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## Dynamics of inductive plasmas in Cl<sub>2</sub>, O<sub>2</sub> and Cl<sub>2</sub>/O<sub>2</sub> mixtures: quantitative diagnostics and numerical modelling

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Inductively-coupled plasmas in molecular, electronegative gases are widely used for plasma processing of surfaces. The complexity of these systems is such that they can only be described by multi-physics models which describe both the plasma physics and the collisional processes between electrons, molecules and atoms. However, there has been little rigorous validation of these models by comparison to quantitative measurements of particle densities over a wide range of parameter space. We have chosen to study the Cl<sub>2</sub>/O<sub>2</sub> system partly because of the industrial process relevance but also because methods exist to measure the density of all the important species occurring in these plasmas.

The experiments were performed in a cylindrical plasma chamber (diameter 55cm, height 10cm) excited at 13.56 MHz (20-500 W) by a planar antenna and with gas pressure between 5 and 100 mTorr. This system mimics a typical plasma etch tool and it is specially designed to perform space and time resolved measurements with various plasma diagnostics. Electron densities are measured by microwave hairpin resonator. Absolute Cl and O atom densities are determined by Two-photon Absorption Laser-Induced Fluorescence. The spatial profile of the neutral gas temperature is measured using Laser Induced Fluorescence of metastable argon atoms (with Ar added in trace amounts). We have constructed a new ultra-low noise broadband UV-visible absorption bench, which allows the measurement of the densities of ground state Cl<sub>2</sub> molecules and ClxOy reaction products, as well as vibrationally excited states of Cl<sub>2</sub> and O<sub>2</sub>. These comprehensive measurements are compared to the predictions of the Hybrid Plasma Equipment Model (HPEM) with the aim to validate/calibrate/improve the physical-chemical models of Cl<sub>2</sub>/O<sub>2</sub> plasmas.

In this talk, a particular emphasis will be made on the neutral gas heating and vibrational kinetics in high density Cl<sub>2</sub>/O<sub>2</sub> plasmas. Using Ar\* LIF we demonstrate the occurrence of strong gas heating, with temperatures reaching 1500 K in the centre of the reactor. We show that in chlorine, gas heating represents the major depletion mechanism of the Cl<sub>2</sub> feedstock. Simulations reveal that neutral density gradients induced by the gas temperature gradients have a strong effect on the electron temperature which in turn affects the gas heating itself (e.g. Frank-Condon heating). This strong coupling implies that gas heating must be simulated self-consistently with the dynamics of charged species; the commonly-used assumption of a constant gas temperature leads to wildly inaccurate predictions of all plasma parameters.

In chlorine, ground state vibrational populations on levels v''=0-3 are measured by broadband absorption spectroscopy of the Cl<sub>2</sub> continuum between 250 and 450 nm. The observed vibrational distributions suggest that the vibrational and translational degrees of freedom in the plasma are close to local equilibrium, which can be explained by the efficient VT relaxation in Cl<sub>2</sub> by interaction with Cl atoms. In contrast in O<sub>2</sub>, highly non-equilibrium vibrational populations over the levels v''=4-19 are demonstrated by absorption spectroscopy of Schumann-Runge band. The work is in progress to elucidate the role of these highly vibrationally excited molecules in the O<sub>2</sub> plasma kinetics.

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