Vibrational and rotational properties of O_2 molecules in very high frequency plasmas with high sensitivity broadband absorption spectroscopy

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Abstract: We present here the measurement of O_2 plasma neutral properties in a 100MHz plasma source by a high sensitivity broadband plasma absorption spectroscopy technology. Vibrational and rotational properties of O_2 molecules are derived from a theoretical fitting to the experimental spectra. Density distribution of O_2 molecule at different vibrationally excited levels are also derived. Effects of VHF power and pressure on these plasma neutral properties are reported. A bi-Maxwellian vibrational distribution is also reported.

Keywords: vibrational and rotational properties, broadband plasma absorption spectroscopy.

1. Introduction

As advanced memory and logic critical dimensions shrink and stack complexity, film quality, and yield requirements increase, precision plasma processes including plasma enhanced atomic layer deposition (PEALD) and atomic layer etch (PEALE) experience more demand. Ideally infinite selectivity and damage-free process with sub-angstrom control are sought. Plasma enhanced processes, particularly plasma enhanced atomic layer deposition rely on plasma generated radicals for much of their perceived benefit. Furthermore, in both atomic layer etch and deposition processes, low or nearly zero energy ions are required. Large-area plasma processing systems capacitively driven at very high frequencies (VHF, e.g. 100 MHz) have attracted much interest for semiconductor device and flat panel display processing. VHF has the additional advantage of generating plasma with more efficiency as power is coupled more into electrons and less into ions in the sheath. Benefits are seen for processes requiring reduced ion bombardment energy, ostensibly to minimize damage and promote high radical flux to the substrate.

Unfortunately, it has been a challenge to measure the neutral plasma species of interest. It would be desirable to use plasma absorption spectroscopy to study plasma neutral species because it can provide direct measurement of the absolute densities of species in their ground state as well as vibrational and rotational properties of neutrals. Lack of intense and stable light sources with wide wavelength coverage and the lack of optical aberration-free spectrographs and detectors with true high resolution has rendered plasma absorption spectroscopy impractical as a solution for industry. Emission based diagnostics such as actinometrical methods are far too imprecise. A recent advance, broadband plasma absorption spectroscopy (BPAS) [1] has been proven to be a very practical improvement of plasma absorption spectroscopy with capability to detect absorbance as low as 1×10^{-4} over a broadband. In order to understand the fundamental plasma chemistry property of VHF plasma, we investigate VHF plasma neutral properties with a high sensitivity BPAS technology. Illustrative measurements were performed in a 100 MHz plasma source with pure oxygen plasma spanning a wide RF power and pressure range. Through a theoretical fitting to the experimental absorption spectra, the vibrational and rotational properties of O_2 molecules in the VHF plasma are derived. Density distribution of O_2 molecule at different vibrationally excited levels of ground electronic state can be obtained. Effects of VHF power and pressure on these O_2 plasma neutral properties are reported. With newly improved experimental optics, we are able to discover experimentally that VHF O_2 plasma exhibits a bi-Maxwellian vibrational distribution that is in agreement with the recent theoretical work on inductively coupled O_2 plasma [2].

2. Experimental setup

The basic configuration of BPAS is schematically shown in Fig. 1. The VHF plasma source has a cylindrical chamber of 50 cm in diameter and 3 cm gap between the powered and ground electrodes. Pure O_2 is injected into the chamber through a shower head at a flow rate of 500 sccm. Turbo-molecular pump and dry pump are used for evacuating the chamber in order to avoid the concerns arising from the contamination of plasma by oil mechanical

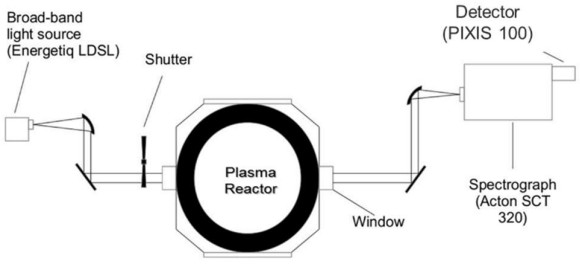

Fig.1 Schematics of broadband plasma absorption spectroscopy setup

pump. A CW laser driven light source (LDLS, Energetiq EQ-99) is used for the plasma absorption, which can provide a broad spectral range with extremely high brightness and excellent spatio-temporal stability. The light emission from the light source is collimated and directed to pass through the plasma chamber and it is then delivered and focused onto the entrance slit of an aberration-corrected spectrograph (Acton Isoplane SCT-320). A PIXIS 100 CCD camera from Princeton Instruments is used as the detector to record the dispersed spectrum at the exit of the spectrograph. The camera has high quantum well capacity and fast spectral rate up to 1300 fps, allowing the detection of bright light beam at a high speed in favour of minimizing the noise and baseline variation. In this experiment, two different gratings (2400 and 300 mm^{-1}) are used. The low resolution (300 mm^{-1}) grating gives a wide spectral range and is used in vibrational absorption experiments. The high resolution grating (2400 mm^{-1}) with the maximum spectral resolution of about 0.05 nm and narrower spectral range is used to study the rotational property at a specific vibrational band. The light source housing and the entire light path are purged with a flow of dry nitrogen in order to eliminate any ozone produced by the UV radiation from the light source and the plasma. An automated beam shutter is incorporated in the light path just before the entrance viewport of the plasma chamber to allow the measurements of the background and the plasma emission spectra. MgF_2 window are used for the chamber viewport and Al/MgF_2 coated broadband VUV reflective mirrors that has optimized reflectance (83%) down to 120 nm are used for the optics in the light path from the light source to the entrance slit of the spectrograph.

The measurement is automated using a LabVIEW code that switches plasma on/off and shutter open/close to acquire spectrum in four modes:

	Shutter Open	Shutter Close
Plasma ON	$L_1(\lambda)$	$L_3(\lambda)$
Plasma OFF	$L_2(\lambda)$	$L_4(\lambda)$

The detector typical reads 150 times at each mode with exposure time of 10 msec and the four-step cycle repeated 50 times with signal accumulation in order to reduce the shot-noise. The standard deviation of noise about 2×10^{-5} can be achieved, allowing us to detect absorbance as low as 1×10^{-4}. To calculate plasma absorbance A(λ), the following expression is used to subtract the plasma emission and background signal:

$$\frac{I_T}{I_0}(\lambda) = \frac{L_1(\lambda) - L_3(\lambda)}{L_2(\lambda) - L_4(\lambda)} = exp\big(-A(\lambda)\big)$$

The experimental absorption spectrum is fitted with the PGOPHER program [3] to extract vibrational and rotational level information of the plasma molecules. Vibrational and rotational temperatures of plasma neutrals can be obtained along with the density in each vibrational level, taking account of the optical path length of the chamber.

3. Results and discussion

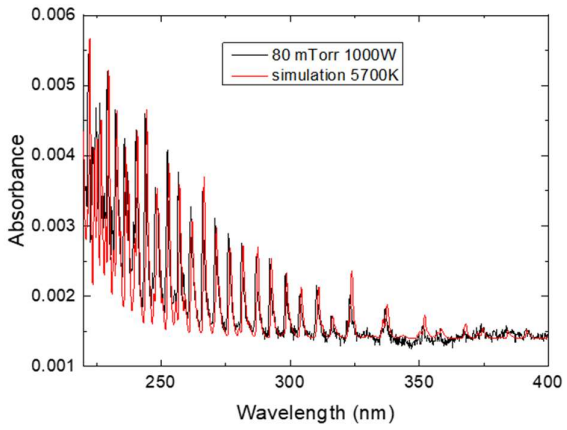

Fig. 2 Experimental (black) and simulated (red) absorption spectrum of VHF O_2 plasma at 80 mTorr and 1000 W.

Figure 2 shows the experimental (black) and the simulated (red) absorption spectra of VHF O_2 plasma at 80 mTorr and 1000 W RF power using the low resolution grating (300 mm^{-1}). Multiple absorption bands are observed in the spectral range of 220-400nm, which represents the Schumann-Runge $B^3\sum_u^-(v') \leftarrow X^3\sum_g^-(v'')$ transitions of O_2 molecules [4]. The vibrational temperature (T_{vib}) of $v'' = 4$ to 19 levels was obtained by fitting the relative intensities of the absorption bands to all the levels of the upper B state, which gives T_{vib} = 5700 K

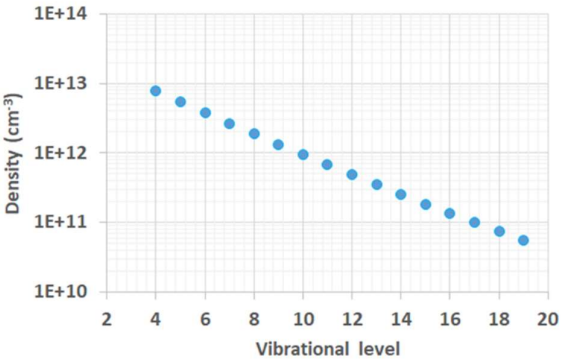

Fig. 3 Vibrational distribution function of $v'' = 4$ to 19 levels (high energy "hot" vibrational tail) of VHF O_2 plasma at 80 mTorr and 1000 W.

at 80 mTorr and 1000 W RF power. The corresponding vibrational distribution function (VDF) is shown in Fig. 3. Because the limitations of optics while this experiment was conducted, only $\nu'' = 4$ and above levels were detectable. It is worth to note that an O_2 molecule in the $\nu'' = 18$ level has an energy that is almost halfway to the dissociation threshold of O_2. Peaks above $\nu'' = 19$ are too low in population to be detectable. Thus, the vibrational distribution shown in Fig. 3 only represents the "hot" vibrational tail, which may account for about 10% of total O_2 population in the plasma. The total density of O_2 molecules in the $\nu'' = 4$ to 19 levels is about 2.64×10^{13} cm^{-3}. Note that this is a line averaged density because of the existence of the radial gradient such as hot gas near the chamber centre and colder gas near the chamber wall.

The pressure and power dependence of the vibrational temperature are shown in Fig. 4 and Fig. 5, respectively. T_{vib} decreases quickly as pressure increases to 300 mTorr then stabilizers at ~4500 K. We think the electron impact excitation balanced by V-T transfer between O_2V and atomic O translation would be one of the mechanisms that controls the vibrational temperature. At lower pressure,

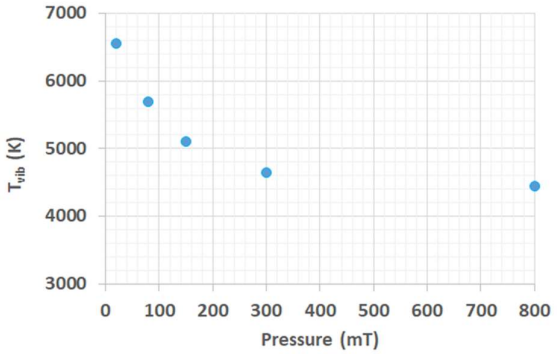

Fig. 4 Vibrational temperature of the "hot" vibrational tail as a function of pressure.

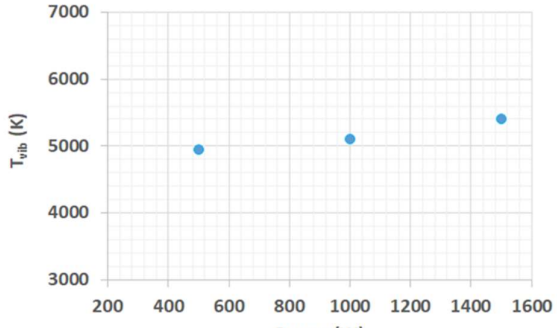

Fig. 5 Vibrational temperature of the "hot" vibrational tail as a function of RF power.

plasma has higher mean electron energy and higher electron density while the atomic O population is low, resulting the higher T_{vib} at lower pressure. At very high pressure e.g. above 300 mTorr, electrons cool down faster causing less dissociation, which may slow down the T_{vib} reduction. As shown in Fig. 5, T_{vib} gradually increases with VHF power, which is understandable because plasma would have higher mean electron energy and electron density at higher power.

With improved optics in the optical path that extends the detectable range down to 170 nm, absorption spectra of $\nu'' < 4$ levels can be obtained. In the VHF O_2 plasma generated at 150 mTorr and 1000 W RF power, besides the high energy "hot" vibrational population (~5% relative abundance, T_{vib} ~ 6300 K), a low temperature vibrational population is observed with 95% relative abundance of the total O_2 molecules. The T_{vib} of this low temperature population is about 990 K. The total O_2 density deduced from the absorption measurement is 2.45×10^{15} cm^{-3}. The fitting to the experimental absorption spectrum also gives the rotational temperature T_{rot} about 555 K. Due to very efficient r-T collisional energy transfer, T_{rot} is expected to be in equilibrium with the gas translational temperature, e.g. the gas temperature. At this gas temperature (555 K) at 150 mTorr, the total molecule density from ideal gas law is about 2.61×10^{15} cm^{-3}. Considering that some O_2 would be in the metastable state that is undetectable and a few percent of O_2 would be dissociated into atomic O, the measured total O_2 molecule density is in a good agreement with that expected in the plasma chamber. The two-temperature (bi-Maxwellian) vibrational distribution observed in the experiment of VHF O_2 plasma is also predicted in a recent modelling work on ICP O_2 plasma [2].

Using the high resolution grating (2400 mm^{-1}), a specific vibrational band can be looked in details. Figure 6 is a typical high resolution absorption spectrum of VHF O_2 plasma. A zoom-in plot of the 11-0 band is shown in Fig. 7. By fitting the high resolution absorption spectrum, the rotational temperature T_{rot} can be obtained. It is found that T_{rot} decreases with decreasing pressure, which supports the prior observation that T_{vib} increases with decreasing pressure and V-T energy transfer is an important mechanism controlling the vibrational temperature of O_2 molecules in VHF O_2 plasma.

4. Conclusions

High sensitivity broadband plasma absorption spectroscopy technology is demonstrated to be a useful method to study the vibrational and rotational properties of VHF O_2 plasma. It has been found that T_{vib} of VHF O_2 plasma increases with decreasing pressure and increasing RF power; while the T_{rot} decreases with decreasing pressure, implying that V-T energy transfer plays an important role in balancing the electron impact excitation in VHF O2 plasma. A bi-Maxwellian two temperature vibrational distribution is also observed, in which a low temperature vibrational component with the relative abundance of 90% has been experimentally observed for the first time.

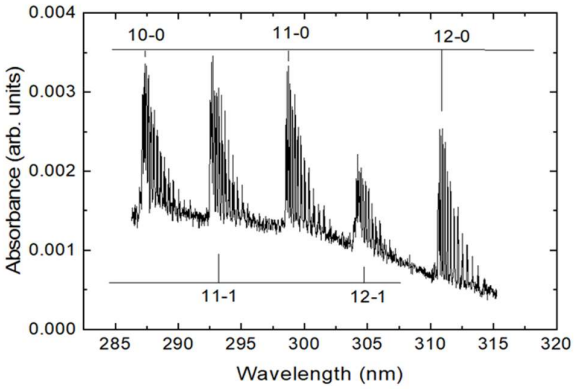

Fig. 6 Typical high resolution absorption spectrum of VHF O_2 plasma.

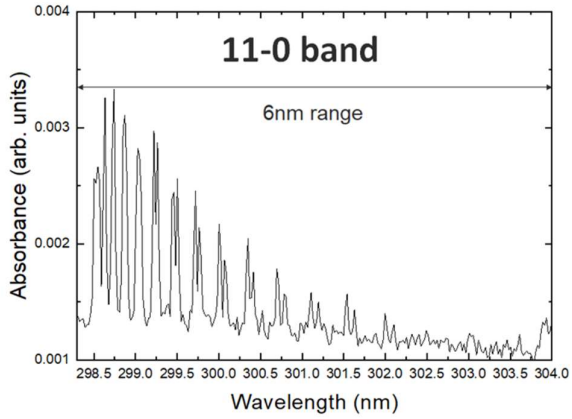

Fig. 7 Details of the high resolution absorption spectrum showing the 11-0 band between 298 and 304 nm.

5. References

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