# Spectrophotometric measurements in an rf capacitively-coupled oxygen discharge

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This article present experimental data on spectrophotometric measurements in an oxygen plasma for different values of radio-frequency 1.56MHz(rf) power and pressure in an asymmetrical industrial OPT Plasmalab 100 system used for semiconductor etching. The method for characterizing ion and atom energies is to examine the Doppler profile of their emission lines. The energies derived from the emission profiles depend on the operating power and pressure. The signals were deconvoluted and the resulting profiles were fit with a Gauss-ian line-shape function whose full width at half-maximum was used as a measure of the Doppler width. While term "temperature" may not accurately describe the ion energetics in an rf plasma source, the Doppler profile does provide a useful basis for a relative comparison of ion motion under a variety of operating conditions. A simple mathematical model was applied to calculate atomic and ionic temperature and a good concordance with Doppler method has been found.

## 1. Introduction

Reactive ion etching is widely used in the fabrication of semiconductor devices. To understand the processes taking place when the surface is exposed to plasma, the temperature of plasma constituents need to be known. A change in plasma input parameters (gas pressure, rf power) causes a change in the velocity at the surface of generated active species [1].

Oxygen plasma have a wide range of applications (surface treatment, polymer etching, biomaterials processing etc) and the investigation of an oxygen plasma led to a better understanding of the medium and of the processes involved in these applications. In particular, plasma temperature plays an important role in all these applications. Spectroscopically, at the present condition of plasma, the predominant broadening mechanism is mainly thermal motion. Therefore, the ion temperature could be determined from the half-width by measuring the Doppler (thermal) broadening of the emitted spectral lines. In our study, optical emission spectroscopy has been used as a non-intrusive and non-perturbative diagnostic technique to determine temperature of plasma heavy particles by the use of selected oxygen atom and ion spectral line intensities. Doppler profile measurements of the emission oxygen plasmas provide a measure of the average energy of ions and neutral species in the rf system. This method has been used previously [2-11] to measure plasma parameters.

## 2. Experimental results and discussion

The rf plasma which was investigated was confined in a plasma chamber of an asymmetrical industrial OTP Plasmalab 100 capacitively coupled system [12]. The top electrode diameter was 295 mm, inter-electrode spacing 50 mm and the driven electrode diameter was 205 mm. The range of powers was 10 – 150 W and of pressure 10 - 90 mTorr. The apparatus was controlled by Oxford Instruments software from a 486 DX33 PC.

Emission spectroscopy measurements coming from the plasma were performed with a spectrophotometer Jobin-Yvon type coupled with a silica-silica high OH-PYROCOATTM fiber. The fiber has a high OH-concentration for efficient power transmission from UV through visible wavelengths, so it provides low-loss transmissions in this domain. The chamber has a quartz window and the silica fiber was positioned outside the chamber very close with this window and fixed in such a manner that detect the maximum light emission. All data presented here were obtained by observing the emission at 90o from the central axis of the electrodes, i.e. parallel to the electrode surfaces. A typical spectrum has been shown

in Fig. 2. A Hiden Analytical rf-compensated Langmuir probe was used to determine plasma potential (Fig. 1)[13].
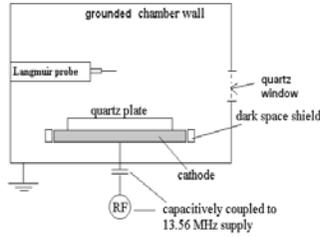


Fig. 1 A schematic diagram of the capacitively coupled discharge.

Oxygen atoms are formed in O2 plasma mainly by electron impact dissociation:

$$O_2 + e \rightarrow O + O + e-$$  (1)
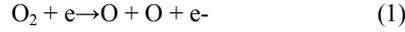
or by dissociative attachment:

$$O_2 + e \rightarrow O + O-$$  (2)

Electron impact excitation of ground-state molecular and atomic oxygen leading to emission at 844,6 nm and 777 nm occurs by two mechanisms:

direct excitation

$$O + e \rightarrow O^* + e-$$  (3)

and dissociative excitation:

$$O_2 + e \rightarrow O^* + O + e-$$  (4)
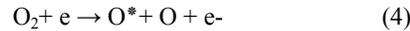
where O* refers to the OI(3p 5P) state which emits at 777 nm and to the OI(3p 3P) state which emits at 844,6 nm. As the power decreases, reaction (4) eventually dominates over reaction (3) [10]. Walkup et al. [10] have shown that reaction (4) leads to a Doppler-broadened emission lineshape, due to the ~1eV spread in the velocities of the O* produced, and because O* spontaneous emission is faster then thermalization.

Two ionization mechanisms are most important in the creation of O+:
direct ionization of O :

$$O + e \xrightarrow{} O+ + 2e$$  (5)
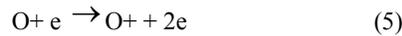
and dissociative ionization of O2:

$$O_2 + e \xrightarrow{} O + O+ + 2e$$  (6)
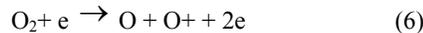
where O+ refers to the OII(3d 3D) state which emits at 558 nm and to the OII(4d 5Do) state which emits at 615.25 nm.
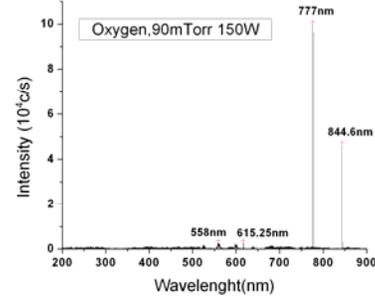


Fig. 2 Optical emission spectrum from 500 to 900 nm

The optical emission intensity of the atomic spectral lines 777 nm and 844,6 nm (Fig.2) are superpositions of 3 spectral lines [14]: 777.1944 nm; 777.4166 nm and 777.5388 nm and 844.6247 nm; 844.6359 nm and 844.6758 nm, respectively. Each of these three components is Doppler broadened [15]. After removal of instrument broadening, the signals were deconvoluted and the resulting profiles were fit with a Gaussian line-shape function whose full width at half-maximum was used as a measure of the Doppler width [6, 8]. At lower pressures (< 1 Torr) the effect of broadening of spectral lines due to atom collisions can be neglected [7], as in the case of our determinations. The thermal motion of ions is predominant and a Maxwellian velocity distribution can be suggested (7). In this case the broadening of spectral lines is determined in principal by Doppler effect and the following equation can be used to determine the atom and ion energies [8]:

$$k_B T = \frac{mc^2}{8 \ln 2} \left( \frac{\Delta\lambda_{1/2}}{\lambda_0} \right)^2$$  (7)

where $\Delta\lambda_{1/2} = 2\Delta\lambda_D$ is the full-width of half-maximum intensity of the line determined from the deconvolution process

$\Delta\lambda_D = \lambda - \lambda_0 = 2(\lambda_0 / c)[\ln(2)(2k_B T / m)]^{1/2}$ is the

Doppler width, $\lambda_0$ is the center wavelength of the emission line, T is the temperature of the emitting species, kB is Boltzman's constant, m is mass unit of the emitting species, c is the velocity of light in vide.

If plasma is at partial Local Thermodynamic Equilibrium (LTE), the distribution of plasma ions or atoms is Boltzmann and the integral intensity of a spectral line can be written [7]:

$$I_{ik} = \eta(\lambda_{ik}) A_{ik} n_0 \frac{hc}{\lambda_{ik}} \frac{g_i}{Z(T)} \exp(-E_i / k_B T)$$  (8)

where η (λik) is transfer function, Aik is Einstein coefficient for spontaneous emission, no is atom density of fundamental energetic state, h is Plank constant, gi is statistical weights of energetic level i, Z(T) is partition

function, Ei is the energy of initial level of electronic transition, kB is Boltzman's constant. The LTE basically demands that the excitation and ionization process have been produced only by electron impact.

The ratio of relative intensities of two spectral lines from the characteristic spectrum of plasma corresponding to transition i→k and respectively j→k is an exponential function as following:

$$\frac{I_{ik}}{I_{jk}} = \frac{\eta(\lambda_{ik})A_{ik}}{\eta(\lambda_{jk})A_{jk}} \frac{g_i}{g_j} \frac{\lambda_{jk}}{\lambda_{ik}} \exp\left(-\frac{E_i - E_j}{k_B T}\right) \qquad (9)$$

where k is the ground state and i, j are the excited states.
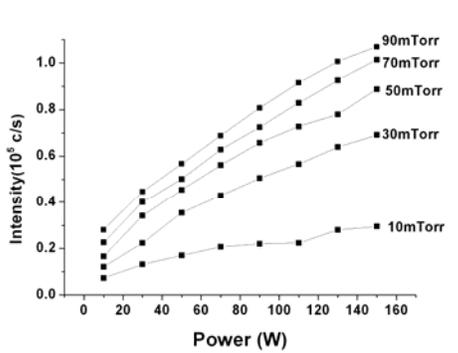


*Fig. 3 Intensity of atomic spectral line 777, 5388 nm at different powers and pressures*

Fig. 3 shows the variation of spectral lines intensities for O 777, 5388 nm at different pressures and rf powers. At lower pressures, the intensities of spectral lines are increasing with increasing of both power and pressure. An exponential dependence of the optical emission intensities with power when the pressure is maintained constant can be observed. At higher pressures and powers the intensity of spectral lines is higher. At lower pressures, a small part of the electrons have sufficient energy for excitation and suffer collisions with the other particles (ions). At higher pressures, the plasma density increases and the frequency of collisions becomes higher. In this case a bigger part of electrons can transfer their energy by impact with the other particles and can excite them. By dezexcitation, atoms and ions emit spectral lines.

A simple theoretical model can be developed to sustain this exponential dependence. By using exponential fit (first order) of the experimental data from Fig. 3, a relation of the type (10) has been obtained.

$$I - I_0 = A \exp\left(-\frac{P - P_0}{t}\right) \qquad (10)$$

In relation (10) P (power supply) and I (line intensity) are experimental data, while I0, A, P0 and t are fitting coefficients.

For two relative intensities of spectral lines, at a given pressure, we obtain the ratio:

$$\frac{I_1 - I_0}{I_2 - I_0} = \exp\left(-\frac{P_1 - P_2}{t}\right) \qquad (11)$$

Considering

$$F_{ij} = (\eta(\lambda_{ik})A_{ik}g_i\lambda_{jk})/(\eta(\lambda_{jk})A_{jk}g_j\lambda_{ik}) \text{ and from}$$

similarities between relations (9) and (11), a new relation was obtained. By applying function ln, on obtains:

$$\frac{\Delta E}{k_B T} + \ln F_{ij} = \frac{\Delta P}{t} \qquad (12)$$

The power P is a physical parameter which determines the nature of emission electronic transition responsible from the studied ionic and atomic lines. Ionic and atomic temperatures from plasma can be calculated from the relationship (12) obtained by fitting the experimental data when the emission electronic transitions and the power discharge are known. A very good concordance between the values of plasma temperature calculated from the proposed model (eq 12) and those calculated from Doppler profiles measurements (eq 1) have been found (Tables 1). The values of Ei, Ej and Fij were obtained from the NIST Atomic Spectral Database [14].
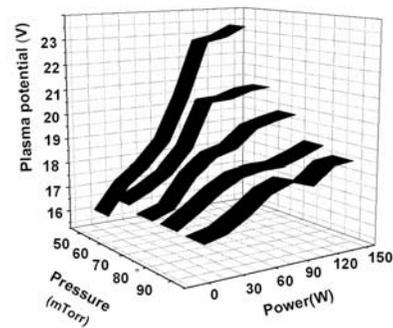


*Fig. 4 Plasma potential obtained from Langmuir probe measurements.*

The plasma potential was determined from the point where the second derivative of the Langmuir probe I-V trace passed trough zero. O'Neill et al. [6] founded that plasma potential measurements show the similarities between its functional dependence on input parameters (operating pressure and rf power) and the ion translational energies determined from optical emission studies. In Fig. 4 the mean values of the plasma potential (in volts) are presented as function of pressure and rf power. It shows that plasma potential is positive with respect to the grounded electrode.

*Table1. Temperatures determined from atomic spectral line 777, 5388 nm using Doppler profiles and the theoretical model.*

| Pressure (mTorr) | $\Delta\lambda_{1/2}$ (nm) | T (eV) | t | $T_{model}$ (eV) |
|---|---|---|---|---|
| 10 | $0.10 \pm 0.009$ | 13.29 | 284 | 19.65 |
| 30 | $0.11 \pm 0.010$ | 14.32 | 227 | 16.29 |
| 50 | $0.12 \pm 0.007$ | 16.13 | 183 | 17.83 |
| 70 | $0.13 \pm 0.003$ | 18.67 | 149 | 19.35 |
| 90 | $0.14 \pm 0.006$ | 21.25 | 122 | 24.43 |

*Table2. Temperatures determined from ionic spectral line 615.2566nm using Doppler profiles and the theoretical model.*

| Pressure (mTorr) | $\Delta\lambda_{1/2}$ (nm) | T (eV) | t | $T_{model}$ (eV) |
|---|---|---|---|---|
| 10 | $0.19 \pm 0.006$ | 172.14 | 439 | 163.89 |
| 30 | $0.17 \pm 0.004$ | 159.32 | 395 | 149.31 |
| 50 | $0.16 \pm 0.009$ | 135.96 | 354 | 125.97 |
| 70 | $0.15 \pm 0.007$ | 111.41 | 292 | 108.26 |
| 90 | $0.14 \pm 0.008$ | 109.75 | 248 | 87.30 |

Doppler linewidth measurements for atoms and ions illustrates that the plasma temperature depends on the power and pressure at which the system is operated. The emission profile for ions broadens as the pressure is reduced, while for the atoms it becomes narrower. The influence of the electrical proprieties of the plasma on ion energies is illustrated by the correlation between the O+ emission linewidth and the plasma potential as function of power and pressure (Fig. 4 and Table 2). With decreasing pressures, the electron temperature increases. At lower pressures the ions suffer few collisions as they traverse the experimental device and the contribution of electric fields to ion motion is expected to be greatest at low pressures and high power since the magnitude of plasma potential increases under these conditions (Fig. 4). It was observed (Table 2) a drop in ion O+ temperature at higher pressure and a corresponding increase in linewidth for neutral O emission (Table 1). The linewidth for neutral species for O plasma is less then that for ions. Similar behavior and high values of particle temperatures have been found in an argon-oxygen rf capacetively-coupled discharge [16].

### 3. Conclusions

Optical emission spectroscopy and Langmuir probe measurements were performed in a capacitively coupled 13, 56 MHz oxygen rf discharge. Those diagnostics are important for characterizing plasma temperature relevant to etching applications. At low pressures, an increase in plasma potential values induces an increase in O+ ion temperature. At high pressures and high rf powers, an increase in the number of ion/ neutral collisions causes Doppler broadening of the emission from O atoms.

An exponential dependence of spectral line intensities with power supply has been founded. A simple theoretical model has been verified to calculate atom temperatures and a very good concordance with Doppler measurements was revealed.

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