Spectroscopic characterization of nitrogen plasma generated by waveguide-supplied coaxial-line-based nozzleless microwave source

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Abstract. In this paper, results of spectroscopic study of microwave (2.45 GHz) plasma at atmospheric pressure and high flow rate are presented. The plasma is generated by waveguide-supplied coaxial-line-based microwave plasma source (MPS). Pure nitrogen was used as working gas. An additional nitrogen flow rate of 50l/min was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. The swirl concentrated near the quartz cylinder wall, stabilized plasma generation and protects the quartz tube wall from overheating. Working gas flow rate and microwave absorbed power varied from 50 up to 200 l/min and from 600 up to 5500 W, respectively. The emission spectra in the range of 300 - 600 nm were recorded. The rotational and vibrational temperatures of N₂⁺ ions and N₂ molecules, as well as the rotational temperature of OH radicals were determined by comparing the measured and simulated spectra. The plasma gas temperature inferred from rotational temperature of heavy species ranged 4000 to 6200 K. It depended on location in plasma, microwave absorbed power and working gas flow rate. The MPS can be used in various gas processing applications.

Keywords—microwave plasma, OES, rotational temperature, gas processing

1. Introduction

Recently, microwave plasma sources (MPSs) operated at atmospheric pressure have been developed [1, 2]. MPSs were used as a light sources [3], in sterilization [4] and technological processes like surface treatment. Various materials could be treated with microwave plasma: metals (steel [5] and aluminium [6]), ceramic [7] and polymers [8]. Plasma can be used for deposition of thin films [9], as well as etching [10]. MPSs also found applications in the processing of various gases [11, 12]. Destruction of Freon CFC-11 [13] and HFC-134a [14] and production of hydrogen via methane conversion [15] in microwave atmospheric pressure plasmas were reported by us elsewhere. In papers [14] and [15] a waveguide-supplied nozzleless MPS was used.

The plasma gas temperature is one of the most important parameter in plasma technology and applications. This temperature can often be inferred from the rotational temperature of the heavy species of the gas [16-23]. The rotational and vibrational temperatures in plasmas are often determined comparing experimental and simulated optical spectra.
In this paper, results of spectroscopic study of microwave plasma at high nitrogen flow rates are presented. The plasma was generated in waveguide-supplied coaxial-line-based nozzleless MPS operated at 2.45 GHz.

2. Optical emission spectroscopy (OES)

Measurements of the plasma parameters in high-pressure plasma environment pose requirements that are different compared to low-pressure plasmas (<10 mbar). The highly collisional nature of atmospheric pressure plasma can significantly modify the data analysis procedure and sometimes questions the applicability of methods used in the low-pressure plasmas. However, as many research showed, well developed low-pressure plasma diagnostics methods for both partially ionized [24, 25] and highly ionized plasmas [26, 27] can be adopted for collisionally dominated plasmas.

In the thermal equilibrium plasmas the temperature measurements using OES are usually based on the absolute or relative intensities of various atomic lines of oxygen and nitrogen. In the case of non-equilibrium plasmas at atmospheric pressure, the techniques used for the temperature measurements in the equilibrium plasmas may not provide reliable information about the gas temperature because the population distribution of internal energy states tends to depart from the Boltzmann distribution. This concerns mainly the case of the electronic and vibrational population distributions, but the rotational populations tend to follow the Boltzmann distribution owing to fast rotational relaxation at atmospheric pressure. Thus, the gas temperature can often be inferred from the rotational temperature of the heavy species of the gas [16-23]. Various transitions of O$_2$, N$_2$, N$_2^+$, and NO (in dry air), OH (in humid air) and other atoms and molecules present in the plasma can be used for the temperature measurements, depending on the level of plasma excitation and interference of the other transitions.

In case of resolved spectra the rotational and vibrational temperatures can be obtain from the Boltzmann plot [21, 22]. But in most experiments obtaining of resolved spectra is impossible due to high spectral resolution requirements. Fortunately, also in case of unresolved spectra some methods were developed to determine temperatures [16, 17]. Rotational and vibrational temperatures in plasmas are often determined comparing relative intensities of experimental and simulated optical spectra [20]. In this work for simulation of the optical spectra the Specair [28, 29] and Lifbase [30, 31] programs were used. The codes of these programs calculate the spectral radiation emitted by gases and plasmas of various compositions at given individually vibrational and rotational temperatures.

3. Microwave Plasma Source (MPS)

The sketch of the nozzleless waveguide-supplied coaxial-line-based MPS is shown in figure 1. The source was based on a standard WR 430 rectangular waveguide with a section of reduced-height preceded and followed by tapered sections. The tapered section assured smooth transition from the standard waveguide dimensions to the waveguide of reduced height. There was an inner cylinder electrode mounted perpendicular to the waveguide in the center of the circular openings on the axis of the waveguide wide wall. The inner cylindrical electrode was surrounded by a quartz tube. Both the inner cylindrical electrode and the quartz tube were surrounded by outer cylindrical shield on the outside of the waveguide. The inner cylindrical electrode and the outer cylindrical shield formed a coaxial line. The working gas was injected to the plasma by the inner cylindrical electrode. An additional gas was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. The swirl concentrated near the quartz cylinder wall, stabilized plasma generation and protects the quartz tube wall from overheating. The plasma in the form of a flame was generated inside a quartz tube above the end part of the inner cylindrical electrode. The plasma could be observed through visualization slit in outer cylindrical shield (see figure 2 and 4). Figure 2 shows the photos of nitrogen plasma at different discharge conditions and figure 3 shows the length of nitrogen plasma (measured from electrode) as a function of microwave absorbed power for two different axial flow rates. Operation of the MPS was described in details in [32].
Fig. 1. The sketch of waveguide-supplied coaxial-line-based nozzleless microwave plasma source.

Fig. 2. Microwave nitrogen plasmas for different conditions.

Fig. 3. The length of nitrogen plasma (measured from electrode) as a function of microwave absorbed power $P_A$ for different axial flow rates.
4. Experiments

The experimental setup is shown in figure 4. It consisted of a 2.45 GHz magnetron generator, microwave power supplying and measuring system, MPS, movable plunger for impedance matching, gas supplying and flow control system, spectrometer [DK-480 (CVI), 1200 and 3600 grooves/mm grating] for spectral emission measurements, equipped with a CCD camera [SBIG ST-6, 750 × 242], and a PC computer. The microwave generator is composed of a high voltage power supply, a control unit and a magnetron head. The magnetron head is equipped with a water cooled circulator which protects it against damages caused by the reflected microwave power. The microwave power measuring system includes a directional coupler, two power meter heads and a digital dual-channel power meter. This system enables direct measurements of an incident $P_I$ and reflected $P_R$ microwave powers. An absorbed power $P_A$ was obtained from the subtraction of $P_I - P_R$.

![Experimental setup](image)

Fig. 4. Experimental setup.

Pure nitrogen was used as working gas. An additional nitrogen flow rate of 50 l/min was introduced to the plasma by four gas ducts which formed a swirl flow inside the quartz tube. A small amount of water vapor was added optionally to swirl gas flow in order to achieve detectable intensity of OH spectra. Working gas flow rate and microwave absorbed power varied from 50 up to 200 l/min and from 600 up to 5000 W, respectively.

To measure the spectra, the light emitted by the plasma was focused with a quartz lens (50 mm in diameter, focal length – 75 mm) onto the entrance slit of the spectrometer (see figure 4). The width of the spectrometer entrance slit was 50 µm (20 mm height). Two opaque screens with pinholes of a 1 mm diameter were placed near the plasma. These pinholes, together with the lens and the pinhole at the spectrometer entrance as well as the entrance slit formed a spatial resolution unit for selection of an area of the plasma, emission of which was recorded by the spectrometer. We estimate that the measured area was about 8 mm diameter. Spectra were recorded and then corrected according to the wavelength sensitivity of CCD camera. The wavelength sensitivity of CCD camera was determined using a tungsten halogen calibration lamp. Using a Hg-Ne low-pressure calibration lamp ($\lambda = 365.02$ nm, 435.84 nm and 546.07 nm, Hg I) we measured that the Gaussian instrumental line profile FWHM was about 0.12 nm and 0.05 nm for 1200 and 3600 grooves/mm grating, respectively. All spectra were measured with 1200 grooves/mm grating. Only for OH (A-X) rotational band measurements the 3600 grooves/mm grating was used.
In this experiment, for the temperatures determination we used the transitions as follows:

- OH ($A^2\Sigma \rightarrow X^2\Pi$, 306-310 nm band),
- $N_2$ second positive system ($C^3\Pi \rightarrow B^3\Pi$, 308-317 nm band),
- $N_2^+$ first negative system ($B^5\Sigma \rightarrow X^5\Sigma$, 380-392 nm and 463-472 nm band).

5. Results

Figure 5 shows spectrum emitted by the nitrogen plasma. As seen, the dominant spectrum is $N_2^+$ first negative system ($B^5\Sigma \rightarrow X^5\Sigma$). The spectrum contained also: $N_2$ second positive system ($C^3\Pi \rightarrow B^3\Pi$) and $N_2$ first positive ($B^3\Pi \rightarrow A^3\Sigma$). The Zn I lines (identified with NIST database [33]) observed in spectrum indicates degradation of the brass inner electrode end. The intensity of all measured systems increased linearly with increasing microwave absorbed power.

Fig. 5. Measured emission spectrum of nitrogen plasma ($P_A = 4$ kW, nitrogen flow rate - 50 l/min, 25 mm below the electrode end)

A small amount of water vapor was added to the swirl nitrogen flow. This addition of water vapor did not change the plasma significantly: the microwave incident and reflected powers, as well as the plasma length remained unchanged. The benefit of such addition was occurring of OH (A-X) rotational band. This band is widely used for gas temperature estimations, e.g. [17, 18, 23].

After having the experimental spectra, a simulations of this spectra was carried out using Specair or Lifbase program. The simulated spectrum was fitted to the experimental one by variation of the rotational $T_{rot}$ temperature. Figures 6 and 7 show the comparisons of the both spectra: experimental and simulated fitted to the experimental one. The comparision of measured and simulated spectra of OH (A-X) (figure 6a), $N_2$ second positive system (figure 6b) $N_2^+$ first negative system for two different bands (figure 7), were performed and rotational $T_{rot}$ and vibrational $T_{vib}$ temperatures were determineted.
The rotational temperatures of OH radicals, N$_2$ molecules and N$_2^+$ ions as a function of distance below the inner electrode end top (distance BIEE) in nitrogen plasma (P$_A$ = 2kW, nitrogen flow rate - 50 l/min, 25 mm below the electrode end) are presented in figure 8. At this condition the plasma length was about 85 mm (see figure 3). Regardless the plasma length it was impossible to determine the temperature of N$_2^+$ ions and N$_2$ molecules at the further area of plasma. The reason of this was low intensities of band of N$_2^+$ first negative system and N$_2$ second positive system used for temperature determinations. As seen in picture we could observe effect of cooling the gas by the inner electrode. The highest temperature occurred at distance of 15 - 25 mm. Further from the inner electrode temperature decreased. Interesting phenomenon could be observed for N$_2^+$ ions temperatures determined from 380-392 nm band. Close to the inner electrode, at excitation region the vibrational temperature was 1000 K higher than the rotational temperature. At the end of plasma flame, due to thermal relaxation both temperatures were in equilibrium [23].

The rotational and vibrational temperatures increased with microwave absorbed power (figure 9). This increase was not significant. As it could been seen in figure 3 the increase of the microwave power caused almost proportional increase of the plasma length and thus the plasma volume. It could be concluded that the microwave power influence the plasma volume and much less the plasma gas temperature. The influence of axial flow was more apparent for higher microwave absorbed powers. Increasing the flow caused slight decrease of temperature (figure 10). For lower
absorbed powers this effect was less apparent. At location in the plasma placed 25 mm below the inner electrode determination of the rotational and vibrational temperatures of N$_2^+$ ions temperatures from 380-392 nm band provided the constant result (figures 8-10). The initial distribution (i.e. distribution just after the excitation) of rotational and vibrational states in this case was non-thermalized, but was the effect of excitation mechanisms [23]. The effect of thermal relaxation was observed at the end of the plasma flame (see figure 8).

![Graph](image1)

**Fig. 8.** Measured rotational and vibrational temperatures of OH radicals, N$_2$ molecules and N$_2^+$ ions as a function of distance below inner electrode end (Distance BIEE) ($P_A$ - 2 kW, nitrogen flow rate - 50 l/min)

![Graph](image2)

**Fig. 9.** Measured rotational and vibrational temperatures of OH radicals, N$_2$ molecules and N$_2^+$ ions as a function of microwave absorbed power (nitrogen flow rate - 50 l/min, 25 mm below the electrode end)
As seen in figures 8, 9 and 10 the results for each selected specie were slightly different for the same discharge conditions. Obtained rotational and vibrational temperatures ranged from 4000 to 6200 K and from 4500 to 7000 K respectively, depending on the location in the plasma, the microwave absorbed power and axial nitrogen flow rate. OH radicals and N2+ ions from 463-472 nm band provided comparable results. N2 molecules in all cases provided slightly lower temperatures. In all conditions $T_{\text{vib}}$ were greater or equal than $T_{\text{rot}}$. It is in good agreement with theory [20]. The rotational and the vibrational temperatures, except these obtained from N2+ ions determined from 463-472 nm band, were in equilibrium in nitrogen microwave plasma. The results gave comparable temperatures to that presented by us [34] measured in similar device: nozzleless waveguide-supplied metal-cylinder-based MPS. Rotational temperature of OH radicals was assumed to be the best estimation of the plasma gas temperature in nitrogen microwave plasma.

6. Conclusion

Spectroscopic study of nitrogen microwave (2.45 GHz) plasma at atmospheric pressure and high flow rates was presented in this work. The study concerns the rotational and vibrational temperatures of selected heavy species present in microwave plasma in order to estimate gas temperature. The plasma gas temperature inferred from rotational temperature of OH radicals ranged 4000 to 6200 K. It depended on location in plasma, microwave absorbed power and working gas flow rate.

The investigated nozzleless, waveguide-supplied, coaxial-line-based MPS works very stable with various working gases. The parameters of the plasma can be changed in wide range. The high gas temperature makes it attractive tool for different gas processing at high flow rates. Owing to high gas temperature MPS was successfully used for Freon destruction [14], as well as for hydrogen production via hydrocarbon conversion [15].

Acknowledgments

This research was supported by The National Centre for Research and Development (NCBiR) under the programme NR14-0091-10/2010.
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