure O_2 at pressures from 1 to 8 Torr. The oxygen atom density and gas temperature are determined by mono-mode laser cavity ringdown spectroscopy (CRDS) at 630nm [1]. These results are complimented with measurements of the plasma impedance (giving the true voltage, current and power absorbed by the plasma) and the ion flux to the grounded electrode.

Figure 1 shows the steady-state oxygen atom density as a function of the gas pressure and the absorbed RF power. At gas pressures above 2 Torr the oxygen atom density increases with pressure and with injected RF power, as expected. However, the dissociation fraction decreases with pressure, reaching a maximum of about 14% at 2 Torr 200W. However, at 2 Torr the oxygen atom density passes through a maximum with power, and at 1 Torr the oxygen atom density decreases with RF power. Since the electron density (and therefore O_2 dissociation rate) increases monotonically with power at all pressures, this is a rather surprising result, indicating that the oxygen atom loss rate (principally due to recombination at the electrode surfaces) increases with power at these lower pressures. This corresponds to conditions where the energy and flux of ion bombardment of the surfaces is increasing, suggesting that this surface recombination is activated by the ion bombardment.

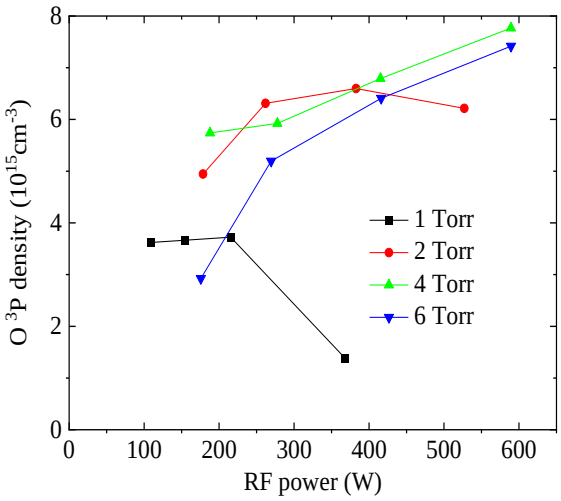

Figure 1. Oxygen atom density as a fuciton of O_2 pressure and injected RF power

In order to investigate this further, we performed time-resolved measurements of the oxygen atom density in pulse-modulated plasmas. Figure 2 shows the results at 2 Torr, clearly showing that the O atom density decay becomes faster as the RF power is increased. Nevertheless, the decays are

surprisingly slow - with decay time constants varying from 207 to 149 ms, corresponding to surface reaction coefficients of the order $3x10^{-4}$. These small values are rather surprising on bare metallic (aluminium) surfaces, and very comparable to the values observed on borosilicate glass[2], showing the importance of surface oxidation. This increase of surface reactivity with ion bombardment energy is also very similar to what is observed in a DC discharge in a borosilicate glass tube at pressures below 1 Torr[2]. The ion energies under these conditions are not sufficient to remove native oxide from an aluminium metal surface. Rather, the ions appear to activate surface reactions. At higher O_2 pressures the oxygen atom decays become faster, suggestion the onset of gas-phase reactions, and with a rate that becomes insensitive to the RF power.

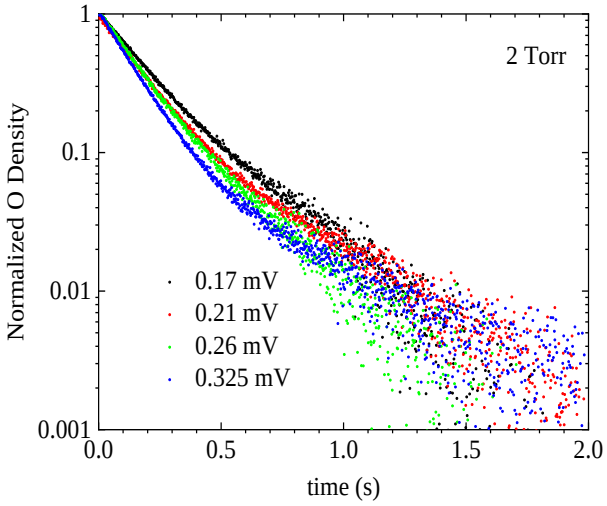

Figure 2. Decay of the oxygen atom density as a functon RF power at 2 Torr O_2 pressure

The time-resolved measurements also allow the O^- negative ion density to be measured, as well as indicating the creation of ozone in the afterglow, both in the gas phase and on the reactor surfaces, as previously observed in DC glow discharges[1]. Analysis and interpretation of this data is on-going.

These observations of oxygen surface recombination probabilities provide an intriguing bridge between surface recombination at higher pressures (where observed recombination coefficients are in the range 10^{-3}-10^{-4}) and lower-pressure plasma experiments where the coefficient can reach several 10s %.

Acknowledgements

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[1] Booth J P, Guaitella O, Zhang S, Lopaev D, Zyryanov S, Rakhimova T, Voloshin D, Chukalovsky A, Volynets A and Mankelevich Y *Plasma Sources Science and Technology* 2023 **32** 095016

[2] Booth J P, Guaitella O, Chatterjee A, Drag C, Guerra V, Lopaev D, Zyryanov S, Rakhimova T, Voloshin D and Mankelevich Y *Plasma Sources Science and Technology* 2019 **28** 055005