Time-discretized extreme and vacuum ultraviolet spectroscopy of spark discharges in air, $\text{N}_2$ and $\text{O}_2$

To cite this article: D Trienekens et al 2016 J. Phys. D: Appl. Phys. 49 035201

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I. Introduction

Photoionization plays an important role in the early stages of streamer and spark discharges, as becomes evident from experiments on discharges in N$_2$/O$_2$ mixtures [1–3]. Discharge models incorporating photoionization generally assume the necessary photoionization capable emission originates from molecular bands of nitrogen in the vacuum ultraviolet (98–102.5 nm) [4–9]. This assumption is based on spectra obtained by measuring the spectra resulting from electron impact in N$_2$ [10, 11]. However, experimental proof that this emission also takes place in the early stages of streamer and spark discharges is lacking.

In a previous paper [12], a system was presented that is capable of performing spectroscopic analysis of spark discharges in the EUV/VUV region (60–160 nm in this case). Using an electrically actuated fast pneumatic gate valve (referred to as a puff valve), a pressure gradient is introduced in a discharge chamber, such that a spark discharge takes place in near atmospheric conditions, whereas the rest of the system remains under vacuum. The latter allows for the propagation of EUV/VUV radiation generated by the discharge. Removing the transparent dielectric barrier separating the discharge chamber from the spectrograph (as was used previously in [13, 14]) enables studying EUV radiation down to 60 nm, which would otherwise be absorbed by the dielectric barrier.

In [12], it was noted that statistical variances significantly affected the measured spectra, leading to physically unresolvable negative values for background corrected intensities. Also, it was noted that spectral lines often appeared to be very broad. Although it was not made clear whether this was due to the apparatus profile or due to physical line broadening mechanisms, it is reasonable to assume that the apparatus profile...
is the dominant contributor to measured spectral line widths. Thirdly, the apparatus sensitivity profile was unknown, making it impossible to directly compare intensity of lines from different positions in a given spectrum.

In general, earlier results obtained using this system have not yet provided us with a clear view of the temporal development of the emission spectrum of spark discharges in the EUV/VUV region. Measurements in air and air-relevant gases and a more extensive analysis of the system are therefore needed.

II. System analysis

To be able to compare line intensities, the obtained spectra have to be corrected using an apparatus sensitivity profile. The fluorescent quantum efficiency of the sodium salicylate scintillator used has been assumed constant throughout the measurement range, as suggested by literature [15].

The grating reflectance was also taken into account. It was found that the percentage of light that is reflected by the grating varies from 5% to 89% through the measurement range (see figure 1) [16, 17]. The grating reflectance is assumed to be the dominant mechanism influencing the sensitivity of the system, and is used to correct the obtained intensity of the lines.

This finding may explain why the spectra presented in [12] show relatively low intensity for lower wavelengths.

It was found before that spectral lines obtained by the system are relatively broad, mostly due to the apparatus profile. This may lead to an overestimation of some lines, especially in the steep parts of the reflectance curve. Therefore, the reflectance curve is convoluted with a triangular profile, yielding a more realistic sensitivity correction.

In order to reduce statistical variances in the obtained spectra, we investigated discharge behavior for a large number of shots using an Andor DH734-25U-03 ICCD camera. Analysis of the obtained images showed the discharge would often propagate along the puff valve cap or on the dielectric surface beneath the electrodes in its early stage, as can be seen in figure 2. Figures 2(a) and (c) show the discharge propagating upwards from the electrodes and along the puff valve cap. Figure 2(b) shows the discharge propagating along the Kel-F surface beneath the electrodes, see reference [12] for geometry details. The close proximity to the discharge ruled out the use of a metal entrance slit. Kel-F (PCTFE) (polychlorotrifluoroethylene (CF₂CC(F)n) was used to construct the entrance slit due to its opacity and high machinability. In both cases, the discharge largely avoids the entrance slit to the spectrometer chamber, which is located directly between the needles. In a later stage, after ~50 ns, the discharge would...
propagate between the needle electrodes. This behavior however did not always occur and was perceived as stochastic in nature.

Due to this stochasticity in the early stage of the discharge, it is obvious this behavior is a cause of statistical variance in the captured signal. In order to increase reproducibility of the discharge, we placed a ~2 mm Kel-F spacer underneath the needles. This forces the discharge along the spacer surface (and across the entrance slit), greatly reducing the statistical variance observed before.

Figure 3 shows the obtained PMT signals for 10 shots at 130 nm, all taken under the same conditions and with the Kel-F spacer beneath the needles. Statistical variation was greatly reduced by the introduction of the Kel-F spacer. However, as can be seen, a significant amount of variation still exists between subsequent shots, most likely due to the stochastic nature of the discharge. No discharge took place at the last shot, therefore it is neglected in the averaging process. Note there is also some jitter in the start of the PMT signal, a result of discharge inception jitter. This was corrected for when averaging over the 10 shots.

In general, we found that correlation between shots was lower for lower wavelengths. This is most likely a result of the increased necessity of background corrections and the lower grating reflectance, leading to relatively higher noise.

III. Experiments

Spectra in the 60–160 nm region were obtained for air, O₂ and ultra high purity (uhp) N₂. All spectra were averaged over 10 shots and have a spectral resolution of 0.5 nm. Background measurements were performed using the method described in [12] and averaged over 5 shots. This results in a total of 3015 shots per spectrum. Although the exact pressure is unknown, it was shown in [12] that for a high voltage pulse delay of 350 μs (with respect tot the puff valve trigger) a pressure of 200–500 Torr is to be expected. This value was derived by comparing the discharge morphology at varying high voltage pulse delays to the discharge morphology at varying static pressures.

Obtained spectra are shown in 50 ns timesteps. Although severe artificial broadening of the lines still complicates interpretation of the data, spectral content can clearly be distinguished. The comparison between air, uhp N₂ and O₂ clearly shows a difference in the 90–110 nm region, especially in the first ~250 ns of the discharge. Moreover, this range is known to correspond to strong emission from the \( b^1 \), \( b^1' \) and \( c^4 \) singlet states of N₂ (i.e., the Birge-Hopfield I and II, and Carroll-Yoshino bands) [10, 11]. Note that for wavelengths below 102.7 nm direct photoionization of the oxygen molecule is possible. Photoionization is always assumed to play an important role in the early stages of discharge inception and propagation [1–9, 18–20]. Molecular nitrogen, having a higher ionization potential than molecular oxygen, is capable of emitting photons with the energy required for this process.

An example of two averaged PMT signals that are corrected for grating reflectance is shown in figure 4.

In order to reduce the effect of statistical variance, we reject shots where the time difference between the start of the PMT signal and the voltage pulse is larger than 50 ns. Also, shots were the PMT signal stays below a threshold value of 1 V are taken as zero to suppress noise.

Combined, the improvement made on the setup and the acquisition of an apparatus sensitivity profile is expected to result in more reliable obtained spectra.

Figure 3. Example of PMT signals for air at 130 nm. Shown are 10 shots over which averaging takes place. Average correlation between two shots is 67%.

Figure 4. Averaged PMT signal for 107 and 120 nm. The signal is corrected by dividing by the grating reflectance percentage.
Our results show that spectra for air and uhp N₂ are very similar in the 90–110 nm region in the first 150 ns, as can be seen in the upper three panes of figure 5. Also, it is evident that emission for O₂ is much lower in this region. This clearly shows that for air and uhp N₂, emission is taking place in the region where direct photoionization of molecular oxygen is possible, whereas this emission is much lower for a discharge in O₂. This implies emission is indeed mostly due to the presence of nitrogen.

In the later stage of the discharge, a large peak at ~107–109 nm can be seen in all three spectra. Although the purity of the oxygen is not known exactly, the fact the peak arises in all three spectra (air, O₂ and uhp N₂) suggests an external factor. Emission from Cl, introduced in the discharge gap by degradation of the C–Cl bond in the Kel-F spacer under the needles, is the most likely reason for the 107–109 nm peak [23, 24]. A peak at 107.5 nm was observed by Stephens et al in additional experiments on the same setup [25].

A comparison between the experimentally obtained spectrum in air (90–160 ns) and the theoretical spectrum obtained by Spectraplot is shown in figure 6. An electronic temperature of 1.6 eV was assumed for this stage of the discharge [25]. Note that only atomic and singly ionized nitrogen and oxygen were taken into account. As can be seen, several of the experimentally observed spectral features are present in the theoretical spectrum as well. The difference in intensities may be explained by the fact that we expect our plasma not to be optically thin, an assumption that is used in SpectraPlot. This might for instance cause the lower intensity for the 120.0 nm line in the experimentally obtained spectrum. This is a transition to the ground state of atomic nitrogen, meaning self-absorption should play an important role here. Also, the assumption of local thermodynamic equilibrium (LTE) used in SpectraPlot can be questioned, as was discussed in [25], and may lead to discrepancies between the experimental and theoretical spectrum.

The most important difference between the theoretical and experimental spectrum however can be observed in the 95–105 nm region. Optically thick or not, we observe strong emission in this region, where atomic and ionic nitrogen and oxygen are not expected to contribute to emission to this extent [24], as is inferred from the spectrum simulated with SpectraPlot. We attribute this emission to N₂ singlet transitions, as was stated earlier. This supports our claim that molecular nitrogen is the most important source of this photoionization capable emission. Follow-up measurements indeed proved this hypothesis [25].

IV. Conclusions

We have experimentally obtained time-resolved spectra for spark discharges in O₂, uhp N₂ and air in the 90–160 nm range. Although the broad apparatus profile complicates line identification, our results clearly show significantly higher emission in the
95–105 nm range in air and uhp N₂ compared to O₂ in the early stages of discharge formation. We conclude this emission originates from N₂ singlet transitions. In this range direct photoionization of oxygen molecules becomes possible. This leads us to the conclusion that this photoionization capable emission originates from molecular nitrogen, a claim that is further supported by comparison with spectra calculated using SpectraPlot. These simulated spectra show atomic and singly ionized nitrogen and oxygen are not expected to contribute heavily to emission capable of directly ionizing molecular oxygen.

Acknowledgments

One of the authors (D T) was supported by project 12119 of Dutch Technology Foundation STW, partly funded by ABB.

References

[17] Fischer B 2014 private communication