

Spatially-resolved electrical and optical study of Townsend Dielectric Barrier Discharges in nitrogen at atmospheric pressure

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Abstract: Current-voltage characteristics and time-resolved optical emission spectroscopy measurements are performed along the gas flow lines in a Townsend Dielectric Barrier Discharge in nitrogen at atmospheric pressure. A detailed analysis of the excitation and de-excitation kinetics of emitting $N_2(C)$ states is also provided.

Keywords: Dielectric Barrier Discharge (DBD), Homogeneous discharge, Atmospheric pressure (AP), Optical emission spectroscopy, current-voltage characteristics.

1. Introduction

Dielectric barrier discharges (DBDs) are extensively used as a way to provide the non-equilibrium plasmas required by many applications. In particular, DBDs represent very attractive tools for plasma-enhanced chemical vapour deposition (PECVD) of functional, nanostructured coatings on heat-sensitive materials and nanomaterials, including polymers derived from the wood biomass [1].

Depending on the gas nature, and the electrical conditions, DBDs can be filamentary or homogeneous [2]. The filamentary regime is obtained through a streamer-type breakdown while the homogeneous regime is obtained with a Townsend breakdown. Since the filaments are randomly distributed in time and space, filamentary discharges often present little interest for uniform surface treatment over large area substrates [3]. For such applications, homogeneous discharges seem more promising. However, in presence of reactive species used for PECVD, the homogeneous regime often fails to provide truly homogeneous coatings. Indeed, depending on the position along the gas flow line, significant variations of the deposition rate as well as the physical and chemical properties of plasma-deposited coatings can be observed [3]. While some of these features could be « smooth » through substrate displacement during plasma deposition, some of these variations obviously remain during static plasma deposition experiments.

In this study, spatially-resolved electrical and spectroscopic diagnostics performed along the gas flow lines are used to provide insights into the underlying physics and chemistry driving Townsend Dielectric Barrier Discharges in nitrogen at atmospheric pressure.

2. Experimental set-up and diagnostics

The experimental setup used in this work has already been described in a previous publication [4]. The DBD is kept in an enclosed vessel in order to control the

atmosphere. Prior to each experiment, the reactor is pumped down to 10^{-3} mbar, before being filled with a given gas at atmospheric pressure. The DBD is ignited between two flat, squared, plane-to-plane electrodes made of metalized paint deposited on thick alumina plates. The gas gap is set to 1 mm. In order to renew the atmosphere, a gas flow is injected from one side of the discharge, and the pressure inside the vessel is maintained constant.

The power supply provides a low frequency sinusoidal voltage signal (3 kHz) to a linear power amplifier whose output is applied to the primary winding of a transformer. The discharge cell is connected to the secondary winding of the transformer. The voltage applied to the electrodes is measured by a high voltage probe (Tektronix P6015A). The discharge current and the gas voltage are deduced from these electrical measurements from an electrical equivalent circuit described by Naudé *et al.* [5]. The measured and calculated discharge current quantifies the processes happening over the entire electrode surface. However, the current density is not necessarily the same at any point on the surface because of the gas flow circulation. In order to measure the variation of the

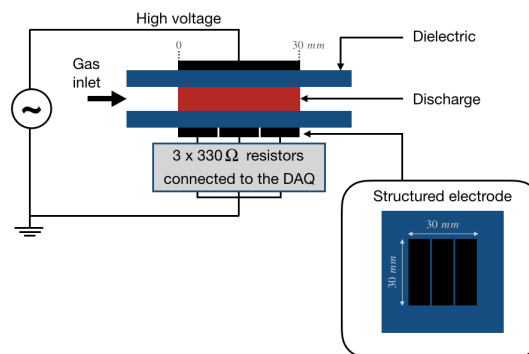


Fig. 1. Schematics of the discharge cell proving spatially-resolved measurements using a structured electrode

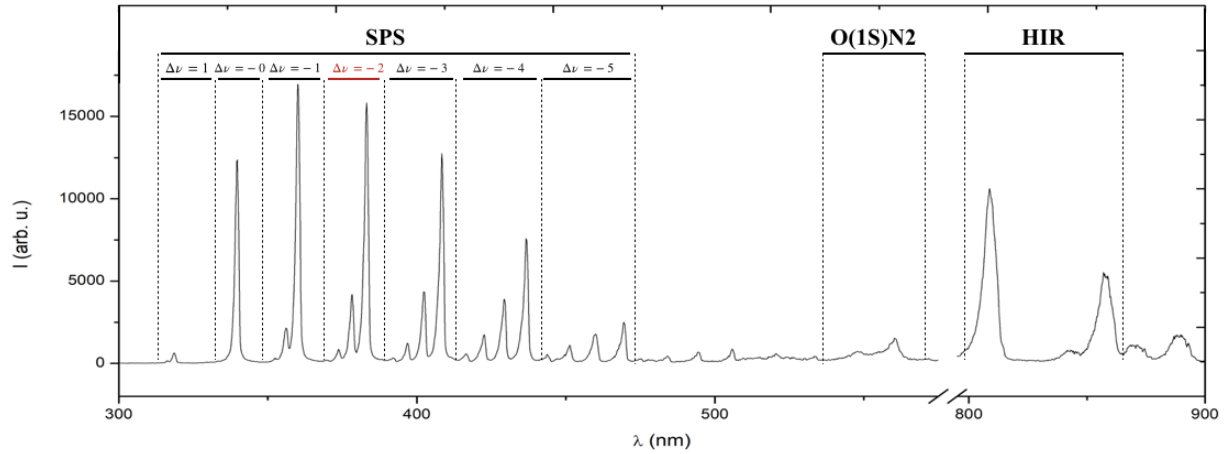


Fig.2 Typical spectrum, main emission systems

current as a function of the position along the gas flow lines, the ground electrode is replaced by an electrode divided into 3 disconnected strips (see Fig. 1) linked to the entrance, middle and exit of the Townsend discharge. Each band is connected to a 330 Ω shunt resistor and the voltage across the 3 shunt resistors is acquired simultaneously to gather the current. In this case, the same method as used in [5] is applied for each strip, considering each zone as independent. The splitting of the ground electrode does not perturb neither the discharge homogeneity, nor the total discharge current.

Spatially-resolved electrical diagnostics are combined to optical emission spectroscopy measurements realized using an optical fiber moving along the gas flow lines. The signal is provided to a high-resolution monochromator (Acton SP-2500) equipped with an intensified charge-coupled device (Princeton Instruments PI-MAX3 ICCD). The optical setup is synchronized with the power supply voltage. A typical spectrum of the Townsend discharge at atmospheric pressure is presented in Fig. 2. Distinct emission systems are depicted : the second positive system (SPS) of N_2 , the $O(1S)N_2$ band and the Herman Infra Red (HIR) system of N_2 .

3. Results and discussion

Current-voltage characteristics for a complete period of the applied voltage are presented in Fig. 3. The discharge current (I_d) and the voltage applied to the gas (V_g) are presented for each of the zones defined by the fractional electrode. The voltage applied to the electrodes (V_a) is also presented. A homogeneous Townsend discharge is characterized by the presence of a single current peak of low amplitude (a few mA.cm⁻²) and long duration (a few tens of μ s), as seen in Fig. 3. When the voltage applied to the gas reaches the breakdown voltage, a significant rise of I_d is observed and the gas voltage reaches a plateau. However, the discharge current never really reaches zero between two cycles of the applied voltage; a feature ascribed to the so-called memory effect in DBDs [6].

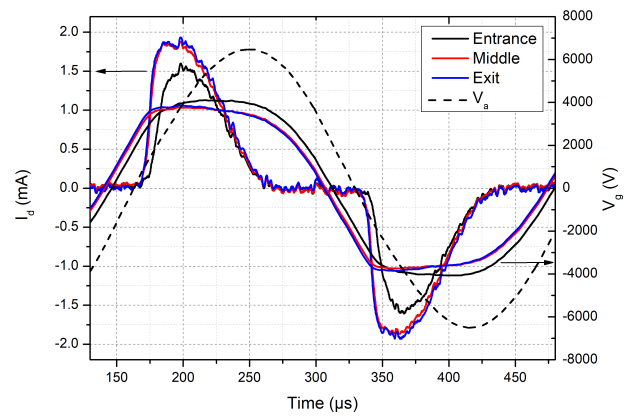
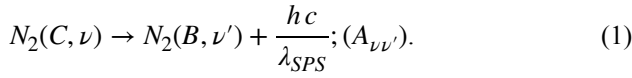


Fig. 3. Electrical characteristics of the discharge as a function of time and position

The use of fractional electrodes further reveals that the current-voltage characteristics differ over the entire discharge zone. More precisely, the discharge first ignites at the exit and then appears at the entrance of the reactor. This can be deduced from the earlier rise at the exit of both the discharge current and the gas voltage for the same value of the applied voltage. As described in previous publications [6], such phenomena can be explained by a change in the memory effect due to a change in the number of the so-called « weak-field electrons » during the rise of the gas voltage. To date, two mechanisms are believed to be responsible for such memory effect: secondary electron emission by the impact of metastable $N_2(A)$ on the charged dielectrics and the associative ionization of NO^+ through collisions between $N(^2P)$ and $O(^3P)$. In presence of oxygenated species, the first mechanism vanishes rapidly due to significant quenching of $N_2(A)$. On the other hand, as detailed elsewhere, the quenching of $N_2(A)$ by nitrogen and oxygen species can promote the formation of $N(^2P)$ and $O(^3P)$ [6]. In such conditions, associative recombination reactions in the discharge volume becomes the dominant source of seed electrons.

Thus, the fact that the discharge first initiates at the exit suggests that the population of $N_2(A)$ is lower (and therefore the memory effect is lower) at the entrance than at the discharge exit. This aspect was confirmed by a rise of the emission intensity of the HIR system along the gas flow lines [6]. Indeed, over the range of experimental conditions investigated, this system is mostly populated by gas phase association of $N_2(A)$ such that the emission intensity scales with the square of the $N_2(A)$ population.

Spatially-resolved electrical measurements were compared to those provided by optical emission spectroscopy, in particular the SPS system (showed on Fig. 2) linked to the radiative de-excitation of $N_2(C)$ towards $N_2(B)$ (equation 1). For the $\Delta\nu = -2$ sequence corresponding to Einstein coefficient $A_{\nu\nu'}$, this radiative decay can be expressed as



The time-resolved evolution of the bandhead emission intensity at 380.4 nm ($\Delta\nu = 0 - 2$) is presented in Fig. 4. As a reference, I_d values (straight line) are also shown. The different emissions are normalized to their maximum.

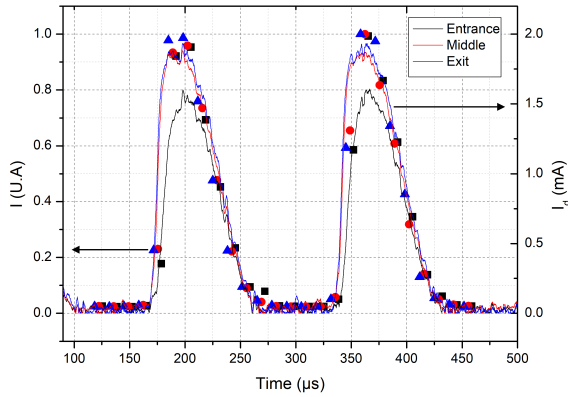
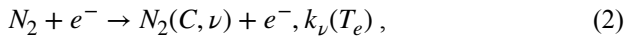


Fig. 4 Time-resolved bandhead emission intensity (normalized units) at 380.4 nm. The discharge current (straight line) is also shown for comparison.

As can be seen in Fig. 4, SPS measurements present the same time evolution than the discharge current: this suggests that the emitting $N_2(C)$ states are mainly created by electron impact on $N_2(X)$ according to



with the corresponding reaction rate $k_\nu(T_e)$. In such case, the SPS emission intensity (I_{SPS}) can be written as

$$I_\nu \propto k_\nu(T_e) n_e n_{N_2}. \quad (3)$$

From Equation 3, assuming that I_d is proportional to the electron density (n_e), the I_{SPS} / I_d ratio becomes linked to the reaction rate and thus to the electron temperature (T_e)

(assuming Maxwellian electron energy distribution function). This I_{SPS} / I_d ratio is presented in Fig. 5 for all data points with the discharge on (when I_d is significantly above zero). It can be seen that the I_{SPS} / I_d ratio is constant during the discharge-on time, with a comparable value for all positions along the gas flow lines. This suggests comparable T_e values over the whole range of experimental conditions investigated.

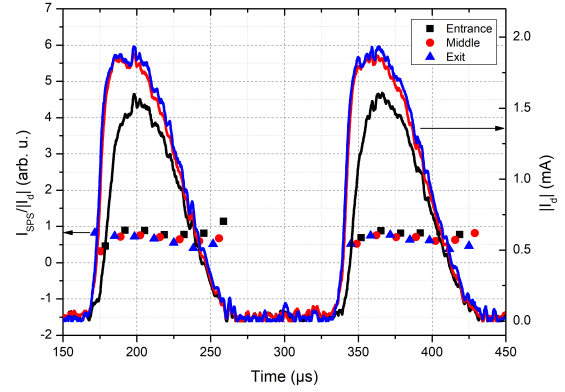


Fig. 5. I_{SPS}/I_d as function of position and time. Absolute values of I_d are also shown for comparison.

The populations of other emitting $N_2(C)$ states from the $\Delta\nu = -2$ sequence were also examined. In the context of Equation (3), bandhead emission intensity ratios (after correction of their optical efficiency) can be expressed as

$$\frac{I_\nu}{I_\omega} \propto \frac{k_\nu(T_e) n_e n_{N_2}}{k_\omega(T_e) n_e n_{N_2}} \propto \frac{k_\nu(T_e)}{k_\omega(T_e)} \quad (4)$$

This ratio is presented in Fig. 6 for two vibrational numbers, $\nu = 1, \omega = 0$, of the emitting $N_2(C)$ states from the $\Delta\nu = -2$ sequence.

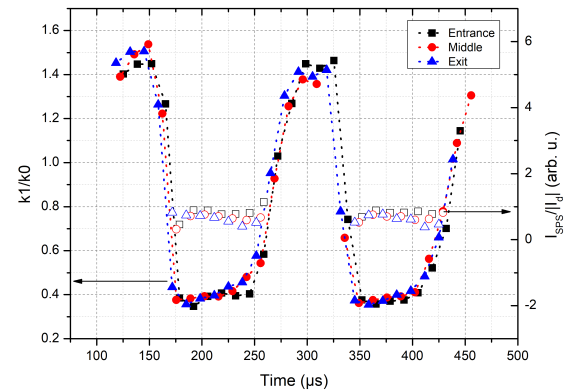


Fig. 6. Rate constant ratios for $\nu = 1, \omega = 0$ and I_{SPS}/I_d as function of position and time.

In the discharge-on period, this ratio seems fairly constant, with comparable values for all positions along the gas flow lines. From Equation (4), this indicates comparable electron-impact excitation rate constant ratios, and thus similar values of the electron temperature.

However, this ratio significantly rises during the off-time period, with a fairly constant value between two subsequent cycles of the applied voltage. As presented in Fig. 7, this rise is even more prominent for other ratios of the $\Delta\nu = -2$ sequence.

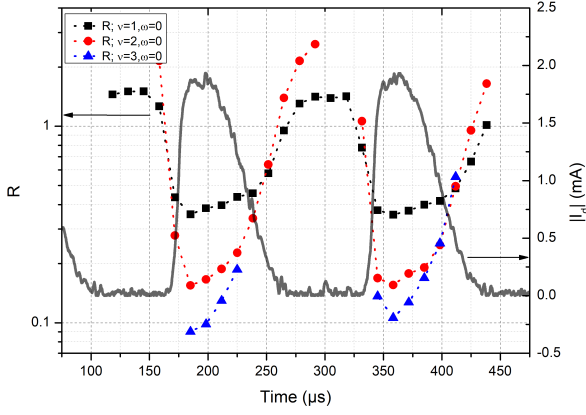
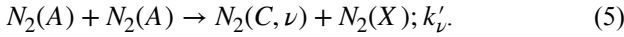


Fig. 7. Emission intensity ratios (after correction of their optical efficiency) for different bands of the $\Delta\nu = -2$ sequence. Absolute values of I_d are also shown.

This result was analyzed in more details considering that the emitting $N_2(C)$ states can also be populated through Penning excitation involving $N_2(A)$ states



This mechanism is characterized by the reaction rate k'_ν . In this framework, the bandhead emission intensity ratio from two vibrational numbers (ν, ω) of the emitting $N_2(C)$ states from the $\Delta\nu = -2$ sequence (after correction of their optical efficiency) can be written as

$$R \propto \frac{k_\nu n_e n_{N_2} + k'_\nu n_{N_2(A)}^2}{k_\omega n_e n_{N_2} + k'_\omega n_{N_2(A)}^2} \quad (6)$$

Therefore, in line with Equation (6), this ratio is expected to differ between the on- and off-discharge periods. In the on-discharge time, i.e. when the electron density is relatively important, R represents the ratio of the reaction rates for electron-impact excitation, and thus the electron temperature. On the other hand, in the off-discharge time, i.e. when the electron density significantly decreases, R provides the ratio of the reaction rates for Penning excitation (a constant for a given set of vibrational numbers (ν, ω)).

From the results presented in Figs. 6 and 7, it is observed that the two mechanisms for population of emitting $N_2(C)$ exist but in different proportions over time. From the energy diagram of $N_2(C)$ presented in Fig. 8, one expects a more significant contribution of Penning excitation for high values of ν due to the smaller energy variation between $N_2(A)+N_2(A)$ and the emitting $N_2(C, \nu)$ state.

Therefore, for the same sequence $\Delta\nu = -2$, a more significant rise is expected for $\nu = 2$ than for $\nu = 1$, as seen in the experiments (Fig. 7).

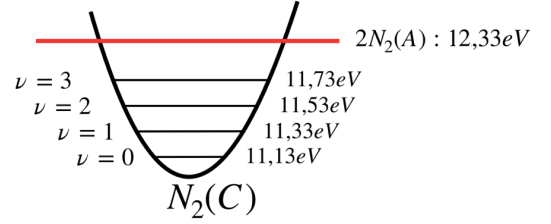


Fig. 8. Energy levels of emitting $N_2(C)$ states.

4. Conclusion

Spatially-resolved analysis of the current-voltage characteristics and time-resolved optical emission spectroscopy measurements are used to examine the physics and chemistry of Townsend Dielectric Barrier Discharge in nitrogen at atmospheric pressure. Significant variations of the breakdown voltage and discharge current were observed between the entrance and the exit of the plasma reactor due to the corresponding variations of the populations of seed electrons. This result was linked to a change in the memory effect due to variations of the populations of $N_2(A)$ states along the gas flow lines. On the other hand, no significant changes in the electron temperature was deduced from detailed analysis of the emission of the second positive of N_2 . For these levels, both electron-impact excitation and Penning excitation were found to play an important role in the excitation kinetics, with a more significant contribution of Penning ionization reactions for higher ν values.

5. References

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