Atmospheric Plasma Analysis by Molecular Beam Mass Spectrometry


Introduction

The use of atmospheric plasma is growing in interest due to their advantages in processing materials, mainly organic, which are not suitable for high vacuum. Such plasmas are commonly studied by optical emission spectroscopy. It is important to understand the surface properties of the treated material. It is important to know the energy and identity of the impinging species.

Atmospheric discharges arise from a number of gas mixtures. These plasmas are typically used to study the chemistry of oxidising and reducing gases. Several plasmas, e.g. O+ + O + 2e (Ei=20.3 eV), 

The discharge was generated by a radio frequency driven atmospheric plasma source and sampled using a multi-stage differentially pumped molecular beam mass spectrometer. Results for gas mixtures containing different percentages of O3, N2O, and CO2 in helium are compared.

Neutrals

Energy distributions of the ions/species are reported as a function of the discharge power and distance between the plasma source and the entrance to the analyser.

Additionally, the pathways for producing radical species in the various mixtures were identified by electron attachment and appearance potential methods.

Experiment

(i) Discharge

The discharge was generated by a radio frequency driven atmospheric plasma source, based upon the design of Stoffels et al. [1]. This original design was adapted to include a second, concentric gas inlet in order to study mixtures of gases. The inner gas inlet delivers helium to the plasma volume and the outer gas inlet carries different percentages of the gas to be studied (oxygen, nitrogen, nitrogen/carbon dioxide). The low power discharge, around 7W, was produced between the plasma source and the entrance of the Molecular Beam Mass Spectrometer (MBMS) analyser as shown in Figure 1.

(ii) Diagnostics

Species created in the atmospheric discharge were sampled using a triple stage differentially pumped molecular beam inlet system and subsequently detected with the Hiden EQP mass/energy analyser. A schematic of the arrangement is shown in Figure 2. The EQP mass/cage analyser is housed in a vacuum chamber with a further two intermediate expansion chambers between it and the plasma. Each of these three chambers, or stages, are separated by slitted slitter cones and continuously pumped by separate turbo molecular pumps. Due to the free expansion from atmospheric pressure to the lower pressure conditions a molecular beam is formed and plasma species are sampled and detected without undergoing further reactions.

Ozone

Ozone produced by atmospheric plasma sources is widely used as a sterilising agent. Ozone is formed in a commercial ozone generator. The internal ionisation source of the EQP mass/energy analyser may also be set to operate at low electron energies in order to study electron attachment processes. The electron attachment scan for the production of O(3P) is shown in Figure 5 when the ozone generator is on and off. For both cases there is a large attachment region between 0.5-1.0 eV which is from direct attachment to O3.

When the ozone generator is switched on, a second, smaller attachment peak is seen around 0.7 eV which is due to the dissociative attachment process; 

The ion energy distribution (O+ ions) was also measured as a function of discharge power as shown in Figure 4. The discharge conditions were He(75%)/O2(25%) at a distance of 3mm, increases and more energetic ions are observed with the tail of the distribution extending to almost 10keV at 10kW.

Conclusions

The Hiden MBMS System and subsequently detected with the Hiden EQP mass/energy analyser. A schematic of the arrangement is shown in Figure 1. The EQP mass/cage analyser is housed in a vacuum chamber with a further two intermediate expansion chambers between it and the plasma. Each of these three chambers, or stages, are separated by slitted slitter cones and continuously pumped by separate turbo molecular pumps. Due to the free expansion from atmospheric pressure to the lower pressure conditions a molecular beam is formed and plasma species are sampled and detected without undergoing further reactions.

Reference


Figure 1. Atmospheric plasma produced between the RF electrode, or needle, and the sampling orifice of the Hiden Molecular Beam Mass Spectrometer.

Figure 2. Schematic of the Hiden Molecular Beam Mass Spectrometer System. The three cones are fitted with apertures of 0.5mm at the first stage, 0.4mm at the second stage and 1.0mm at the entrance of the EQP mass/energy analyser.

Figure 3. Figure shows a representative positive ion spectrum from a He(75%)/O2(25%) discharge. The discharge was produced at low power (7W) and at a distance of 4mm from the MBMS sampling orifice.

Figure 4. Ion energy distributions for O+ ions from the He/N mixture as a function of distance from the sampling orifice.

Figure 5. Ion energy distributions for O+ ions from the He/O2 mixture as a function of discharge power.

Figure 6. Neutral mass spectra for plasma on (red trace) and plasma off (green trace).

Figure 7. Appearance potential scans for O with the plasma on and off. The threshold for the dissociative ionisation of O3 is 20 keV.

Figure 8. Appearance potential scans for N with the plasma on and off. The threshold for the dissociative ionisation from N2 is 25 keV.