Density and temperature measurements in inductively-coupled plasmas in Cl₂/O₂, pure gases and mixtures, using a new high sensitivity ultra broad-band absorption spectroscopy setup

M. Foucher¹, D. Marinov¹, E. Carbone¹, J.P. Booth¹ and P. Chabert¹

¹ Laboratoire de Physique des Plasmas, Ecole Polytechnique, Route de Saclay, 91128 Palaiseau, France

Abstract: A new high sensitivity ultra broad-band absorption spectroscopy setup is used to analyse inductively-coupled plasmas in pure Cl₂, pure O₂ and mixtures. The high signal-to-noise ratio and baseline stability ($2 \times 10^{-5}$) allows the measurement of rotational and vibrational temperatures in pure O₂ plasmas, of Cl₂ density, vibrational temperature and negative ion density in pure Cl₂ and of oxychloride densities and temperatures in mixtures.

Keywords: ICP, Cl₂/O₂, absorption spectroscopy

1. Introduction

The experimental study of Inductively-Coupled Plasmas (ICP) in pure Cl₂, pure O₂ and in mixtures is of great interest for model validation. Moreover, plasmas of Cl₂/O₂ are widely used (often with HBr) in the fabrication of CMOS transistor gates. Numerous simulations of these plasmas have been developed, but only a few experimental results exist to validate them.

In this paper we provide results obtained using a new high sensitivity broad-band absorption spectroscopy setup. It uses an intense, stable and broad-band (200 - 800 nm) light source (Energetiq LDSL-EQ99), achromatic optics and an aberration-free spectrograph (Acton SCT-320).

In a plasma of pure O₂, highly vibrationally excited molecules were observed via the Schumann-Runge absorption bands [2], allowing the O₂ vibrational and rotational temperatures to be determined. In pure Cl₂, the vibrational temperature is determined and negative ions are detected. In Cl₂/O₂, oxychloride reaction product densities and temperatures are measured.

Measurements were made over a range of experimental parameters: total gas pressure [5 - 80] mTorr, injected radio-frequency (RF) power [100 - 500] W and gas composition (in the Cl₂/O₂ case).

2. Experimental setup

The reactor used for all the experiments has been presented elsewhere by Booth et al. [1]. Briefly, it is a cylindrical chamber (55 cm diameter, 10 cm high) with a 4-turn planar coil that produces the plasma through a dielectric window. The power is injected by a RF generator that can be pulsed. The pressure is regulated between 5 and 80 mTorr by a valve above the turbo-molecular pump. Mass flow controllers are used to regulate the gas flow or specify a particular ratio in Cl₂/O₂ plasmas.

The absorption spectroscopy setup is presented in Fig. 1. The spherical beam of the light source (Energetiq LDSL-EQ99) is collimated with a parabolic mirror and directed through the reactor by a flat mirror. This light source is very broad-band (200-800 nm), intense and highly stable (after two hours heating). The light beam crosses the reactor at mid-height and is focused onto the entrance slit of an aberration-free spectrograph (Acton SCT-320). Three gratings (2400-1200-300) l/mm provide spectral ranges of (30-60-240) nm respectively in a single measurement. The light is then analysed by a 1024 element photodiode array. All these items are mounted on a single chassis in order to reduce the noise due to vibration.

Absorbance spectra are recorded using a LabView program which controls a shutter and the plasma extinction/ignition.

The absorbance, $A(\lambda)$, is determined using a four-stage procedure:

- 1 : $L_1(\lambda) = $ Plasma on/Light on
- 2 : $L_2(\lambda) = $ Plasma on/Light off
- 3 : $L_3(\lambda) = $ Plasma off/Light on
- 4 : $L_4(\lambda) = $ Plasma off/Light off

$A(\lambda) = - \ln \left( \frac{L_1(\lambda) - L_2(\lambda)}{L_3(\lambda) - L_4(\lambda)} \right)$

Signal averaging over a few minutes allows the (wavelength independent) shot noise to be reduced below...
10^5, allowing absorbancies as low as 10^{-4} to be easily seen. For longer integration times residual fluctuations in the lamp spectrum become the limiting factor; typically the baseline is flat to within 2.10^{-5} across the spectral range 210-450 nm, but with a fluctuating (but wavelength independent) offset of the order of ±2.10^{-4}. This vertical offset does not impact the spectra shape. This setup has significantly improved sensitivity compared previous studies using Xe arc lamps [2]; more recently UV light-emitting diodes (UV-LED) have shown improved noise levels [3], but only have spectral ranges of a few 10’s of nm.

3. Results and discussion

Fig. 2 shows an example spectrum obtained in pure O_2 at 10 mTorr 500 W. Numerous bands corresponding to vibrational transitions within the Schumann-Runge bands [4] can be seen (some transitions have been indicated on the figure showing the presence of molecules in vibrational levels up to ν” = 19) over a wide spectral range [250-400] nm (other bands or present further but more difficult to distinguish). These transitions would not be visible in room-temperature O_2. In order to determine the vibrational distribution we simulated the absorption of various vibrational bands using the PGOPHER freeware [5], with spectroscopic constants from the literature [4]. Fig. 3 shows the vibrational state populations (ν = 9 to 15) at 80 mTorr 500 W. A change in slope is clearly visible around ν = 12; this could be explained by spatially-varying vibrational temperatures. A full investigation as a function of experimental conditions is ongoing.

Using the 2400 g/mm grating to analyse the (0-11) band around 300 nm at higher resolution shows the rotational structure, as shown in Fig. 4 (80 mTorr 500 W). By fitting these results with simulated spectra (PGOPHER) the O_2 rotational temperature (which can be considered to be in equilibrium with the gas translational temperature at this pressure) was determined as a function of gas pressure and RF power, as shown in Fig. 5.

The gas temperature is significantly above ambient, and increases both with power and pressure, reaching up to 900 K. Various mechanisms can be invoked to explain these high vibrational and rotational temperatures, including electron impact excitation of O_2 molecules and the energy released by recombination of O_2 at the reactor walls, combine with (V-T) energy transfer processes.

Fig. 6 shows absorption spectra measured in pure Cl_2 plasmas at 10 mTorr for power varying from 100 to 500 W. The Cl_2 absorption continuum centred around 330 nm is clearly visible. The absorbance decreases as a...
function of RF power, due both to Cl₂ dissociation and to gas heating and dilation (at constant pressure). The line-integrated Cl₂ density first drops quickly with power, but then does not decrease much below 50% as power is increased. It is possible there is near-complete dissociation of Cl₂ at the reactor centre, with residual absorbance due to cold, undissociated Cl₂ close to the reactor walls.

Fig. 6. Absorption continuum spectra of the Cl₂ molecule at 10 mTorr for injected powers comprised between 100 and 500 W. Cl⁻ ions as well as CCl₄ can be seen.

At the long wavelength side (> 450 nm) the absorbance tends towards zero under all conditions. However below 275 nm an offset appears which increases with RF power. This continuum absorption can be attributed to Cl⁻ photodetachment [6], corresponding to a negative ion density of the order 5x10¹¹ cm⁻³.

Between 200 and 250 nm, another broad absorption band can be seen. This appears to correspond to CCl₄ molecules, formed by reaction of chlorine with carbon in the O-ring seals.

As for the pure O₂ case, we wanted to measure the vibrational temperature of the Cl₂ molecule. Fig. 7 shows the absorption cross sections form the four lowest vibrational levels of the Cl₂ molecule. The experimental spectra are dominated by the v = 0 level, indicating the vibrational temperature is quite low. Fig. 8 shows the same data as Fig. 7 but normalized, showing a slight increase of the width of the absorption band with RF power, indicating the presence of vibrationally excited molecules. The vibrational distribution was deduced by fitting experimental spectra using the cross-sections of Fig. 7. The population densities for the different vibrational levels were then determined and plotted as a function of the vibrational number. Fig. 9 shows a result for 10 mTorr and 500 W. A bi-Maxwellian distribution is observed, with a cold (435 K) distribution with a high temperature (1000 K) tail.

Fig. 10 show the absorption spectrum in a plasma of 50% Cl₂/ 50% O₂ at 10 mTorr 500 W. In addition to the Cl₂ absorption continuum and the Schumann-Runge bands of O₂, we can see the appearance of other vibrational structures. These correspond to oxychloride reaction products, especially ClO and OCIO. Fig. 11 shows a first estimation of the variation of the densities of these species as a function of the gas composition was made using cross sections found in the literature [7]. We can see that both oxychlorides are formed when Cl₂ or O₂ is added. ClO reaches a maximum at 50% Cl₂ and 50% O₂. OCIO increases monotonically with O₂ content but has much lower density than ClO.
4. Conclusion

Gas rotational and vibrational temperatures have been measured in ICP’s of pure O$_2$; vibrational temperatures were measured in ICP’s of pure Cl$_2$ as well as the negative ion density; in Cl$_2$/O$_2$ mixture the densities of oxychlorides were measured for the first time (to our knowledge) by absorption spectroscopy. These results provide a comprehensive data set for model validation. Finally we have demonstrated the potential of our new absorption spectroscopy setup: its high sensitivity and signal to noise ratio as well as excellent baseline stability open many new possibilities for plasma chemical analysis.

5. Acknowledgements

This work was performed within the LABEX PLas@par project and received financial state aid, managed by the Agence National de la Recherche, as part of the programme “Investissements d’avenir” (ANR-11-IDEX--0004--02). It was also supported by the Agence National de la Recherche project INCLINE (ANR-09 BLAN 0019) and by the Applied Materials University Research Partnership Program.

6. References