Optical spectrum of the coaxial DBD forming the plasma jet in fast air flow at atmospheric pressure

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Abstract. The non-thermal plasma source based on the high-frequency (100 kHz) sinusoidal dielectric barrier discharge (DBD) generating the plasma jet in air at atmospheric pressure is described. This source uses the electrode system of a coaxial geometry and able to work at the low- and high-power regimes. A narrow plasma jet was generated in airflow at the velocities in the range of 20-80 m/s. The emissive UV-Visual spectra of the discharge zone and plasma jet are presented. The change of the emissive spectrum along the length of plasma jet and on the surface of the quartz substrate to be treated is studied as well. The spectrum reflects the composition of reactive species generated by DBD. The presented experimental results give insight into the properties of the gas discharge plasma inside the coaxial DBD and the spatial characteristics of plasma jet outside the discharge zone as well.

1. Introduction
Non-thermal plasma jets at atmospheric pressure are widely used for many applications [1-11]. In most cases, plasma jets being formed by discharges using the inert gases (He, Ar, N₂ and their mixtures) as work gases. The ambient air contains the electronegative components (oxygen and water molecules) which are the efficient quenchers of electronically excited species and, besides, they diminish the concentration of electrons in plasma due to strong attachment processes. This circumstance leads to diminishing the concentration of reactive species and shortening the action range of these air plasma jet. Therefore, there was always a strong doubt - whether the plasma jet in the ambient air as work gas can provide the concentration of reactive species which is sufficient for effective plasma processing. On the other hand, atmospheric pressure air plasma jets are of great interest because the replacement of the expensive inert gases by the ambient air promises a high profit for the plasma-based technologies.

In this paper, we present the newly developed gas discharge system generating the plasma jet using the ambient air as the working gas at atmospheric pressure. This system is based on the usage of the coaxial high-frequency (100 kHz) sinusoidal DBD in fast flow velocity (20-80 m/s) of the ambient air with a high-volume flow rate of 4-24 L/min per tube. High flow velocity provides faster delivering of reactive species from discharge zone to the surface that reduces their loss due to the quenching or other plasma-chemical processes in the jet and increases the total amount of the delivered reactive species onto the surface to be treated. The latter leads to the intensification of the plasma surface processing. We used the high-voltage sinusoidal power supply with a frequency of 100 kHz and output
power about 1 kW. Note that high-frequency DBD is able to provide a high specific energy deposition into the working gas. Due to fast quenching processes at atmospheric pressure, it leads to strong air heating that, in its turn, can lead to a positive synergy effect of the simultaneous action of hot air and reactive plasma species at the surface treatment.

Note that the effectiveness of the wanted plasma-chemical processes happening at the interaction of plasma jet with the surface depends on the composition of the reactive species delivered by plasma jet onto the surface. However, the reactive species interacting with the substrate are not the same as those generated by the gas discharge itself. A reason is that there is a plasma-chemical transformation of the primary reactive species into the secondary (and so on) ones in the course of their transportation by the plasma jet from the gas discharge zone onto the substrate to be treated. So, to evaluate correctly the efficiency of the surface treatment by plasma jet, it is necessary to take into account the properties of the used gas discharge generating the primary reactive species and also the transformation of reactive species in the course of their transportation by plasma jet on the surface. This task was implemented by us with use of the spectroscopic method. Information on the composition of the reactive species generated by the DBD plasma has been obtained from their emissive spectra in UV-Visual region. Of course, such information cannot satisfy this question in full because some species do not emit in this spectral region or the intensity of their emission either is too weak (for instance, metastable) or overlaps with the strong lines (bands) of other species. Nevertheless, some conclusions can be done.

2. Experimental setup

General scheme of the single-tube reactor is shown in figure 1. The barrier discharge was generated in the airflow inside thin quartz or ceramic tube. The sizes of tubes were chosen close to each other as much as possible. The inner and outer diameters of the quartz and ceramic tubes are of 2.0 and 4.5 mm and 2.5 and 4.5 mm, respectively. At given inner diameters of tubes and gas flow velocities (20-80 m/s) Reynolds number of flows inside tubes exceeds the critical number \( Re \approx 2320 \). It means that flow of the ambient air inside tubes is turbulent one.

![Figure 1 Setup of the coaxial DBD in fast air flow at atmospheric pressure. The inner and outer diameters of the dielectric tube are 2 and 5 mm. The discharge zone length is 20 mm.](image)

The applied high voltage was measured by HV divider PINTEK HVP-39 (1000:1, 40 kV, 200 MHz). The discharge current was measured by a low-inductive shunt with resistance of 50 Ohm. All electrical signals were recorded by the digital oscilloscopes such as Tektronix TDS 520, Tektronix DPO2024 and Tektronix TDS 2012 with the bandwidth of 500, 200 and 100 MHz. The current and voltage waveforms were used to calculate the average discharge power \( < W > \):

\[
< W > = \frac{1}{nT} \int_0^{nT} I(t)U(t)dt,
\]

where \( I(t) \) and \( U(t) \) are the current and voltage waveforms of the sinusoidal DBD recorded in the experiment by the digital oscilloscope, \( n \) is the number of periods \( T \) taken into consideration.

To register the UV and visual spectrum of the discharge and plasma jet, the spectrometers AvaSpec-2048FT-6-RM and AvaSpec-2048-L were used. The first of them has a low sensitivity to the registered light but high spectral resolution \( \Delta \lambda = 0.1 \) nm in the region \( \lambda = 240 – 400 \) nm and \( \Delta \lambda = \)
0.2 nm in the region $\lambda = 400 - 800$ nm. The second one has a high sensitivity to the registered light but low spectral resolution $\Delta\lambda = 1$ nm in the region $\lambda = 200 - 1000$ nm. The optical system was focused in such a way to collect the light either from the middle of discharge zone or from different parts of the plasma jet.

The data capture time was different and has been determined by the intensity of the registered light and sensitivity of the spectral device. The emissive spectra were used to determine the sorts of reactive species in the gas discharge zone and different parts of plasma jet. The second positive system of N$_2$ was used to determine the rotation and vibration temperature in plasma using the SpecAir code [12]. The average translation gas temperature $T$ inside the non-equilibrium plasma jet was measured by the thermocouple located 5 mm away from the tube exit.

3. Experimental results and discussion

The coaxial DBD in fast airflow exhibits two regimes: the low-power (LP) and high-power (HP) regimes which being happened at low and high amplitudes of the applied voltage. The images (a) and (b) in figure 2 show the side view of the plasma structure inside the discharge zone of DBD in quartz tube at the LP and HP regimes respectively. These images are averaged over many half-cycles. The UV-Visual spectra of the discharge zone of the airflow DBD in the LP and HP regimes are shown in figures 2c and 2d. The $I - U$ waveforms of DBD in LP and HP regimes are given in figures 2e and 2f.

![Figure 2](image)

**Figure 2** Images of plasma structure inside discharge zone of DBD in quartz tube at low-power (a) and high-power regime (b); airflow is directed from left to right. The UV-Visual spectra of the discharge zone at low-power (c) and high-power regime (d). Images and spectra were taken under the exposure time of 1 ms (a, b) and 20 ms (c) and 10 ms (d). The current-voltage waveforms of DBD in
LP (e) and HP (f) regimes. Parameters: (a, c, e) $V = 60$ m/s, $U = 5.3$ kV, $<W> = 6.4$ W; (b, d, f) $V = 60$ m/s, $U = 7.6$ kV, $<W> = 86$ W. Quartz tube. The length of discharge zone is 20 mm.

One may see in figure 2 that the emissive spectrum of the discharge zone of DBD in HP regime is formed by such excited species as $\text{N}_2$, $\text{Ar}$, $\text{O}$, $\text{NO}$, $\text{OH}$. It is surprising that argon contributes to the plasma chemical kinetics in the discharge zone as well. The reason is that the concentration of $\text{Ar}$ in ambient air is high and equal to 0.93% (vol.) or $2.3 \cdot 10^{17}$ cm$^{-3}$ at normal atmospheric condition.

Figure 3 presents information about the image of air plasma jet in HP regime, its emissive spectrum in different parts of jet and the intensity distribution of $\text{N}_2(2+)$ system ($C^3\Pi_u \rightarrow B^3\Pi_g$, $\Delta \nu = 0-0$, $\lambda = 337$ nm) along the plasma jet.

The exposure time of the dim plasma jet is 3 s.

![Figure 3 Image of free air plasma jet (a).](image)

Figure 3 Image of free air plasma jet (a). The intensity distribution of $\text{N}_2(C^3\Pi_u \rightarrow B^3\Pi_g$, $\Delta \nu = 0-0$, $\lambda = 337$ nm) along the plasma jet. Two examples of the UV-Visual spectra taken at $L = 1$ mm (c) and $L=5$ mm (d) away from the tube exit. Parameters of DBD: $V \approx 60$ m/s, $U = 5.3$ kV, $<W> \approx 60$ W. Exposure time for all spectra is 40 s.

Figures 4 and 5 show the radial distribution of both the UV-Visual spectrum emitted by plasma sheet being formed at striking the substrate by plasma jet and the intensity of emission of $\text{N}_2(C^3\Pi_u \rightarrow B^3\Pi_g$, $\Delta \nu = 0-0$, $\lambda = 337$ nm), $\text{NO}(\gamma$-band, $A^3\Sigma^+ \rightarrow X^2\Sigma^+$), O($^5P \rightarrow 5S$, $\lambda = 777$ nm).
The arrows show several points at the plasma sheet from which the spectra were observed.

Figure 4 The image of plasma sheet being formed by the air plasma jet on the quartz substrate (a). Radial distribution along plasma sheet of the emission intensity for the excited species (b):

$N_2(C^3Π_u \rightarrow B^3Π_g, \lambda = 337 \text{ nm})$ (1), $NO(γ\text{-band}, A^3Σ^+ \rightarrow X^2Π, \lambda = 236 \text{ nm})$ (2), $O(^5P \rightarrow ^5S, \lambda = 777 \text{ nm})$ (3).

a) b) c) d)
Figure 5 Evolution of the spectrum along radius $R$ of the plasma sheet on the quartz substrate placed at 5 mm away from the tube exit. $V \approx 60$ m/s, $U = 5.3$ kV, $<W>\approx 60$ W. a) $R = 0$ mm, $\tau = 40$ ms; b) $R = 1$ mm, $\tau = 500$ ms; c) $R = 2$ mm, $\tau = 500$ ms; d) $R = 3$ mm, $\tau = 3$ s; e) $R = 4$ mm, $\tau = 3$ s; f) $R = 5$ mm, $\tau = 10$ s; g) $R = 6$ mm, $\tau = 20$ s; h) $R = 8$ mm, $\tau = 20$ s.

The probe measurements revealed that the electric field strength in plasma jet is very low ($E/N \approx 1$ Td). The features of the probe measurements at an elevated gas pressure are described in detail in [13,14]. Based on the analysis of the possible reactions in the plasma jet with a low electric field, one may state that the plasma chemical reactions in the jet are induced not by electrons but metastable $O_2(a^1\Delta)$, $O(\,^1D)$, $N_2(\,^3\Sigma^+)$ and Ar($\,^3P$) being formed in the discharge zone and blown out by flow. Besides, the non-excited species such as $O(\,^3P), OH, O_3, NO$ present also in the air plasma jet. The close examination of the possible reactions in the air plasma jet leads to the following list:

\begin{align}
Ar(\,^3P) + N_2(X^1\Sigma^+) & \rightarrow N_2(A^3\Sigma^+) \\
N_2(A^3\Sigma^+) + O_2 & \rightarrow N_2(X^1\Sigma^+) + O(\,^3P) + O(\,^3P) \\
N_2(A^3\Sigma^+) + H_2O & \rightarrow N_2(X^1\Sigma^+) + OH(X^2\Pi) + H \\
N_2(A^3\Sigma^+) + O(\,^3P) & \rightarrow NO(X^2\Pi) + N \\
N + O_2 & \rightarrow NO(X^2\Pi) + O(\,^3P) \\
O(\,^3P) + O_2 + N_2(X^1\Sigma^+) & \rightarrow O_3 + N_2(X^1\Sigma^+) \\
OH + OH & \rightarrow O(\,^3P) + H_2O \\
O(\,^1D) + H_2O & \rightarrow OH + OH \\
O(\,^1D) + O_2 & \rightarrow O_2(a^1\Delta) + O(\,^3P) \\
O(\,^1D) + O_2 & \rightarrow O_2 + O(\,^3P)
\end{align}
\[
O(^1D) + N_2(X^1Σ^+) \rightarrow N_2(X^1Σ^+) + O(^3P) \\
O_3 + O(^1D) \rightarrow O(^3P) + O_3, \quad O_2 + O_2 \\
O_3 + O_2(α^3Δ) \rightarrow O(^3P) + O_2 + O_2 \\
O_3 + NO(X^2Π) \rightarrow NO_2 + O_2
\]

One may see in the above list that primary reactions in the jet are induced by metastable \(O_2(α^3Δ), O(^1D), Ar(^3P)\) and \(N_2(Δ^3Σ^+)\). According to the above list, the excitation of these species happens due to collisions with metastable \(N_3(Δ^3Σ^+)\). However, there is a question: how these metastable themselves are being generated in the plasma jet and the plasma sheet. We assume this mechanism is based on bimolecular reactions between the highly excited \(N_2(X, ν > 12)\) molecules having the rate coefficient \(k_{ν1, ν2} ≈ 10^{-16} \text{ cm}^3 \text{ s}^{-1}\) [15]:

\[
N_2(X, ν_1) + N_2(X, ν_2) \rightarrow N_2(X) + N_2(Δ^3Σ^+)
\]

To prove the existence of highly vibration excited nitrogen molecules, we have performed the spectroscopic measurements of the average vibration \(T_{vib}\) and rotation \(T_{rot}\) temperatures of the electron-exited state \(N_2(C)\) in the discharge zone and the translation gas temperature \(T\) in the plasma jet as well. The gas temperature was measured by the thermocouple located 5 mm away from the tube exit. The obtained results are presented in figure 6. The behaviour of the averaged DBD power \(<W>\) in dependence of gas flow velocity is shown in this figure as well. The dotted arrows denote the back transition of DBD from the high-power regime into the low-power regime. This transition is induced by high velocity of airflow inside the discharge zone.

In air at the atmospheric pressure there is a fast exchange between rotational and translation degrees of freedom, therefore, the rotation temperature is equal to the gas temperature: \(T_{rot} = T\). Also, due to fast exchange between vibration degrees of freedom of \(N_2(X, ν)\) and \(N_2(C, ν)\), vibration temperatures of these states can be equal to each other. The spectroscopic measurements showed that, despite the high gas temperature \((T ≈ 900 K)\), the air inside the discharge zone is non-equilibrium, \(T_{vib} > T_{rot}\), and in some cases the measured vibration temperature reaches up to 4600-4800 K. High gas temperature leads to that the rate of electron detachment from negative ions practically overcomes the rate of electron attachment to oxygen and the role of negative ions in the charged particles kinetics is negligible. In other words, the main role in the generation and excitation of reactive species in the discharge zone belongs to electrons. However, because of very low electric field in the plasma jet, the role of electrons in the kinetics of reactive species in this zone is negligible.

![Figure 6](image1.png)

**Figure 6.** a) The dependence of the spectroscopically determined \(T_{vib}\) (curve 1) and \(T_{rot}\) (curve 2) of the electron-exited state in the discharge zone inside the ceramic tube on the air flow velocity \(V\). b) The dependence of gas temperature \(T\) inside the plasma jet (curve 1) measured by the thermocouple located 5 mm away from the tube exit vs air flow velocity \(V\), \(<W> = 65 W\); the behaviour of the averaged DBD power \(<W>\) in dependence of gas flow velocity (curve 2).
4. Conclusion
We have developed novel plasma source of the "efflux" type that is based on the usage of the coaxial high-frequency (100 kHz) sinusoidal DBD in fast flow velocity (20-80 m/s) of the ambient air at atmospheric pressure with a high volume flow rate of 4-24 L/min per tube. This discharge exhibits two regimes (low-power and high-power ones). The information on composition of the reactive species generated by airflow DBD has been obtained from the emissive spectra of the discharge zone plasma jet and plasma sheet in the UV-Visual region. The obtained spectral data allowed us to trace the composition of reactive species being generated inside the discharge zone and the change of this composition along both the plasma jet and plasma sheet on the surface formed by plasma jet on the substrate. The basic set of the elementary plasma-chemical processes responsible for the generation of reactive species in the discharge zone and their further changes in plasma jet is offered. Our findings promote more insight into physics of the airflow DBD at atmospheric pressure.

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