Windowless VUV spectroscopy of atmospheric pressure plasmas

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Abstract: Measuring plasma-emitted VUV photons can provide useful information about excitation processes in the plasma and about the presence of atomic and molecular species. In this contribution, the windowless VUV spectroscopy will be introduced in details and the VUV spectra of variety of atmospheric plasmas will be presented. These measurements will be compared to densities of O, N and other species as measured by mass spectrometry.

Keywords: VUV spectroscopy, atmospheric plasma

1. Introduction

Atmospheric pressure non-equilibrium plasmas (APPs) are effective source of large densities of reactive radicals, metastables and ions and also high fluxes of photons. Among those are also highly energetic vacuum UV (VUV) photons with wavelengths below the cutting edge of LiF or MgF₂ window materials. The resulting high reactivity of these APPs can be used in many surface treatment applications such as activation of polymer surfaces, treatment of living tissues (decontamination, acceleration of wound healing) or in deposition of thin films or nanostructured materials. To gain insights into the effects of the different plasma components, a microscale Atmospheric Pressure Plasma Jet (µ-APPJ, Fig. 1) operated in helium with a small (up to 1%) admixture of a molecular gas (e.g. O₂) can be used.

With this plasma source, the treated substrates are not directly immersed in plasma but they are exposed to the effluent, which main reactive parts are plasma generated reactive species and emitted photons. This source has been described and studied extensively in the past by several groups and quantitative measurements of O, N, O₃ and O₂(a¹Δg) densities and qualitative information about ions in the effluent are available [1-5]. Most of the in-plasma-generated ions and electrons recombine in the effluent and only some in photochemical reactions induced water cluster ions has been measured by MS near the substrate. [6]

2. Windowless VUV Spectroscopy

Many excited species in APPs are emitting photons in the vacuum ultraviolet (VUV) wavelength region with wavelength below 200 nm. This photons cannot propagate through air, but since many of the APP sources are operated in argon or helium, they can propagate through the gas channel formed by the noble gas and can therefore reach the surface even at the distance of several tens of mm from the jet. It is, therefore, important to investigate at least qualitatively the VUV spectra of APPs. To achieve that a windowless VUV spectrometer has been designed for this measurements and is schematically shown in Fig. 2.
The principle of coupling the plasma emitted VUV and UV photons into the He-filled VUV spectrograph without necessity of having any window between the plasma and the spectrograph function as follows: all the potentially absorbing species in the plasma (such as molecules introduced into the plasma as precursor gas) are steered by the additional helium flow into the side and cannot enter the spectrograph. Additionally, controlled atmosphere around the jet is used to prevent air to diffuse into the light path. Fig. 3 shows the measured spectrum of the μ-APPJ operated with helium gas in the 50 to 140 nm wavelength range. Next to the few atomic oxygen lines, resulting from the excitation of the gas impurities, the clear emission of the 1st and 2nd helium excimer continuum is visible.

Fig. 3. VUV spectrum of the μ-APPJ operated in the 5.0 grade helium gas.

These photons can propagate through the helium gas without being absorbed, since the first photon absorption by ground state helium is possible to the (1s)(2p) level corresponding to the wavelength of 58.44 nm only. The spectrum in Fig. 2 is very similar to the spectrum reported for a micro-hollow cathode discharge in helium [7]. The windowless VUV spectrograph have been used to record emission spectra of several gases admixed at concentrations below 1% into the helium in the μ-APPJ. Three examples of the plasma with O2, N2 and Ar are compared to the spectrum of helium gas only from Fig. 3 in Fig. 4.

It should be noted that the spectrometer grating is optimized for 130 nm and its efficiency decreases both at shorter and longer wavelengths. Worth to mention is especially the spectrum of the He/0.14%Ar mixture, where the He excimer emission is fully replaced by atomic lines of argon. The plasma is maintained by argon ion atoms, since it has much lower ionization and excitation energy than He, without formation of Ar2+ ions and argon excimers. This mechanism was nicely demonstrated and explained by Castaños-Martínez et al. [8] in surface wave tubular discharge at atmospheric pressure operated with Ne and Ar gases.

Fig. 4. Exemplary VUV and UV spectra of μ-APPJ with He, Ar, He/0.07%O2, He/0.14%H2 and He/0.14%Ar gas mixtures.

The VUV spectra, and their dependence on the variety of plasma parameters, can be used as an additional information for the analysis of the plasma-chemical processes in APPs. Special feature of this high energy VUV photons is that they can photo-ionize or dissociate species at larger distances from the jet, as was already suggested in the past [9]. These in photochemistry generated species should be considered for example in the treatment of biologically relevant substrates. We have reported recently the possible effect of protonated water cluster ions, which formation was initialized through photoionization, on bacteria [6].

3. Summary

Atmospheric pressure plasmas operated with noble gases can generate vacuum UV photons, which are then transported through the noble gas to substantial distances. The windowless vacuum UV emission spectroscopy was introduced and applied to atmospheric pressure plasmas measuring photons down to the wavelength of 58 nm. These measurements provide useful information about possible reaction mechanisms in the discharge (excimers or atomic species), about excitation processes in the plasma and about the presence of atomic and molecular species. The parameter dependencies for helium and argon containing plasmas with small admixture of molecular gases will be presented and compared to available mass spectrometry data.

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5. References