VACUUM ULTRAVIOLET TO VISIBLE EMISSION OF SOME PURE GASES USED FOR PLASMA PROCESSING

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Abstract

The vacuum ultraviolet (VUV) to near infrared (IR) emission ($112 \leq \lambda \leq 880$ *nm) from molecular gases* (H_2, O_2) *and molecular gas - noble gas mixtures* (H_2-*Ar*, O_2-*Ar) have been investigated with two separate spectrophotometric instruments. We report the influence of plasma parameters such as gas composition, pressure and microwave power upon the plasma emission. In the case of mixtures with noble gases, we selected a range of plasma parameters so as to obtain very intense VUV emissions, which can be useful for the photochemical treatment of polymer surfaces. The mechanisms involved are briefly discussed.*

Introduction

Low pressure glow-discharge plasmas are increasingly used as an effective method for the surface modification of polymers (to increase the adhesive strength, the wettability, etc.) without affecting the bulk properties of the material. However, because of the complexity of chemical reactions both in the gas phase and at the polymer surface, the mechanisms underlying such plasma treatments are not yet well understood.

Low pressure plasmas comprise a complex mixture of charged particles (electrons, ions) and neutrals (ground- and excited-state molecules, free radicals) but they can also be efficient sources of electromagnetic radiation [1]; the radiation in the vacuum ultraviolet (VUV, $\lambda < 200$ nm) corresponds to photon energies twice the covalent bond strength of most molecules, and it plays a vital role in the initiation of photochemical processes, both at the polymer surface and in the gas phase.

The literature on plasma-solid interactions deals mostly with the effects of ions, electrons and neutral species, and only a few studies have focused on the effects of UV/VUV radiation. However, before investigating the influence of VUV radiation from "real" plasmas, those including gaseous reaction products, one must know the influence of the plasma parameters such as the power, pressure and flow rate on the emission spectra from pure gases or controlled gas mixtures. In this paper we have chosen to discuss the cases of plasma in oxygen and argon/oxygen mixtures, because of the synergistic effects of VUV and atomic oxygen on polymer surfaces, known from space flight experience [2], and in hydrogen and hydrogen/argon mixtures, since these are very suitable for studying the VUV photochemistry of saturated polymers [3].

Experimental Procedures

The experimental system used, shown schematically in Fig. 1, currently comprises four major parts, in line-of-sight arrangement: the plasma source, the sample chamber, the VUV-spectrophotometer, and the optical multichannel analyser (OMA). We have used a microwave (MW) resonant cavity with a 2.45 GHz power supply as the plasma source, the plasma being excited in a quartz tube with an internal diameter of 13.5 mm and a length of 400 mm. The gas flow and pressure are controlled with electronic mass flow controllers and a capacitive pressure gauge (all MKS Instruments), and UHP gases (Canadian Liquid Air Ltd.) have been used without additional purification. The 0.2 m VUV/visible spectrophotometer ($30 \leq \lambda \leq 500$ nm, Acton Research Corp. VM 502, with a nominal resolution of 0.4 nm), is separated from the plasma reactor by a calibrated MgF_2 window (cutoff wavelength $\lambda_C = 112$ nm, item (6) in Fig. 1); entrance and exit slit widths of 250 μm and 100 μm have been used, respectively; the sample chamber and monochromator are pumped independently of the plasma reactor by a turbomolecular pump, to less than 5×10^{-4} Torr. The spectrophotometer, in the "z" configuration, uses a photomultiplier with a sodium salicylate-coated window as the detector. A photomultiplier voltage of 1.1 kV has been used. The grating movement and the data acquisition are computer controlled [4]. The OMA (Princeton Instruments, model ST120-IRY700, spectrograph model SPEX 1681) has been used in the range $250 \leq \lambda \leq 900$ nm, the optical emission being transmitted to the entrance slit of the instrument via an optical quartz fiber.

The dependence of VUV-visible emission spectra on the pressure ($0.5 \leq p \leq 10$ Torr) and power ($50 \leq P \leq 500$ W) can help to interpret the chemistry of plasma treatment of polymers, especially the role of the VUV radiation. The plasma was first allowed to stabilize for 15 minutes before measurements were started; following this, VUV spectra were recorded five times in the range $100 \leq \lambda \leq 500$ nm with a sweep rate of 0.5 nm/s, and then averaged. All spectra are background corrected.

Results and Discussion

In the case of pure gases, the excitation of the molecules by electron collisions, the dominant mechanism in low pressure plasma, depends upon the particular excitation cross-sections and the electron energy distribution function (EEDF). For energy thresholds above 10 eV (most of the atomic excitation processes), the excitation is produced by the high-energy electrons in the tail of the EEDF [5].

In Figs. 2 and 3 the VUV to visible spectra of hydrogen and oxygen plasmas are shown, respectively, as recorded by the two spectrographic instruments; the good overlap in the spectral features in the region $250 < \lambda < 500$ nm is particulary noteworthy.

For oxygen, beside the atomic lines, the O_2^+ negative system is observed, superposed with less intense Herzberg and Schumann-Runge systems [6]. The presence of OH bands is due to the formation of the electronically excited OH via the reaction of $H(^2P)$ with O_2 [7]

$$H(^2P) + O_2(^3\Sigma) \rightarrow OH(^3\Sigma) + O(^3P) \tag{1}$$

or by the reaction of metastable atomic oxygen $O(^1D)$ with residual H_2O molecules and hydrogen atoms [5]. Electron impact excitation occurs via three main processes with thresholds at 4.5, 8.0 and 9.7 eV [8], the latter two of which lead to dissociation; in addition, photochemical reactions can generate atomic oxygen in different energetic states by resonance absorption [9]. Hydrogen plasma (Fig. 3) shows the lines of the Balmer series, the molecular continuum, and below 170 nm an intense emission due to the Werner and Lyman bands, and the Lyman α line [6, 10].

Atomic line intensities in both oxygen and hydrogen plasmas are observed to decrease monotonically by one or two orders of magnitude with rising pressure in the range studied ($0.5 \leq p \leq 10$ Torr). This can be attributed, to an important extent, to a change in the EEDF: with increasing p, a higher fraction of the power that is coupled into the plasma gas is consumed by vibrational and rotational excitation, and by elastic collision processes [5]. Competing phenomena are the recombination of atoms in the gas phase and at the reactor walls.

A rise in atomic line intensities is expected with increasing power absorption in the plasma, due to the resulting rise in electron density and in the rate of the dissociation reaction [11]. While a monotonic rise is indeed observed for O_2 plasma in the applied MW power range studied ($50 \leq P \leq 500$ W), the emission intensity from H_2 plasma levels off above 250 W, presumably due to a rapid increase in the recombination rate with increasing reactor wall temperature [12].

For H_2-Ar and O_2-Ar mixtures, in which the molecular gas content is maintained below 5% [12], the EEDF of the noble gas is mildly perturbed but still close to Maxwellian, and it has a richer high energy tail. Under the present experimental conditions, argon metastables $^2P_2$ (11.55 eV) and $^3P_2$ (11.72 eV) [5] play a very important role in the overall excitation mechanism. In the case of H_2-Ar mixture, we observe the most intense Lyman α emission at 1% H_2 in Ar. The metastables increase the ground state H atom concentration by collisional dissociation of H_2 molecules (Penning transfer) through low-lying repulsive states like $b^3\Sigma_u^+$. Also, by collisional energy transfer to ground state $H(^2S)$ atoms, they can enhance the Lyman α emission (121.5 nm; $2p^2P\text{->}^2S$) and even Balmer α (656.3 nm; $3p^2P\text{->}2p^2P$) [14]. For pressures above 1 Torr, the intensity increase of the atomic lines is less pronounced, presumably due to a decrease in the metastable population resulting from the higher rate of collision.

A similar behaviour is observed for O_2-Ar mixtures, for which the atomic line intensity maximum occurs near 2.5% O_2 in Ar. This increase in 130.4 nm and 844.5 nm atomic line intensities may result from collisional excitation of dissociative states (for example to $B^3\Sigma^-_u$ - 8.741 eV and $1^3\Pi_u$ - 10.403 eV states), which can increase the concentration of ground state (^3P) atoms, and the excitation by further collisions to ^3S (9.52 eV) and ^3P (10.98 eV). These proposed mechanisms are now being further investigated by titration measurements [11].

Conclusions

Optical emission spectroscopy from plasmas of pure gases and gas mixtures has revealed intense emissions in the VUV spectral region. The pressure and power dependence can be correlated with changes in the EEDF, and with the rates of wall and volume recombination.

The known sensitivity of Ar plasma emissions towards the presence of impurities can be put to use in generating very intense atomic emissions, stronger even than those resulting from plasmas in the pure molecular gases. This can be attributed to efficient collisional energy transfer from metastable Ar atoms. The mixtures that we have investigated can therefore be used as powerful light sources, for example, for the VUV treatment of polymer surfaces, an important objective in our future research. In our plasma system, the VUV emission can be well correlated with the OMA measurements in the region of overlap ($250 \leq \lambda \leq 500$ nm); in view of the similar behaviours of spectral features in the VUV and at longer wavelengths we have reported here, the far more convenient OMA can therefore be used as an overall monitor.

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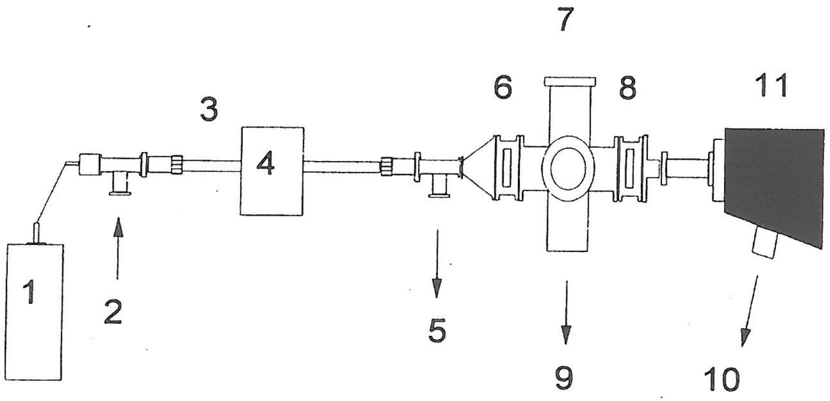

Fig. 1: Apparatus for the investigation of VUV - VIS emission from MW plasma: 1-OMA; 2-gas inlet; 3-quartz tube; 4-MW cavity; 5-mechanical pumping unit; 6,8-window supports for MgF_2 filters; 7-sample chamber; 9,10-to turbomolecular pumping unit; 11-VUV monochromator.

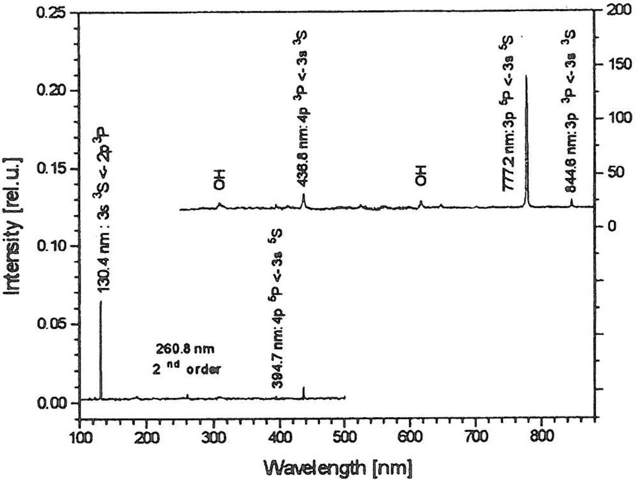

Fig. 2: VUV-visible oxygen spectra obtained with the two spectroscopic instruments; p = 1 Torr, P = 250 W, Φ = 100 sccm.

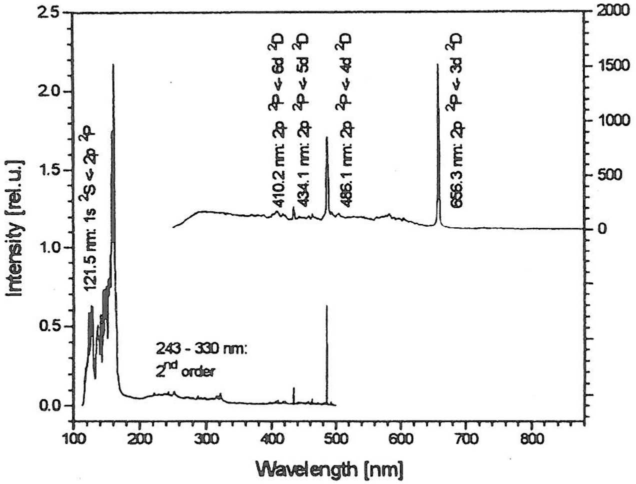

Fig. 3: VUV-visible hydrogen spectra obtained with the two spectroscopic instruments; p = 1Torr, P = 250 W, Φ = 100 sccm.