Emission spectrometry for discharge plasma diagnosis

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Abstract

Emission spectrometry in the atmospheric pressure discharge was carried out to understand the reaction mechanisms of active species because the discharge plasma process is significantly affected by gas components. In this research, $N_2$ second positive band and two band systems of NO such as NO-$\beta$ band and NO-$\gamma$ band were investigated by using a digital controlled spectrometer and an ICCD camera. When the dielectric pellets were placed on the needle-plate type electrode, emissions from both $N_2$ second positive band and NO-$\gamma$ band were reduced along the electrode axis. The emission ratio between $N_2$ second positive band and NO-$\gamma$ band was significantly different due to the existence of dielectric pellets. One dimensional analysis of emission spectral showed that NO-$\gamma$ band and $N_2$ second positive band lay between the needle-plate electrodes, while emission spectral of NO-$\beta$ band existed around the needle electrode. Two-dimensional analysis of the emission spectrum showed that NO-$\gamma$ band and $N_2$ second positive band exist between needle-plate electrodes. Observation by the time resolution of the emission spectrum showed that $N_2$ second positive band emission was extinguished within 200 ns, while that from NO-$\gamma$ band continued for more than 1 $\mu$s. © 2001 Published by Elsevier Science Ltd.

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1. Introduction

The atmospheric pressure discharge plasma process for air pollution control has been studied. Removal process of polluted gas, such as chemical reactions of active species, has not yet been clear. The emission spectroscopy has been used to analyze the discharge plasma for various gas conditions or discharge conditions such as pulsed corona discharge and glow corona discharge [1–6]. In this paper, the emission spectrum of the atmospheric discharge plasma was observed by using the ICCD camera and a spectrometer. Reducing reactions in the atmospheric discharge could be enhanced by excited species or active species, which were observed in this study, namely, $N_2$ second positive system ($N_2$ second positive band, 337.1 nm mainly appeared), NO-$\beta$ band (304.3 and 320.7 nm), NO-$\gamma$ band (247.9 nm mainly appeared) [7], and $O_2$ Herzberg I band (312 and 323 nm) [8] which could be generated after the reducing reactions of NOx.

$N_2$ second positive band is directly excited by the electron impact, while NO-$\gamma$ band is excited by the collisions of the $N_2$ metastable state by the following process [9,10]:

\[ N_2(A) + NO(X) \rightarrow N_2(X) + NO(A) \]  

\[ NO(A) \rightarrow NO(X) + h\nu(NO-\gamma \text{ band}) \]  

Emission of NO-$\beta$ band is used for measuring the N atom density by NO titration [2,11,12]. The following reactions occur at low NO flow rates:

\[ N + NO \rightarrow N_2 + O \]  

\[ N + O + M \rightarrow NO(B) + M \]  

\[ NO(B) \rightarrow NO(X) + h\nu(NO-\beta) \]  

These reactions do not occur by direct electron attachment or dissociation and take several microseconds to complete. In this experiment, the observation period of these species consisted of 1–10 $\mu$s after the trigger signal. NO(B) generated through these reactions was different from NO(B) generated by direct electron attachment. In this study, oxygen gas was not used to observe nitrogen relative species since larger $O_2$ percentages would decrease the number of N atoms due to destructive processes involving NO and $O_2$ molecules [13].

The time resolution of the two-dimensional emission

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spectrometry of a needle-plate electrode by using a pulse generator and a MOSFET switch is also reported in this paper. Trigger timing is described in Section 3.

2. Experimental apparatus

2.1. Measurement system for emission spectrometry

Fig. 1 shows the experimental set up for emission spectrometry. Emission from a needle-plate electrode in a chamber was dispersed by a 0.5 m digitally controlled monochromator (Chromex, 500I) with a resolution of 0.07 nm via two plano-convex lenses. A CCD camera (Hamamatsu Photonics, M6296-01) was used for taking images of target species within a wavelength of 40 nm at the same time. The ICCD camera (Oriel Instruments, AT510) was used for taking images for one- or two-dimensional emission spectrometry of a needle-plate electrode system. The microchannel plate of the ICCD camera was controlled by using a pulse generator (Stanford Research Instruments, DC535).

The chamber depicted in Fig. 1 was made of stainless steel (110 mm × 150 mm), and had a needle-plate electrode. The plate electrode was fixed in the chamber and the needle electrode was movable. Three-dimensional micrometerheads were used to control the position of electrodes in order to obtain the strongest emission intensity.

2.2. Needle-plate electrode

Fig. 2 shows the needle-plate electrode. A plate electrode (an earth electrode) had a dielectric barrier that was made of 1 mm-thick plate of glass without fluorescence. A gap between the needle electrode and the plate electrode was 5–7 mm. In this study, dielectric pellets (NaZSM-5, diameter 2–3 mm) were used to observe effects on the discharge mode. This electrode simulates one portion of the pellet filled reactor which we have already reported [14,15].

2.3. Power source for pulse generation

Positive high voltage pulse with a rise time of 40 ns and a pulse width of 700 ns was applied to the needle electrode. The pulse voltage was generated by using a MOSFET switch (Behlke, HTS 650). Pulse repetition frequency can be controlled from 200 to 1000 pps. The circuit diagram is shown in Fig. 3. The tail register, Rt was varied from 500 to 10 MΩ, and the charging capacitor $C_b$ was 3000 pF. Voltage waveform, current waveform and their product (electric discharge power consumption) were measured or
calculated by using a digital oscilloscope (Tektronix TDS3054), a high voltage probe (Tektronix, P6015A), and a current transformer (Pearson, 2878). An analog power meter (Yokogawa 2041) was used for measuring the input power to the power supply.

2.4. Gas flow system

Standard gas (NO 1000 ppm/N2) was used for the experiments. Concentrations of nitric oxide and nitrogen dioxide were measured using a chemical luminescence NOx analyzer (Shimadzu NOA-7000). Measurement of emission intensity of nitrogen related bands were also carried out with pure N2 gas (99.99%). Gas flow rate was set to 1 l/min in both cases. Before inserting the standard gas into the chamber, residual gas such as O2 was evacuated by a rotary pump connected to the chamber, then purged by pure N2 gas. This process was repeated three times.

3. Results

3.1. Waveforms and trigger timing

Fig. 4 shows waveforms of discharge voltage, discharge current, and trigger timing of microchannel plate for the ICCD camera. The microchannel plate of the ICCD camera was turned on for 5–100 ns by using a pulse generator. Measurement period was selected after the end of the discharge current to distinguish NO related species, which are shown in Eqs. (1)–(5), from the electron excited species of NO. The shortest gating time of the ICCD camera was 5 ns, and the emission image shown in Section 3.2 was obtained by one pulse.

Fig. 5 shows the rising part of discharge voltage, discharge current, and discharge power. The rising time of the discharge voltage was about 40 ns, and the corresponding discharge current was observed within 100 ns. Oscillation of the discharge current was observed by charge and discharge phenomena in the circuit. Strong discharge and the corresponding emission by the nitrogen species between the needle-plate electrodes occurred during this period.

3.2. Analysis of emission spectrometry (N2 second positive band)

Fig. 6 shows an example of the emission band of N2 second positive band (discharge power was constant at 0.3 W). Strong emission lines were observed at 315.9 and 337.1 nm. Significant differences were observed with the existence of dielectric pellets on the plate electrode at the discharge power of 0.3 W.

3.3. Analysis of emission spectrometry (NO-γ band)

Fig. 7 shows an example of the emission band of NO-γ band (discharge power was constant at 0.3 W). Emission intensities were strongly observed at 237.0, 247.9, and 259.6 nm. Similar to the N2 second positive band, significant differences were also observed with the existence of the dielectric pellets on the plate electrode.

These intensity ratios with or without dielectric pellets were investigated as functions of the discharge power.
Relation of the emission intensity for N₂ second positive band, NO-γ band and the discharge power with or without the dielectric pellets is shown in Fig. 8. Discharge power of each pulse was calculated from the discharge power waveform. In this figure, discharge power is defined as the product of the discharge power and pulse repetition frequency.

When the discharge power was around 0.3 W, significant differences of emission intensities were observed with the existence of the dielectric pellets already shown in Figs. 6 and 7. Emission intensity increased linearly with the discharge power as shown in Fig. 8. The ratio between the N₂ second positive band and the NO-γ decreased with the dielectric pellets, while the decrement of ratio between N₂ second positive band and NO-γ without the dielectric pellets was small compared to the catalyst. Existence of pellet catalyst could change the discharge mode or the decrement of generated ratio of specific excited species.

3.4. One-dimensional analysis of emission spectrum

In order to confirm the influence of dielectric pellets on the spatial distribution of discharge, one-dimensional analysis of emission intensity was carried out. Fig. 9 shows the emission intensity of wavelengths ranging from 200 to 400 nm without the dielectric pellets. Zero nm in this figure stands for the tip of the needle electrode and 5 mm stands for the surface of dielectric barrier. Discharge power was constant at 0.15 W.

In this wavelength range, emission intensities of N₂ second positive band (297.7, 315.9, 337.1, 357.7, and 380.5 nm etc.) and NO-γ band (237.0, 247.9, and 259.6 nm etc.) were strong. The intensities of these bands were strong from the tip of the needle electrode to the surface of dielectric barrier, while emission intensities of NO-β band (304.3 and 320.7 nm) and O₂ Herzberg I band (312 and 323 nm) were weak. They were only observed around the needle electrode.

Fig. 10 shows one-dimensional analysis of emission intensity with the dielectric pellets. The other conditions, such as gas composition or discharge power, were the same as those of Fig. 9.

Strong emission intensities of N₂ second positive band and NO-γ band were observed at the region near the needle electrode, and, however, they were not observed near the plate electrode with the dielectric pellets. When the streamer, which generates the excited species, reached the surface of the dielectric pellets, it might not have had enough energy to generate these species. Emission intensities of NO-β band and O₂ Herzberg I band were very weak in this case, and they were hardly observed at the surface of the dielectric pellets, which could be responsible for the NO reducing reactions.

3.5. Two-dimensional analysis of emission spectrum

Fig. 11 shows two-dimensional images of N₂ second positive band without the dielectric barrier (discharge
Fig. 9. One-dimensional analysis of emission intensity for electrode direction without the dielectric pellets.

Voltage and power were 14.5 kV and 0.5 W, respectively. Strong emission was observed at 20–40 ns, while strong NO-γ band emissions were observed at 200–600 ns (Fig. 12). In these experiments, 0 ns is defined as the time when the pulse voltage is applied to the needle-plate electrode. Delay time of observation by the ICCD camera can be neglected. This result suggested that N₂ second positive band was excited by electron collisions, and NO-γ band was energized by collisions of N₂(A) state which is shown in Eqs. (1)–(2). (Both corona discharge.)

Fig. 10. One-dimensional analysis of emission intensity for electrode direction with the dielectric pellets.
and power was 14.5 kV and 0.5 W, respectively). Strong emission was observed after discharge until 40 ns. Emission region was widened by the existence of the dielectric pellets. NO-γ band was also observed in a wide area around the dielectric pellets during the time interval 200–600 ns (Fig. 14). The dielectric pellets could affect the discharge mode resulting in the wide discharge area. Electric field of each pellet’s contact point could increase, where the
Fig. 13. Two-dimensional image of N₂ second positive band after barrier discharge with the dielectric pellets.

Fig. 14. Two-dimensional image of NO-γ band after barrier discharge with the dielectric pellets.
dielectric constant of the pellets (about 10) was higher than the background gas.

3.6. NO initial concentrations on emission spectra

Fig. 15 shows NO concentration dependence on N₂ second positive band without the dielectric pellets. The gate time of the ICCD camera was set at 50 ns, and the discharge voltage was 8 kV. Emission intensity of N₂ second positive band increased with NO initial concentration. The emission intensity of NO-γ band increased with NO initial concentration (Fig. 16). The gate time of the ICCD camera was set at 1 μs, and discharge voltage was 16 kV. From these results, it can be concluded that the NO initial concentration does influence the emission intensity of both N₂ second positive band and NO-γ band.

4. Conclusions

Two-dimensional image of N₂ second positive band and NO-γ band were obtained. The following results were obtained by the observation of emission spectrum of excited species by one-dimensional analysis.

1. When the streamer, which could emit both N₂ second positive band and NO-γ band, reached the surface of the dielectric pellets, it could lose energy to generate these species. Emission spectrum of NO-β band and O₂
Herzberg I band was hardly observed at the surface of plate electrode even without the dielectric pellets.

2. Both N₂ second positive band and NO-γ band emissions were declined, when the streamer reached the surface of electrode or dielectric barrier. Significant difference was observed with the dielectric pellets on the plate electrode. Existence of the dielectric pellets could change the discharge mode and affect the spatial distribution of discharge or the decrement of specific excited species generated by the discharge.

3. N₂ second positive band emitted light by electron collisions. (The light was extinguished within 100 ns.) The spatial distribution of discharge with the barrier was larger than without the dielectric barrier (corona discharge).

4. NO-γ band emitted the light by N₂(A) (metastable state) collisions. (The light lasted more than 1000 ns.) The spatial distribution of discharge was quite different by the dielectric barrier at same discharge power (0.5 W, 14.5 kV).

5. Time dependence of these excited species could be one of the important key factors not only for NO reducing reactions but also for other oxidizing reactions. We should measure the other excited species and their time dependence to understand the general reaction mechanisms of non-thermal plasma combined with the dielectric pellets.

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