Diagnostic of atmospheric-pressure He discharges controlled by dielectric barriers in presence of porous wood samples

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Abstract: A porous wood sample was placed on the bottom electrode of an atmospheric-pressure dielectric barrier discharge in pure helium to examine the influence of substrate outgassing on the plasma properties. Optical emission spectroscopy revealed strong emission from N_2, N_2^+, O and OH impurities. Detailed analysis of the time evolution of the emission spectra indicates that the release of products from the wood substrate yields to an increase of the electron temperature as well as to a significant quenching of He metastables.

1.Introduction

Application of dielectric barrier discharges (DBDs) to the modification of "novel" materials such as wood is much more challenging than for conventional substrates such as Si or SiO_2. This can be attributed not only to the highly complex chemical nature of this polymer but also to its highly porous microstructure which can release impurities either from plasma-substrate chemical reactions or from sample outgassing (if not pumped-down beforehand). In this work, we examine in details the influence of substrate outgassing during wood treatment on the time evolution of DBDs operated in He.

2.Experimental details

Experiments were performed in an atmospheric-pressure He plasma controlled by dielectric barrier, the details of which can be found elsewhere [1]. Two types of substrates that were not outgassed beforehand were used: sugar maple and black spruce. The 3.2 mm thick wood samples were placed on one of the alumina-covered electrodes and the plasma was sustained by applying a 3.5 kV_{pk-pk} signal at 12 kHz. The discharge gap was fixed to 4 mm. The He mass flow rate was set at 4.35 SLM.

3.Results and discussion

Figure 1 presents the line-and time-integrated emission intensities from 300 to 800 nm for various treatment times, *t*, after the first discharge. In addition to the expected strong He emission at 588 and 707 nm, a noticeable emission from the second positive system (SPS) of N_2 and the first negative system (FNS) of N_2^+ was observed due to outgassing of air entrapped in the porous microstructure of wood. In He plasmas, impurities are easily excited by energy transfer reactions with the high-energy (19.82 and 20.61 eV) He metastables [2]. As a result, OH and O emissions are present at 309 nm and 777 nm respectively. While the oxygen emission also results from air outgassing, the OH emission is ascribed to etching of the weak boundary layer and humidity desorption from the wood samples and chamber walls. In Fig. 1. the emission intensities from He I at 588 and 707 nm remain fairly constant with plasma exposure time whereas those from N_2 (337 nm), N_2^+ (391 nm), and O sharply decrease. This can be attributed to the "pumping" of the wood sample following plasma exposure. On the other hand, the OH emission increased slightly throughout the whole process, suggesting that the contribution of surface etching reactions and humidity desorption rised with *t*.

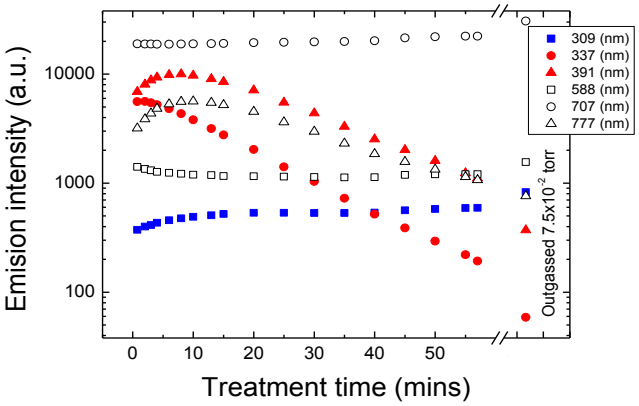

Figure 1: Emission intensity of He, N_2, N_2^+, O and OH as a function of exposure time to a He DBD with a non-degassed sugar maple substrate.

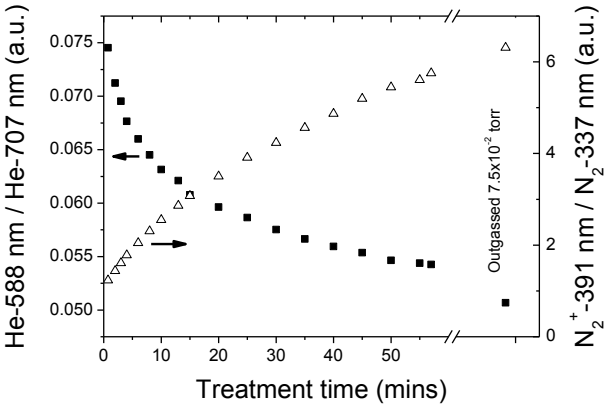

Figure 2: He-588 nm-to-He-707 nm line intensity ratio and N_2^+-391 nm-N_2-337 nm bandhead intensity ratio as a function of exposure time to a He DBD with a non-degassed sugar maple substrate.

We have calculated the He-588 nm-to-He-707 nm line ratio, $I_{588/707}$, and N_2^+-391 nm-N_2-337 nm bandhead ratio, $I_{391/337}$; the results are shown in Fig. 2. Assuming that the He ^{3}D and ^{3}S levels (L•S coupling) giving rise to the emission at 588 and 707 nm are populated by stepwise excitation through the most populated metastable He $^3S_1$ levels and are lost by spontaneous emission, $I_{588/707}$ can be written as

$$\frac{I_{588}}{I_{707}} = \frac{f_{588\,nm}}{f_{707\,nm}} \frac{\theta_{588}}{\theta_{707}} \frac{B_{He\,3D}}{B_{He\,3S}} \frac{k_{3D}(T_e)}{k_{3S}(T_e)}, \quad (1)$$

where f_i is the relative response of the monochromator and detector, θ_i is the escape factor, $B_{He\text{-}3D}$ = 0.74 and $B_{He\text{-}3S}$ = 1 are the branching ratios of the emitting He ^{3}D and ^{3}S levels, and $k_i(Te)$ is the rate for stepwise excitation (a function of the electron temperature T_e). The ratio $k_{3D}(Te)/k_{3S}(Te)$ was calculated using the set of cross sections reported in ref. [3] and was found to increase with T_e (not shown). From this result and the measured He emission intensity ratio displayed in Fig. 2, one readily concludes that in optically thin conditions (i.e. $\theta \approx 1$), T_e must decrease when going from rightafter the first discharge where substrate outassing effects are important to longer treatment times where "pumping" of the wood samples is nearly complete. Since the intensities of the He 588 and 707 nm emission lines are fairly independent of treatment time and that the discharge current (linked to the electron density n_e) increases only slightly with t (not shown), one can further deduce from the decrease of T_e that the number density of He metastables must strongly increase with t. This can probably be attributed to a decrease of their loss frequency by quenching reactions on N_2 and O_2 as wood outgassing evolves.

Figure 2 further shows that $I_{391/337}$ increases with t. Assuming that the N_2^+-B level giving rise to the emission at 391nm is populated by energy transfer reactions through Penning excitation (reaction rate k_1, independent of T_e) with He metastables (number density $n_{He\text{-}m}$) while the N_2-C level giving rise to the emission at 337 nm in populated by both energy transfer reactions through collisions with He^m (reaction rate k_2, independent of T_e) and by electron-impact excitation on the ground state of N_2 (reaction rate k_3 (a function of T_e), number density n_{N2}), $I_{391/337}$ can be written as

$$\frac{I_{391}}{I_{337}} \propto \frac{k_1 n_{N_2} n_{He^m}}{k_2 n_{N_2} n_{He^m} + k_3(T_e) n_{N_2} n_e} = \frac{k_1 n_{He^m}}{k_2\, n_{He^m} + k_3(T_e) n_e}, \quad (2)$$

Based on Eq. (2) and the results presented above, $I_{391/337}$ should first increase with t due to the corresponding increase of $n_{He\text{-}m}$ and the decrease of $k_3(T_e)$. At higher exposure times, $I_{391/337}$ should reach a plateau when electron-impact excitation becomes negligible with respect to energy transfer reactions ($I_{391/337} \propto k_1/k_2$). This behavior is in excellent agreement with the data presented in Fig. 2.

4.Conclusion

We have analysed the characteristics of an atmospheric-pressure dielectric barrier discharge in pure helium in the presence of porous sugar maple and black spruce wood samples. Strong outgassing of nitrogen an oxygen ascribed to wood outgassing as well as OH impurities from wood surface etching and humidity desorption were observed. Analysis of the nitrogen and helium emission intensity ratios revealed that substrate outgassing yielded to (i) higher electron temperature and (ii) lower He metastable densities. These effects however vanish at longer treatment times.

References

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