Surface recombination in Pyrex in oxygen DC glow discharges

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In most plasma processes, surfaces interact with either the active discharge or its afterglow. Heterogeneous surface kinetics plays a role there, affecting both the plasma and surface properties. In particular, in oxygen-containing discharges the adsorption and recombination of atomic oxygen on reactor surfaces determine the gas composition, the availability of O for important volume reactions (e.g.: $CO_2 + O \rightarrow CO + O_2$; $CO + O + M \rightarrow CO_2 + M$) and eventually the flux of reactive oxygen species (ROS) towards target surfaces.

In the work by Booth et al. (2019) [1], the wall loss frequencies of O atoms were measured in the positive column of an oxygen DC glow discharge in a Pyrex tube (borosilicate glass) of 10 mm inner radius, for several pressures and discharge currents. However, the surface mechanisms determining recombination are not fully known yet. In particular, the increasing atomic oxygen recombination frequency and probability with decreasing pressure (see fig. 1) for a plasma operating in the pressure range between 0.27 mbar (0.2 Torr) and 1 mbar (0.75 Torr) is not fully understood. It is complemented by an increase of the recombination probability with current observed in the same pressure range, which is not the case at higher pressures. In our previous publication [2] we showed, via numerical simulations and comparisons with experiments (see fig. 1), that this change in regime results from a modification of the Pyrex surface, which may impact intermediate pressure plasma reactors where plasma-surface interactions are present. The simulations were obtained from a mesoscopic model employing deterministic and Kinetic Monte Carlo methods [3-5].

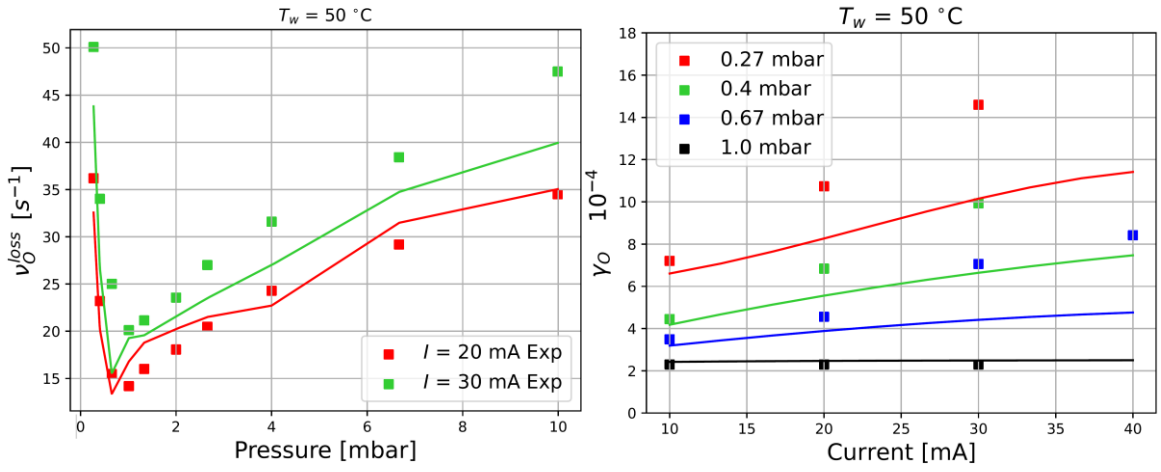

Fig. 1: Atomic oxygen loss frequency as function of pressure for 20 mA and 30 mA discharge current values (on the left), and atomic oxygen recombination probability as function of current for several pressure values (on the right), for a wall temperature of 50 ºC. Results from experiments [1] (square symbols) and simulations employing the deterministic method [2] (full lines).

In this work we employ the LisbOn Kinetics (LoKI) simulation tool [6-8], including the description of surface kinetics of oxygen species, to highlight the most relevant mechanisms and simulate self-consistently the evolution of those species in both gaseous and adsorbed phases in the experimental conditions of [1] and further experimental conditions at wall temperatures between -20 ºC and 50 ºC. The description of surface kinetics proceeds via the kind of mesoscopic modelling employed in the past [3-5], with a new reaction scheme including O+O and O+O_2 surface recombination reactions and a wall temperature dependent desorption frequency. The employment of this description in a coupled model that does not require fluxes and temperatures as input parameters allows to verify the appropriateness of the new reaction scheme and rates in the context of a self-consistent model that simulates the plasma-wall system as a whole in experimental conditions.

Through the self-consistent approach, the fluxes of species from the plasma directly affect the surface, and the surface processes directly affect the available densities in the gas phase, as well as the gas temperature. In particular, the flux of ions from the plasma induces the production of metastable chemisorption sites at the surface. As such, the Langmuir-Hinshelwood (L-H) and Eley-Rideal (E-R) recombination mechanisms take place involving not only physisorption and stable chemisorption sites, but also metastable chemisorption sites, produced by the impact of fast O_2 ions and neutrals, and where recombination can take place with lower energy barrier [9]. The production of metastable chemisorption sites decreases with pressure due to the incident energy of these particles and increases with current due to the flux of incident particles. The presence of metastable sites can be reversed by increasing the plasma pressure, since the destruction of these sites takes place through the collision of incident neutrals from the plasma, which increases with pressure.

The coupled model is validated for a total of 106 experimental conditions, accurately describing the experimental dependence of the atomic oxygen recombination probability on pressure, current, gas temperature and wall temperature. This shows not only the robustness of the model when facing different conditions, but also its versatility bridging different timescales from electron kinetics (below ns) to surface kinetics (up to seconds). The analysis of the simulation results highlights that for wall temperatures of -20 ºC and 5 º C the dominant recombination mechanisms involve physisorbed oxygen atoms (O_F) in L-H recombination $O_F + O_F$ and in E-R recombination $O_2 + O_F$, while for wall temperatures of 25 ºC and 50 ºC processes involving chemisorbed oxygen atoms (O_S) in E-R $O + O_S$ and L-H $O_F + O_S$ also play a relevant role. Moreover, this work demonstrates that the plasma has important effects on the surface at low pressures and that surface recombination processes lead to high ozone wall production rates at high pressures.

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