

INFLUENCE OF GAS TEMPERATURE ON GASEOUS PRODUCTS GENERATED BY COPLANAR BARRIER DISCHARGE IN AIR AND N₂/O₂ MIXTURES

V. MAZANKOVÁ^{a,*}, D. TRUNEC^b, Z. NAVRÁTIL^b, F. KRČMA^c,
A. ZAHORANOVÁ^d

^a Faculty of Military Technology, University of Defence Brno, Kounicova 65, 662 10 Brno, Czech Republic

^b Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

^c Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic

^d Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F1, 842 48 Bratislava, Slovakia

* vera.mazankova@unob.cz

Abstract. Absolute densities of gaseous products generated by coplanar dielectric barrier discharge in N₂/O₂ mixtures and in ambient air were determined by UV and VIS optical absorption spectroscopy (OAS). Ozone (O₃) and nitrogen oxides (N₂O, NO₂ and N₂O₅) were identified as the stable products of the discharge. It was found that the actual product composition strongly depends on the gas temperature. At low input power with a low gas temperature, O₃ density was high and the NO₂ density was very low. When the input power increased and the gas temperature also increased, then O₃ disappeared, while NO₂ density started to increase steeply.

Keywords: absorption spectroscopy, coplanar barrier discharge, nitrogen oxides, ozone.

1. Introduction

Low-temperature plasma (LTP) at atmospheric pressure is currently widely studied as a tool for plasma treatment of the surfaces of various materials. The reason for the wide interest is the potential of plasma applications associated with low costs and environmentally friendly technologies. Plasma interaction with the surfaces of materials depends on plasma composition. Therefore, plasma diagnostics plays an important role in the study of the effect of the plasma treatment. Currently, there is increasing interest in the use of LTP generated by different types of dielectric barrier discharges (DBDs), widely used are surface dielectric barrier discharges (SDBDs) of various electrode configurations. In our work, we focus on the diagnostics of coplanar surface barrier discharge plasma, which is often used in the surface treatment of various materials, in order to elucidate better the key components affecting the treated (for example biomaterial) surfaces.

2. Experimental

The coplanar dielectric barrier discharge (CBD) is a type of dielectric barrier discharge operated typically in air at atmospheric pressure. The coplanar electrode arrangement contains both electrodes on one side of the dielectric barrier. In the used setup, 19 parallel electrode pairs, connected alternately in parallel, were deposited on 0.7 mm thick Al₂O₃ ceramics with dimensions 20 × 8 cm. The electrodes (1.5 mm wide with 1 mm gap) were immersed in oil and cooled by the oil

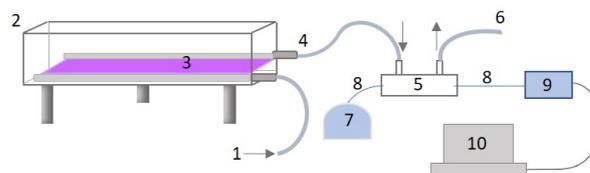


Figure 1. The experimental setup. 1 – gas input; 2 – CBD reactor chamber; 3 – plasma; 4 – output of gaseous products to the cuvette; 5 – cuvette; 6 – output of gaseous products; 7 – deuterium halogen lamp; 8 – optical fibres; 9 – spectrometer; 10 – computer.

cooling circuit. The electrode system was placed in a box with dimensions 16 × 30 × 8 cm made of plastics. The electrodes were supplied with AC high voltage (20 kV peak-to-peak, frequency 14 kHz). The input power to high voltage power supply was measured by FK Technics power meter. The ratio of the power delivered to the plasma and the input power of high voltage power supply is then 0.95. In this work, the CBD plasma source was operated in the closed reactor as described above. The discharge was generated in ambient air, oxygen, nitrogen and in mixtures of nitrogen and oxygen in ratios N₂:O₂ of 80:20, 60:40 and 40:60. The gas flow rate was kept at 31/min in all cases. The ambient air was first compressed to ensure the gas flow. The relative humidity of the air was approximately 50%.

Optical absorption spectroscopy (OAS) of the discharge products in UV and VIS regions was carried out using a standard experimental setup, see Figure 1. The working gas flowed first through the plasma reac-

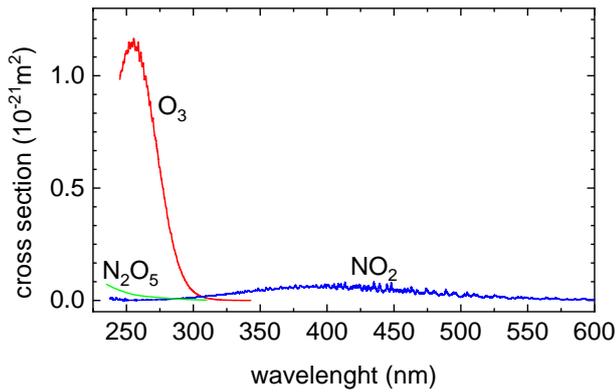


Figure 2. The absorption cross sections for O_3 , NO_2 and N_2O_5 .

tor chamber and then through a quartz cuvette (length $l = 10$ cm), located between a deuterium halogen lamp (Ocean Optics DT-Mini-2-GS) and grating spectrometer (Ocean Optics Red Tide USB 650UV, 650 enabled pixels and 2.0 nm FWHM). The light was transmitted into and from the cuvette by the optical fibers with achromatic collimating lens on their ends. The OAS spectra were measured in the 200–850 nm range for various discharge parameters (discharge power and gas composition). The absorbance $A(\lambda)$ was calculated as $A(\lambda) = -\log(I(\lambda)/I_0(\lambda))$, where $I_0(\lambda)$ is the incident light intensity and $I(\lambda)$ is the transmitted light intensity. The spectra were measured with an integration time of 0.1 s. The ozone and NO_2 densities were determined using the Beer-Lambert law $A(\lambda) = \sigma(\lambda)nl/\ln(10)$, where $\sigma(\lambda)$ is the absorption cross section, n is the density and l is the cuvette length. The absorption cross sections, see Figure 2, were taken from Hitran database [1] for O_3 and NO_2 and from [2] for N_2O_5 .

The temperature of the electrode dielectric was measured by an infrared thermometer through CaF_2 window in the upper part of the box and the gas temperature was measured by a thermocouple thermometer. The thermocouple was placed inside the reactor chamber in the gas. The temperatures measured by these two methods do not differ more than $2^\circ C$.

3. Results

3.1. Measurement at stationary state of CBD

The OAS provided limited access to the discharge chemistry compared to the FTIR spectroscopy. However, OAS enables fast measurements in time, which was used for the measurement of discharge products after immediate change of discharge power (see next subsection). Typical optical absorption spectra, measured at specific powers and in $N_2:O_2$ mixture 40:60 and in ambient air, are shown in Figure 3. For the 40:60 gas mixture and powers up to 200 W, the light in the 200–300 nm wavelength region was dominantly absorbed by the O_3 molecule, see the curve **a** in Fig-

ure 3. Although the absorptions by N_2O_5 and N_2O molecules also fall in this region, they were not observed, as their densities (see the results of FTIR measurement in [3]) as well as their absorption cross sections were significantly lower than those of O_3 . Due to almost complete light extinction around O_3 absorption maximum (at 254 nm), the measured absorbance in this wavelength region is weighted with a large error. Also the absorbance at wavelengths below 225 nm has a large error due to the low intensity of incident light at these wavelengths. So, the O_3 density was calculated from the 285–310 nm wavelength region.

At discharge powers above 233 W, the O_3 absorption peak was missing and the absorption peak of NO_2 spreads from 280 nm to 600 nm in the spectra, see curve **b** for 300 W in Figure 3. The NO_2 density was calculated from 399–401 nm wavelength region. A small absorption band around 225 nm is caused by N_2O molecules. Similar absorption spectra were observed for the discharge burning in the air even at low discharge powers, see the curve **c** in Figure 3. Besides N_2O_5 and N_2O molecules, HNO_3 with the pronounced part of the cross section within 180–240 nm can contribute to the UV light absorption in humid air plasma. Nevertheless, the similarity between curves **b** and **c** suggests that the nitric acid is not present at 200 W, in agreement with the FTIR measurement [3]. Power dependencies of the O_3 and NO_2 densities are along with the results of FTIR spectroscopy [3] shown in Figure 4. In order to improve the image clarity, very low densities obtained by OAS and FTIR are not shown in the plot. Although the measured density values are slightly different, both OAS and FTIR spectroscopy provide a similar picture of plasma chemistry development. As the FTIR and OAS spectra were not recorded in the same experiment, the deviations between the OAS and FTIR values were attributed to worse experiment repeatability, especially in the case of laboratory air. Generally, the OAS measurement had a lower sensitivity (at least due to the used instrumentation), and it also suffered more from the spectra overlap compared to FTIR measurement.

The measurement with other gas mixtures revealed that with decreasing oxygen content in the mixture the transition between the ozone and NO_2 production moves to lower discharge powers. For the discharge in air, ozone was produced only at lowest discharge power of 100 W (not shown in Figure 4). Also with decreasing oxygen content in the gas mixture the ozone and NO_2 densities decrease. The absence of the absorption peak in the spectrum could be used to estimate the upper-density limit. For example, no absorption was observed at 662 nm, where NO_3 absorption cross section has a maximum [2]. The NO_3 density was therefore below $2 \times 10^{20} m^{-3}$. The uncertainty of the densities obtained by OAS was estimated to be about 10%.

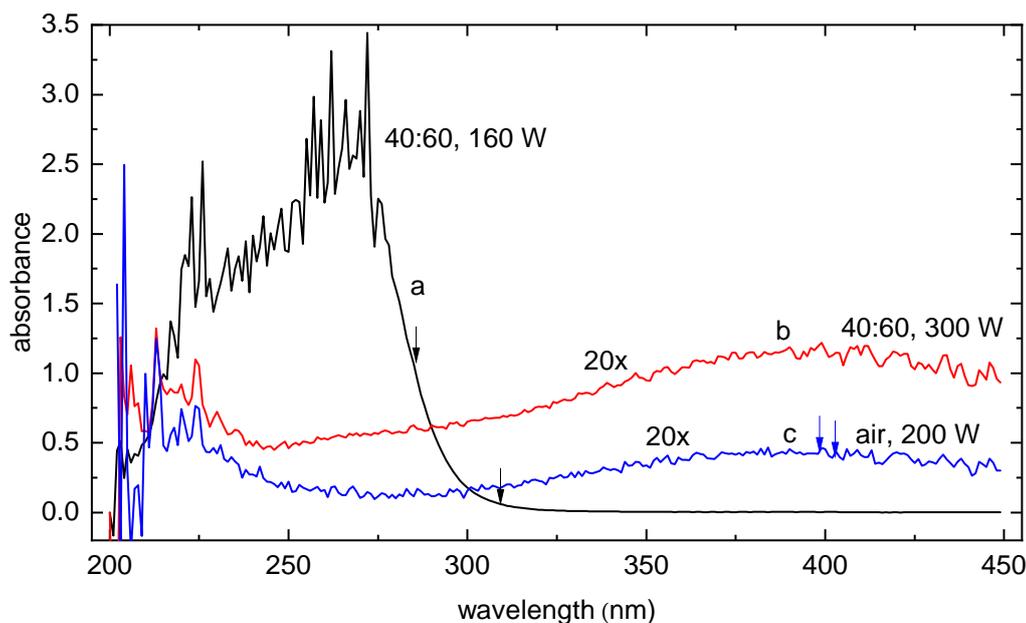


Figure 3. The optical absorption spectra of gaseous plasma products for gas mixture $N_2:O_2$ 40:60 and air at various discharge powers. The red and blue curves were multiplied by 20 in order to improve their readability. The black and blue arrows show the edges of the wavelength intervals used for O_3 and NO_2 density calculation.

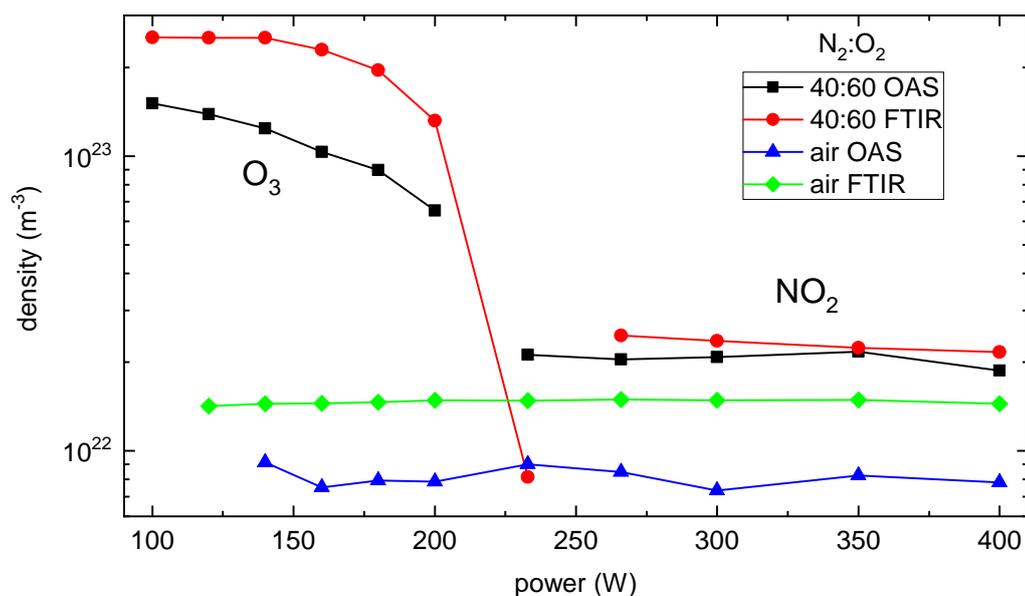


Figure 4. The comparison of power dependencies of O_3 and NO_2 densities obtained using OAS and FTIR spectroscopy (see [3]).

3.2. Measurement after immediate change of CBD discharge power

The time dependencies of ozone and NO_2 densities and gas temperature were measured after an immediate change of applied power to CBD. The results are shown in Figures 5 and 6. When the applied power changes from 150 W to 250 W or to higher applied power, the discharge changes the ozone production to NO_2 production. When the applied power changed from 150 W to 250 W only, the decrease of ozone density lasted 570 s. When the applied power changed from 150 W to 400 W, this decrease took place in 70 s,

which is just the time needed to replace all gas in the discharge chamber. The temperature of CBD ceramics and also gas temperature increased faster after the change of applied power to 400 W than after the change of applied power to 250 W, see Figure 6. The gas temperature at applied power of 400 W reached in 10 s the value of 48 °C, which is enough to destroy the ozone production in the discharge. On the other hand, the gas temperature of 48 °C was reached in 500 s at applied power of 250 W, which corresponds after adding 70 s for gas exchange in discharge chamber to the time obtained from ozone density measurement.

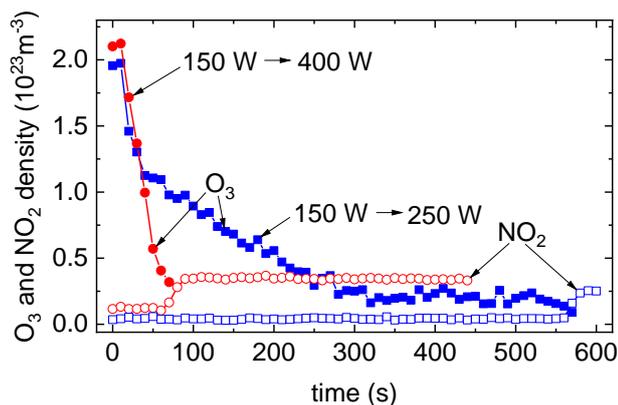


Figure 5. The time dependence of O_3 and NO_2 densities after power increase for gas mixture $N_2:O_2$ 40:60. Blue symbols – 150 → 250 W; red symbols – 150 → 400 W.

These results show that the gas temperature is the only major parameter that controls the composition of gaseous products from the discharge.

4. Conclusion

The absolute densities of stable gaseous products generated by coplanar dielectric barrier discharge in N_2/O_2 mixtures and in ambient air were determined by absorption spectroscopy. Ozone (O_3) and nitrogen oxides (N_2O , NO_2) were identified as the stable products of the discharge in N_2/O_2 mixtures. The product densities were determined for a wide range of applied input powers (100–400 W). The actual product composition was found to depend strongly on the gas temperature. At low input power, when the gas temperature is low, O_3 density is high and NO_2 densities are very low. At specific input power the gas temperature increases too much and O_3 disappears, while NO_2 density rises steeply. These findings are also supported by kinetic models [3, 4], which explained this behavior by the temperature dependencies of chemical reactions in volume.

Acknowledgements

This work was supported by CEEPUS network AT-0063. V.M. was supported by institutional support for the research organization development awarded by the Ministry of Defence of the Czech Republic.

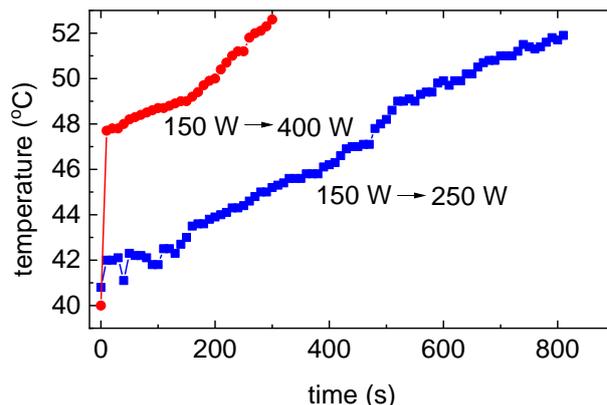


Figure 6. The time dependence of ceramics temperature after power increase for gas mixture $N_2:O_2$ 40:60. Blue squares – 150 → 250 W; red circles – 150 → 400 W.

References

- [1] R. V. Kochanov, I. E. Gordon, L. S. Rothman, et al. Infrared absorption cross-sections in HITRAN2016 and beyond: Expansion for climate, environment, and atmospheric applications. *JQSRT*, 230:172–221, 2019. doi:10.1016/j.jqsrt.2019.04.001.
- [2] R. A. Graham and H. S. Johnston. Photochemistry of NO_3 and kinetics of $N_2O_5-O_3$ system. *J. Phys. Chem.*, 82(3):254–268, 1978. doi:10.1021/j100492a002.
- [3] D. Trunec, Z. Navrátil, J. Tomeková, et al. Chemical composition of gaseous products generated by coplanar barrier discharge in air and N_2/O_2 mixtures. *Plasma Sources Sci. Technol.*, 31:11501, 2022. doi:10.1088/1361-6595/ac9c8f.
- [4] K. Liu, W. Geng, X. Zhou, et al. Transition mechanisms between selective O_3 and NO_x generation modes in atmospheric-pressure plasmas: decoupling specific discharge energy and gas temperature effects. *Plasma Sources Sci. Technol.*, 32(2):025005, 2023. doi:10.1088/1361-6595/acb814.