

An In Situ Comparison between VUV Photon and Ion Energy Fluxes to Polymer Surfaces Immersed in an RF Plasma

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Absolutely calibrated vacuum ultraviolet (VUV) spectroscopy has been used to determine the energy fluxes of VUV photons at an electrically floating substrate in a low-pressure 13.56-MHz radiofrequency plasma reactor used for polymer surface treatments. These fluxes have been compared with the positive ion flux that was reported in an earlier study. At the typical operating parameters of 10-mTorr pressure and 10-W power, the total VUV energy flux is 2.2 mW cm^{-2} , compared with a value of 3.3 mW cm^{-2} from the ions. With increasing power (from 0.5 to 12 W), both the ion and VUV energy fluxes increase monotonically. However, as the pressure increases, (1–100 mTorr), the ion energy flux declines, while the VUV component increases. At discharge powers of 10 W, and pressures greater than 25 mTorr, the greater part of the energy flux to the surface is from the VUV photons. These measurements are used to determine which of the plasma components, VUV or ions, will be most effective in the treatment of polystyrene surfaces in a pure Ar plasma. Because of the low VUV absorption coefficient of polystyrene most of the photon flux penetrates through the outermost 2 nm of the polymer surface without attenuation. Consequently, we calculate that under typical plasma operating parameters, the ions play the major role in the modification of polystyrene surfaces because of their shorter stopping distances.

1. Introduction.

The use of low-pressure, radiofrequency (RF)-coupled, wire-wound plasma discharges is widespread,¹ both for polymer surface modification and polymerization. Polymer surface modifications are performed for various reasons, including improving polymer surface wettability, adhesion, and biocompatibility, which can be achieved without altering the bulk polymer properties. For surface modification purposes both inert gases (e.g., Ar) and reactive gases (e.g., O₂) are used. The use of inert gases is extremely widespread, perhaps because inert gases offer greater process control. However, even Ar plasma treatments of short duration (1 s to 5 min) can alter polymer surface topography² and activate the polymer surface such that there is a significant uptake of oxygen in the polymer surface.^{3,4} Whether this oxygen is incorporated on exposure of the polymer surface to atmosphere, or from plasma impurities remains unclear, and is probably very reactor-dependent.

The Ar plasma treatment of polystyrene is the subject of this article. Polystyrene is an important biomedical material. Tissue culture plastics are typically polystyrene as are many other important biomedical plastics. The surface properties of polystyrene are generally not suited for biomedical applications, and plasma modification is one option to improve upon these poor surface properties. As the plasma simultaneously bombards the polymer surface with several energetic species, there is some debate as to which plasma particles are chiefly responsible for the surface modification. In particular, the respective roles of positive ions and VUV photons are still unresolved, with both species being shown to produce the observed surface modifica-

tion independently. For example, Ada et al.⁵ used a low-energy (10–100 eV) ion beam to fluorinate polystyrene samples. The VUV treatment of polyethylene has been studied by Holländer et al.,⁶ who observed increases in the surface O/C ratio after several minutes exposure to the VUV emission of a microwave discharge in a variety of gas mixtures. It must, therefore, be recognized that the VUV may be an important agent in promoting surface modification in the plasma treatment of polystyrene.

In this study, we have undertaken to measure the VUV photon transitions present in a radiofrequency (RF) “barrel” reactor. Such measurements have not been made previously. These measurements complement those of plasma particle flux measurements made in the same reactor in an earlier study,⁸ and allow us to present a direct comparison of the energy fluxes due to positive ions and VUV photons for a range of generator powers and gas pressures which has not been previously performed.

These plasmas, often mistaken for inductively coupled devices, have been the topic of some recent studies. For instance Beck et al.⁷ measured the ion flux to surfaces inside such a reactor in a deposition plasma. Using electric probes, Barton et al.⁸ obtained the intrinsic plasma parameters of plasma potential, electron temperature, and plasma density as functions of input power, neutral pressure, and spatial position within the chamber for an Ar plasma. These measurements allowed the ion energy flux to a polymer surface (which is electrically floating) to be calculated and compared with a theoretical estimate of the VUV energy flux made by Piejak et al.,⁹ for a parallel plate discharge. There is growing interest in making such in situ measurements. For example, recently, Fozza et al.¹⁰ measured the VUV emission from a microwave discharge and obtained the VUV energy fluxes to surfaces immersed in their reactor.

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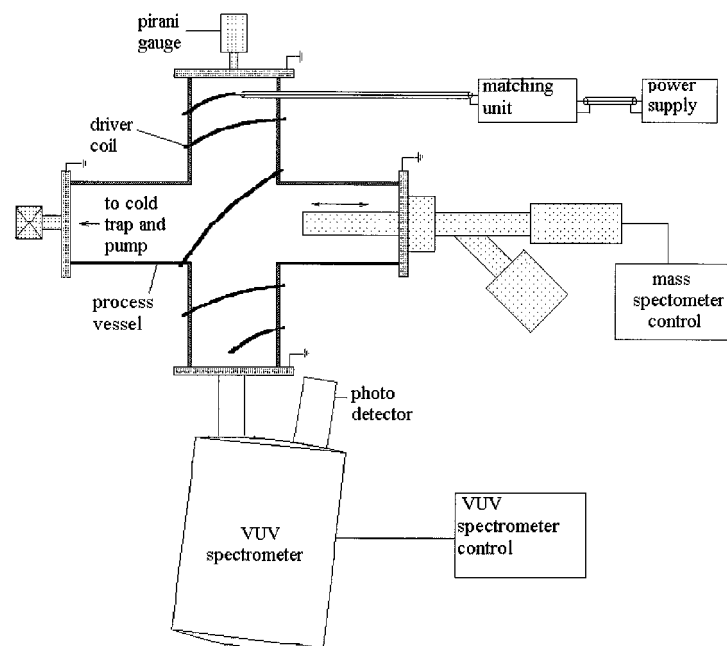


Figure 1. A schematic diagram of the experimental apparatus.

2. Experimental Procedure

The experimental rig is described in detail elsewhere,⁸ and is shown in Figure 1. It comprises a glass cross-piece vessel, with an excitation coil wound around one axis. RF (13.56 MHz) power (between 0.5 and 70 W) is applied to the coil, causing breakdown of the Ar gas across a pressure range of 1–100 mTorr. A full survey of the plasma parameters of self-bias (V_{sb}), floating (V_f), and plasma (V_p) potentials, electron temperature (T_e), and plasma density (n_e) is given in ref 8. In this study, the only difference made to the system described in ref 6 is the addition of the spectrometer to one arm of the vessel (Figure 1).

The spectrometer entrance slit is decoupled from the plasma at the flange face by a stainless steel gauze, which prevented the plasma from penetrating into the instrument flight tube. The instrument is a normal incidence, 1-m focal length device supplied by Rank Precision Industries Ltd. To inhibit VUV absorption within the instrument, the spectrometer body is evacuated to a pressure of about 5×10^{-6} Torr by a turbo molecular pump. Light entering the instrument is reflected from a grating onto the output slits, behind which a sodium salicylate scintillator plate converts the VUV photons to visible wavelengths, which are then detected by a photomultiplier tube. Overall, the spectrometer was capable of detecting wavelengths in the range 50–600 nm, with a measured wavelength resolution of 0.35 nm. The calibration procedure showed that, near the wavelength of the predominant VUV lines, the instrument was capable of detecting photon fluxes above 5×10^{14} photons $s^{-1} cm^{-2}$. This photon flux corresponds to a minimum energy flux of about $7 mW cm^{-2}$.

The calibration procedure was performed as a separate experiment, away from the discharge chamber, but using the same spectrometer optics. The calibration source (Optronic Laboratories model No OL455–12) was a stabilized quartz halogen filament placed inside an integrating sphere. The sphere's luminance is monitored by a silicon detector with an accurately known photonic response, which is mounted into the sphere wall. The overall source has certificated calibrations, traceable from the National Institute of Standards Technology (NIST) for both color temperature and spectral radiance.

This type of source provides a photon flux calibration in the visible region. The extension of the calibration into the VUV was performed using a branching ratio technique.¹¹ This technique compares the ratio of two lines, one in the visible and one in the VUV, which share a common upper atomic level. The intensity ratio of the lines is given by the ratio of the known transition probabilities, which permits calibration into the VUV range. For convenience, we used a 150 W, 20-mTorr hydrogen discharge, on the basis that the Balmer β H_β ($n = 4-2$) and the Lyman γ L_γ ($n = 4-1$) lines were sufficiently intense, and the L_γ transition had a wavelength of 97.3 nm, which is close to the observed argon transitions at 104.8 and 106.7 nm.

3. Results

A complete survey of the spectral lines between $\lambda = 70$ and 600 nm was made for generator powers between 1 and 12 W and argon pressures in the range 1–100 mTorr. The dominant transitions were identified as Ar(I) 3p₆–3p₅ ($2P_0 < 3/2 >$) (106.7 nm) and 3p₆–3p₅ ($2P_0 < 1/2 >$) (104.8 nm). Other Ar lines were observed at about 420 nm, most noticeably the 4s–5p transition at 420.1 nm, which had an intensity of about twice that of the 106.7-nm transition. However, the energy carried by photons at these longer wavelengths is only about 2.9 eV, which is below the bond strength of most polymers.⁸ Also, many polymer materials, polystyrene, polypropylene, and polyethylene, for example, have very low absorption coefficients at these longer wavelengths.¹² Because of these considerations, we concentrate our energy flux analysis on the 106.7-nm and 104.8-nm lines. The only impurity line in the VUV range detected by the instrument was the hydrogen L_α transition at 121.5 nm. We attribute the presence of hydrogen in the discharge to desorbed water from the chamber walls, which is dissociated in the plasma. This line had an intensity which was comparable with the Ar lines, as shown in Figure 2. The energy flux of this line is significant (the photon energy being 10.2 eV) and has been included in our calculations. We did not identify any Ar(II) transitions, which may be explained as the Ar⁺ concentration is 3 orders of magnitude below that of the neutral atoms.

Figure 3 shows the experimentally derived energy flux of the 106.7, 104.8, and 121.5 nm Ar and H lines compared with

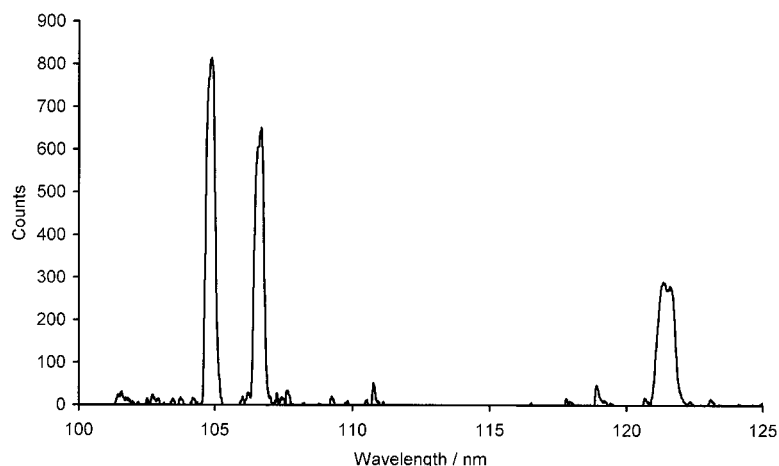


Figure 2. Measured VUV spectrum showing the dominant Ar transitions (106.7, 104.8 nm) and the single hydrogen line at 121.5 nm. The argon pressure was 10 mTorr and the discharge power was 10 W.

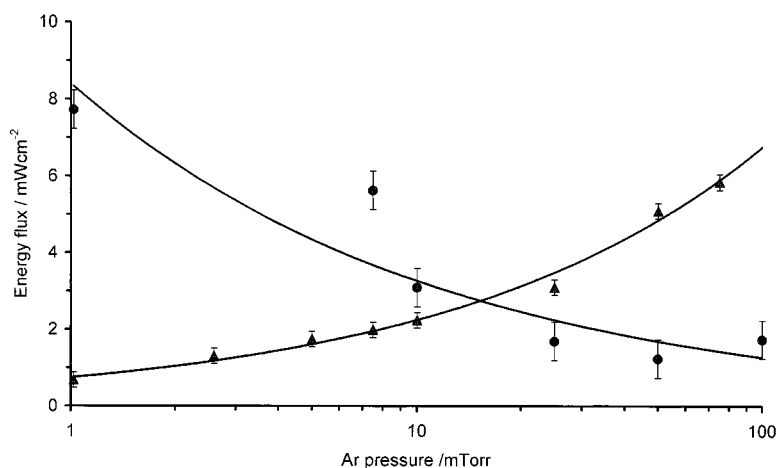


Figure 3. Total VUV photon energy flux (triangles) compared with the ion energy flux⁸ (dots) as a function of argon pressure at a generator output of 10 W. The error in the photon fluxes is the standard deviation of a data set taken under standard conditions over several experimental runs. The error in the ion fluxes is associated with the energy spread of the ion energy distribution function, caused by collisions in the sheath region.⁸ The curves are a guide to the eye only.

that due to ions, which were derived from Langmuir probe and IEDF studies.⁸ The graph shows that as the argon pressure increases, the VUV flux increases because of the increasing neutral density. Conversely, the ion energy flux declines as the plasma density and potential decrease with increasing pressure.⁸ Above about 25 mTorr, the VUV energy flux to a surface exceeds that from the ions. Under the typical operating conditions⁸ of about 10-mTorr pressure, 10-W input power, the ion flux exceeds the photon flux to the polymer surface by a factor of 1.5. The positive ions are neutralized at the polymer surface, thereby releasing the recombination energy (ionization potential) to the polymer. We therefore estimate the ion energy flux by summing the bombarding (kinetic) energy and the argon recombination energy (15.76 eV). From elastic collision theory¹³ the proportion of ion kinetic energy transferred to the polymer molecule is a function of the respective masses, the proportion decreasing with increased target mass. The collisions are atomic, so the proportion of the kinetic energy transferred depends on which atomic species is struck. However, even considering an Ar ion colliding with the styrene repeat unit ($m/z = 104$), about 80% of the argon kinetic energy is transferred to the polymer, which we take as a lower limit.

Figure 4 shows the VUV flux as a function of generator power at a constant pressure of 10 mTorr. Both the ion and photon energy fluxes increase with the plasma density across the

experimental power range.⁸ This is expected because the ion flux to a surface is given by the product of ion density and velocity at the plasma-sheath boundary,¹³ whereas the VUV production rate is also an increasing function of electron density.

The results indicate that, in general, in these plasmas, the VUV energy flux of the dominant lines is of the same order as the ion energy flux to electrically self-biased surfaces. However, in polystyrene, the VUV absorption coefficient^{14,15} is sufficiently low that the distance through which a photon is absorbed is an order of magnitude greater than the ion-stopping distance. Consequently, energy absorption of the VUV photons is distributed throughout several atomic layers, whereas most of the ion energy deposition is within the outermost 1 nm of the polymer surface. This view may be supported by X-ray photoelectron spectroscopic (XPS) measurements made of Ar plasma-modified polystyrene surfaces presented in earlier studies.^{3,4} These reveal a marked oxygen gradient in the polystyrene surfaces, with most of the oxygen located in the top 1 nm of the polymer surface. If the principal agent of surface activation were the VUV, one might anticipate more even oxygen incorporation across the XPS sampling depth.

As well as obtaining the steady-state VUV fluxes, the line intensities were obtained as a function of discharge run time immediately after a vacuum break. This represents 'real' process conditions, in which samples are introduced to the chamber,

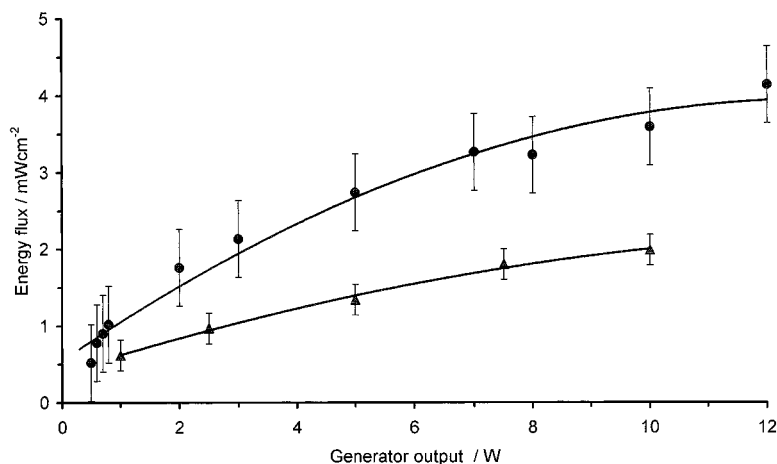


Figure 4. Total VUV photon energy flux (triangles) compared with the energy flux from ions⁸ (dots) as a function of generator output at an argon pressure of 10 mTorr. The curves are a guide to the eye only.

and processing takes place within the first few minutes of discharge operation. We observe a 20% increase in the VUV intensity during the first few minutes of discharge operation until steady-state conditions are reached after about 20 min. These time scales are comparable with desorption of air and water from the vessel walls, which was previously observed using a mass spectrometer. Our measurements of the time evolution of the 121.5-nm hydrogen line (not shown) also support this view.

These measurements do not resolve the issue of whether the oxygen incorporation observed in Ar plasma treatment of polystyrene^{3,4,8} occurs within the reactor during plasma treatment (from residual water, atmospheric gases) or on exposure of the 'activated' polymer surface to atmosphere.

4. Conclusions

Using absolutely calibrated VUV optical spectroscopy, we have determined which atomic transitions give the dominant spectral lines in Ar plasmas used in the surface modification of polymers. By performing an absolute calibration of the spectrometer we have transformed the line intensities to give energy fluxes to such surfaces immersed in the plasma. We observe that almost all the VUV flux to the polymer surface may be accounted for by the 3p6–3p5 ($2P_0 < 3/2 >$) (106.7 nm) and 3p6–3p5 ($2P_0 < 1/2 >$) (104.8 nm) Ar transitions, and the impurity hydrogen L_{α} transition at 121.5 nm. Under typical operating conditions of about 10 mTorr argon pressure and 10 W generator output, the energy flux caused by these two lines is $2.2 \pm 0.2 \text{ mW cm}^{-2}$. This value is about two thirds the energy deposition flux caused by the ions under these conditions. However, we observe that as the argon pressure increases, the VUV flux also increases, while the ion energy flux declines. Consequently, at pressures greater than about 25 mTorr, the VUV energy flux is greater than that of the ions.

However, in the plasma treatment of polystyrene, the efficient transfer of ion energies close to the polymer surface, compared

with deeper penetration of the VUV photon flux, makes their role more important in the modification of this particular polymer.

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