VUV-VISIBLE EMISSION SPECTROSCOPY INVESTIGATION OF FREQUENCY EFFECTS IN LOW PRESSURE PLASMAS

A.C. Fozza[1], M. Moisan[2] and M.R. Wertheimer[1]

[1]Groupe des Couches Minces and
Department of Engineering Physics and Materials Engineering, École Polytechnique,
C.P. 6079, Succursale Centre-ville, Montréal QC H3C 3A7, Canada.
[2]Département de Physique, Université de Montréal, C.P. 6128, Succursale Centre-ville,
Montréal QC H3C 3J7, Canada.

Abstract

The vacuum ultraviolet (VUV) to visible emission from SWD plasmas in pure hydrogen or 7 % H_2 in Ar mixture has been investigated over a broad range of excitation frequency ($50 \leq f \leq 200$ MHz) using a spectrophotometer with a known (calibrated) transfer function. We interpret the f-dependence of emission intensity (atomic lines and molecular bands) in terms of changes in the electron energy distribution function (EEDF) as f is increased.

1. Introduction

The expanding use of low pressure ($p \leq 10$ Torr), high frequency (HF) plasmas in various domains (for example, microelectronics, polymer processing) is demanding increased operating efficiency. In order to optimize a particular plasma process, the operator can vary several "external" (operator-set) parameters, among which the excitation frequency, f, has received relatively little attention in the literature over the years. This is probably due to the difficulties encountered in designing meaningful frequency-dependent experiments: changing f in most cases calls for a change in configuration and dimensions of the reactor and/or the power applicator, thus leading to a change of the plasma volume and HF field conditions; working either at constant electron density, n_e, or at constant HF power density, $\mathcal{P}_a$, is not an easy task when using "conventional" plasmas. These difficulties can be avoided by the use of surface wave discharges (SWDs): in SWD technology, a specifically-designed HF field applicator is used to launch an electromagnetic wave along the dielectric surface of a tubular plasma reactor; the vessel wall and the plasma column thus created, jointly become the propagating medium for the electromagnetic surface wave, which loses power as it travels away from the launcher [1]. SWDs possess great flexibility: a very broad (continuous) range of excitation frequencies, and wide ranges of operating pressures and plasma densities, under non-critical, almost perfect impedance matching with the power source.

In earlier experiments in these laboratories, f-dependence of plasma deposition and etching experiments using SWDs in the range 10 MHz $\leq f \leq$ 2450 MHz have been reported [2]. The plasma polymerization experiments were carried out in gas mixtures comprising

mostly argon, with only a few percent of the reactive "monomer" gases admixed; the observed frequency-dependent effects could therefore be interpreted on the approximate basis of a "pure" Ar discharge. The major changes in reaction kinetics observed in previous experiments in the region 40 MHz $\leq f \leq$ 150 MHz were attributed to changes in the stationary EEDF.

Optical emission spectroscopy provides a reliable "fingerprint" of the plasma bulk. The objective of the present study has therefore been to examine VUV-to-visible emission from H_2 and Ar/H_2 plasmas, excited over the frequency range (40 MHz $\leq f \leq$ 200 MHz), where changes in reaction kinetics for the earlier-mentioned etching and deposition experiments have been observed.

2. Theoretical background

The influence of the field frequency f on plasma parameters can be related to various phenomena, namely: 1) the penetration depth of the high frequency (HF) field in a lossy or overdense plasma, which decreases with increasing f; 2) the variation of plasma density when varying f; 3) at low enough f values, the electron energy distribution function (EEDF) varies with time, closely following the HF field intensity through its period; 4) the power transfer from the HF field to the electrons can vary when ν_m/ω (where $\nu_m(u)$ is the collision frequency for momentum transfer, and $\omega = 2\pi f$) is swept across unity as f is varied: this has the effect of inducing a dependence of the stationary (or time averaged) EEDF on f. The first two phenomena mentioned are, in our case, minimized by the experimental design.

At low enough f values, the shape of the EEDF varies considerably as a function of time within the HF field period. The EEDF is actually non-stationary as long as $\nu^e(u) > \omega$, where $\nu^e(u)$, the characteristic relaxation frequency for energy transfer from electrons of energy u to heavy particles. As f is increased, the EEDF first becomes stationary for the low energy electrons (the bulk of the EEDF); then, gradually, stationarity extends toward higher energy electrons [3].

If the gas pressure is not too high, the degree of ionization is low enough (less then 10^{-4} for argon), the electron-neutral collisions cross-section for momentum transfer varies significantly with u (as for argon, due to the Ramsauer effect); it is then possible for $\nu_m(u)/\omega$ to vary from > 1 to <1. Conditions are created for a frequency effect on the steady-state EEDF to occur. As shown in greater detail in [2], it suffices to consider only three limiting situations: case "A": low enough field frequency, so-called "DC" case ($\nu_m\langle u\rangle/\omega \rightarrow \infty$); case "H": high frequency ($\nu_m\langle u\rangle/\omega \rightarrow 0$), and dominating electron-neutral collisions; this is the so-called "microwave" (MW) case; and case "M": dominating electron-electron collisions, hence a Maxwellian EEDF.

3 Experimental apparatus and methodology

The experimental system used, shown schematically in Fig. 1, comprises the plasma source and the VUV spectrophotometer in a line-of-sight arrangement. The surface wave launcher used was a Ro-Box with a plunger and the capacitive coupler as matching elements; the power supply was a VHF oscillator with an amplifier. The frequency was measured using a frequency counter. The measuring circuit for incident and reflected power was composed of a directional line, attenuators and a thermistor detector (power meter). The directional line and

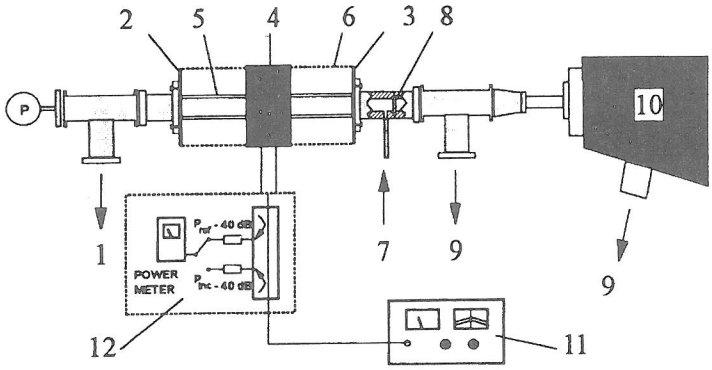

Fig. 1 Apparatus for the investigation of VUV-UV emission from surface-wave plasma: 1 - mechanical pump; 2, 3 - metal plates (short circuits); 4 - surface wave launcher (Ro-Box); 5 - quartz tube; 6 - Faraday cage; 7 - gas inlet; 8 - MgF_2 window; 9 - turbomolecular pump; 10 - VUV monochromator; 11 - variable frequency generator; 12 - power-detection circuit.

the attenuators were calibrated over the entire frequency range of interest. Only results where the reflected power was less than 20 % were taken into consideration. The plasma was excited in a tubular reactor of fused silica with an internal radius, R, of 13 mm, and a length of 320 mm; in order to confine the surface wave plasma to a known volume, and to minimize the axial gradient of the electron density, we placed conducting reflective planes at the ends of the tubular reactor, as shown in Fig. 1 [4]. The gas flow and pressure were regulated with electronic mass flow controllers and an absolute (capacitive) pressure gauge, respectively (all MKS Instruments), and UHP gases (Air Liquide Canada) were used, without additional purification.

The VUV-visible spectrophotometer ($30 \leq \lambda \leq 500$ nm, 0.2 m focal length, Acton Research VM 502, with a nominal resolution of 0.4 nm) was separated from the plasma reactor by a spectrally calibrated MgF_2 window (cut-off wavelength $\lambda_c = 112$ nm, item (8) in Fig 1); the monochromator was pumped independently of the plasma reactor by a turbomolecular pump, to less then 5×10^{-4} Torr (0.07 Pa). Since the window holder comprised a 5 cm long collimation region with an internal diameter of 6 mm, most of the measured signal was collected from the central (near-axis) portion of the reactor. Details about the monochromator setup and calibration were reported elsewhere [5].

For the case of H_2 plasmas, we used a gas flow of 10 sccm and a constant absorbed power of 50 W, while for the H_2/Ar mixture the gas flow was 15 sccm (gas flow ratio, $\phi_{H2} : \phi_{Ar} = 1 : 14$) and the power delivered to the plasma, 25 W; the pressure, p = 0.5 Torr, was kept constant in all experiments.

The plasma was first allowed to stabilize for 15 minutes before measurements commenced; following this, VUV spectra were recorded five times in the range of $100 \leq \lambda \leq 500$ nm with a sweep rate of 0.5 nm/s, and then averaged. All spectra are background corrected.

4. Results and discussion

The observed spectra comprise, in order of decreasing wavelength, several lines of the Balmer series, some molecular continuum followed, below 170 nm, by an intense emission due to the Werner ($C^1\Pi_u \rightarrow X^1\Sigma_g^+$) and Lyman ($B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$) molecular bands; and, finally, the Lyman α (Ly_α) atomic line. The molecular bands displayed by the H_2/Ar mixture are less intense, most of them belonging to the Lyman system.

The atomic emissions arise by direct electron impact on ground state hydrogen atoms, and also from the dissociative excitation of hydrogen molecules through electron impact.

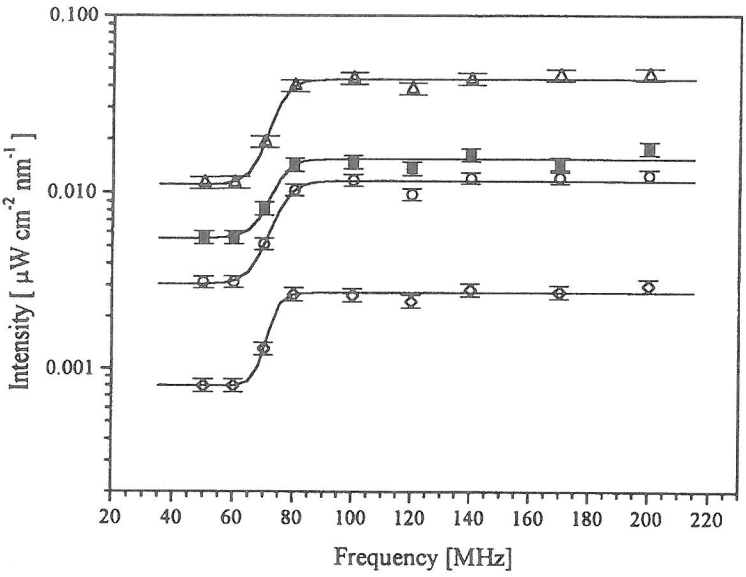

Fig. 2 Frequency dependence of the intensities of atomic hydrogen lines for hydrogen plasma (P = 50 W, p = 0.5 torr): ■ Ly_α (121.5 nm), ◇ H_δ (410.2 nm), ○ H_γ (434.1 nm), △ H_β (486.1 nm).

Figure 2 shows the absolute emission intensities for the Ly_α line, and for the Balmer H_β, H_γ and H_δ lines. With increasing f and a constant $\mathcal{P}_a$ value, the main features of the spectra show a sharp increase in intensity between 60 and 80 MHz, but above and below this frequency interval their intensity is approximately constant; in other words, within the 50-200 MHz frequency range considered, the emission intensity of each line rises from a lower to a higher plateau value. The high level of self-absorption of the Ly_α line explains why its intensity is lower than that of H_β. The observed evolution may be explained by an increase in the population density of H-atoms with rising f, due to a transition from a non-stationary to a

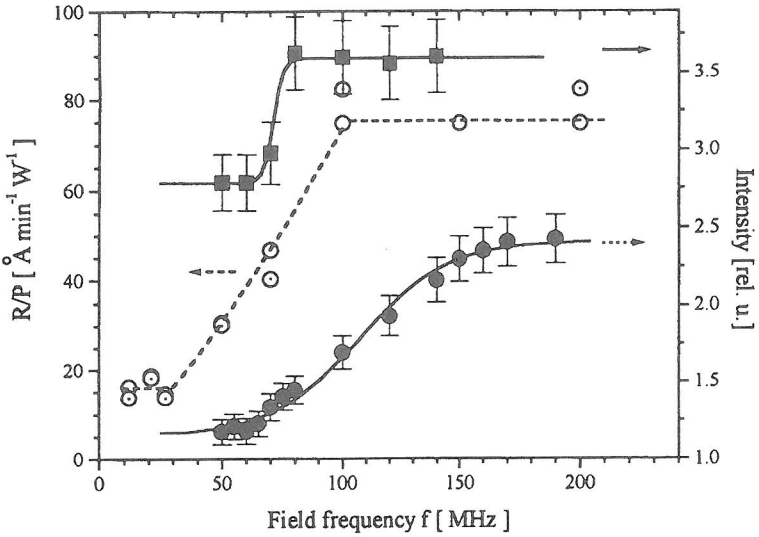

Fig. 3 Frequency dependence of the total emission intensity in the investigated VUV region (100-200 nm), at constant absorbed power, for plasmas in hydrogen (■) and hydrogen-argon mixture (●); the deposition rate normalized to the absorbed power, R/P, for (⊙ , ○) plasma polymerized isobutylene at "low" and "high" power (after Ref. [3])

stationary EEDF [3]. This interpretation is in agreement with the H_γ line upper level population density increase reported by St-Onge [6].

Figure 3 compares the total (molecular spectra and Ly_α line) VUV emission from the H_2(7%)/Ar discharge with that of the pure H_2 discharge. The variation in emission intensity with f is different, in that the transition extends over a much wider f interval for the H_2/Ar discharge. The atomic emission line intensity changes (not shown) also occur over a broader f range: after an initial sharp increase comparable with that of pure hydrogen, the line intensities increase at a much slower rate.

To the best of our knowledge, there is no published theoretical study dealing with possible modulation of the EEDF for argon-hydrogen mixture plasma in a HF electric field. As can be calculated from [7], and as estimated before in [2], the EEDF for pure Ar should be stationary for the investigated frequency range; however, the presence of H_2 may considerably alter the discharge characteristics, so a modulation of the high energy tail of the EEDF should not be excluded as a possible interpretation of our results. As explained in detail in [2], f may have a very strong influence on the power, θ, required to maintain an electron in the discharge: for the range of f investigated here, we are likely to witness the EEDF transition from a low frequency (case "A") to a Maxwellian (case "M") regime (designated "A"→"M" scenario).

5. Conclusions

We have confirmed our view that the observed *f*-dependence in low-pressure HF plasma processes can be correlated with changes in the electron energy distribution function (EEDF), namely with:

i) a cessation of modulations at low and intermediate electron energies, and an increase of the relative EEDF population at higher energies; and/or

ii) a transition from a low-frequency (case "A") to a Maxwellian (case "M") EEDF (A $\rightarrow$ M scenario).

The present results may help to explain the *f*-dependence of the deposition rate for plasma polymerized isobutylene (from a mixture of 23% C_4H_8 + Ar), also shown in Fig. 3. In all these discharges, hydrogen is an important constituent, and they are all likely to be governed by the same *f*-dependent EEDF behavior, as explained above. In the deposition experiment, VUV photochemistry may also conceivably have raised the concentration of active species in the gas phase, and may have enhanced activation of the depositing polymeric surface, especially through Ly_α irradiation [8].

References

[1] M. Moisan and J. Pelletier, Eds., *Microwave Excited Plasmas*, Elsevier, Amsterdam (1992)

[2] M. Moisan, C. Barbeau, R. Claude, C.M. Ferreira, J. Margot, J. Paraszczak, A.B. Sá, G. Sauvé, and M.R. Wertheimer, J. Vac. Sci. Technol. **B9**, 8 (1991)

[3] R. Winkler in *Microwave Discharges: Fundamentals and Applications*, C.M. Ferreira and M. Moisan, Eds., NATO-ASI Series B: Physics, **302**, Plenum Press, New York (1993) pp. 339-357

[4] Z. Rakem, P. Leprince, and J. Marec, Rev. Phys. Appl. **25**, 125 (1990)

[5] A.C. Fozza, A. Kruse, A. Holländer, A. Ricard, and M.R. Wertheimer, J. Vac. Sci. Technol. **A16**, 72 (1998)

[6] L. St-Onge, Mémoire M.Sc. (M.Sc. thesis), Université de Montréal (1992)

[7] P.A. Sá, J. Loureiro, and C.M. Ferreira, J. Phys. D: Appl. Phys. **27**, 1171 (1994)

[8] M.R. Wertheimer, A.C. Fozza, and A. Holländer, Nucl. Instrum. and Methods B (in press).