Emission Spectroscopy of Pulsed Power Microplasma for Atmospheric Pollution Control

Kazuo Shimizu, *Member, IEEE*, Tatsuya Ishii, and Marius Blajan

***Abstract*— Pollution of the atmosphere from various sources including factories and automobiles are serieous problem all over the world and should be controlled. Non themal plasma is studied by various groups as one of the pollution control method. Microplasma, which is atmospheric pressure nothermal plasma, has been used as a method for exhaust gas treatment, and indoor air purification. Microplasma is the relatively recent research field, diagnosis of microplasma and its mechanism are not sufficient. Though, the nonthermal plasma diagnosis by emission spectroscopy has been studied and analyzed by many authors.**

In this paper the diagnosis of the microplasma discharge in N_2 gas, and N_2/ NO gas mixture is presented. An experimental Marx Generator with MOSFET switches was used to generate pulsed output voltages of up to -1.8 kV. Emission spectra were observed by a spectrometer with ICCD camera and a photomultiplier tube. NO-γ band, N_2 second positive band and N_2 first negative system were confirmed. Time evolution of light emission measured by the photomultiplier tube shows differences between NO-γ band and N_2 second positive band. This could the difference of light emission mechanism, N_2 second positive band is excited by direct electron impact and NO-γ band by the collisions of the N_2 metastables.

***Keywords*— Microplasma, Emission Spectroscopy, Pulsed Power, Marx Generator**

I. Introduction

NONTHERMAL plasma is used in applications of cleaning the exhaust gases from various sources such as factories or automobiles [1-7]. Microplasma is a kind of dielectric barrier discharge (DBD) with relatively narrow discharge gap less than 100 μm. It is generated at relatively low discharge voltage, the reactor has small dimensions and requires only small size power supplies. Most of the microplasma research has been application driven like air treatment, NOx removal or sterilization [8-11]. Therefore, the fundamental phenomena of microplasma such as electron energy, generation of radicals are not fully understood.

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The aim of this paper is to analyze the characteristics of microplasma generated by a pulsed power supply using emission spectroscopy. The pulsed power supply consisted in an experimental Marx generator which uses MOSFET switches. Also the ozone generation was analyzed by using pulsed power supply and high frequency (25 kHz) AC voltage. The gases used in experiments were N_2, NO/N_2 gas mixture and air. Emission spectroscopy analysis of microplasma was performed with an ICCD camera and a spectrometer, and the time evolution of microplasma discharge was observed by a photomultiplier tube.

II. Generation of Microplassma

Fig. 1 shows a schematic image of the electrodes used in the experiments. It is a stainless steel covered with dielectric materials as a microplasma electrode. The electrodes are faced together with a discharge gap of 0 μm and 50 μm. Since the discharge gap is small compared to that of other silent discharges, nonthermal plasma occurred about a discharge voltage of 1 kV.

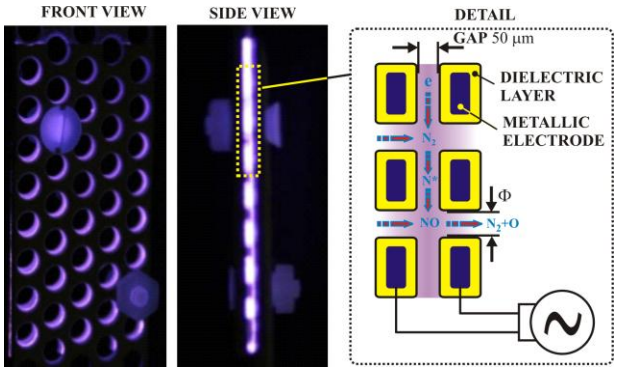

Fig. 1. A schematic images of microplasma electrodes(40 mm x 20 mm, hole size 2.5 mm). The pressure loss between the electrodes is very small (5mmH_2O at gas flow rate of 5 L/min).

III. Marx Generator

The microplasma was generated by applying pulse voltage using a Marx generator as a power supply. The experimental circuit is presented in Fig. 2. An experimental Marx generator generates negative pulses triggering by semiconductor switches. When the MOSFET switches are opened, the capacitors linked in parallel connection are charged at a given voltage V.

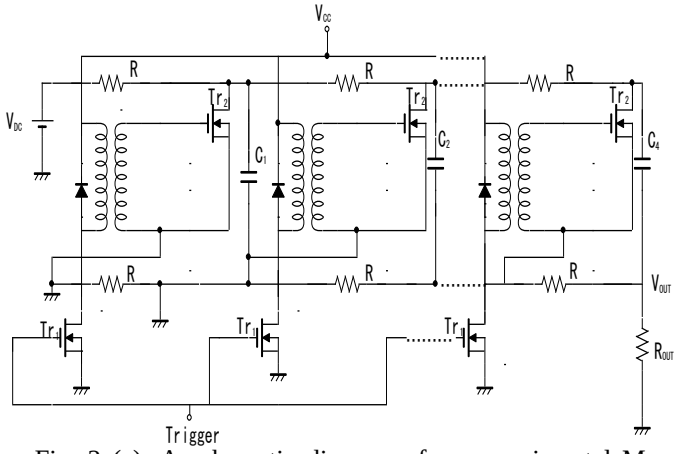

Fig. 2 (a). A schematic diagram of an experimental Marx generator with MOSFET switches.

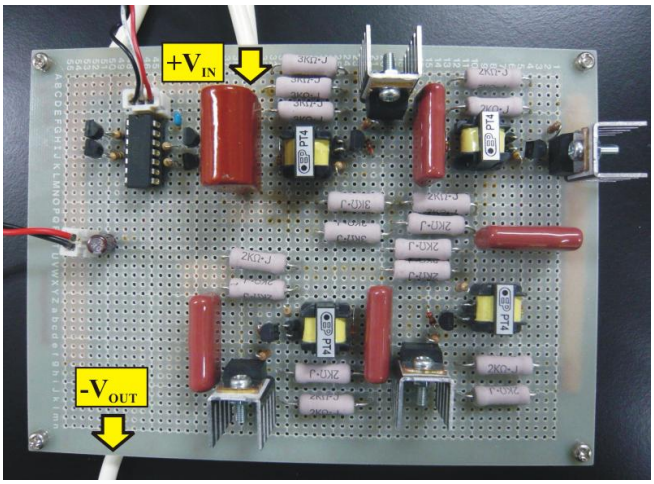

Fig. 2 (b). An Image of an Marx generator circuit.

By turning on the MOSFET switches, the capacitors discharge in a series connection. The voltage will have a value of the voltage V multiplied with the number of capacitors from the circuit. The experimental circuit consists of 4 capacitors. Charge voltage V was set to 500V, and a tail resistor Rout = 2 kΩ was used for pulse frequency of 4 kHz.

IV. Experimental Setup

The experimental setup is presented in Fig. 3. The emission spectrum from microplasma reactor was measured by an ICCD camera (Ryoushi-giken, SMCP− ICCD 1024 HAM-NDS/UV), a spectrometer (Ryoushi-giken, VIS 351) and a photomultiplier tube (Hamamatsu, R 3896). A pulse generator (Tektronix, AFG 3021B) was used to trigger an experimental Marx generator and a ICCD camera. The obtained data were transferred to a computer to be analyzed.

Emission spectroscopy experiments were performed with microplasma electrodes size 40mm x 20 mm and aperture ratio 36 %. The discharge gap between the electrodes was set to 50 µm with dielectric spacer. Ozone and NO_X generation were confirmed with different microplasma electrodes which is diameter 45 mm and aperture ratio 8.7 %.

Discharge gap between the electrodes was set to 0 µm. Ozone concentration was measured with an ozone monitor (Ebara Jitsugyo, EG-2001B). NOx concentration was measured by using a NOx monitor (Shimadzu, NOA-7000A).

Discharge voltage and its corresponding discharge current were measured by a high voltage probe (Tektronix, P6015), an AC current transformer (Tektronix, P6021) and a digital oscilloscope (Tektronix, TDS 2014B).

The composition of the discharge gas used in experiments was pure nitrogen and NO 1000 ppm, N_2 balance for the emission spectroscopy experiments and air for the generation of ozone. The gas flow rate was set at 2 L/min.

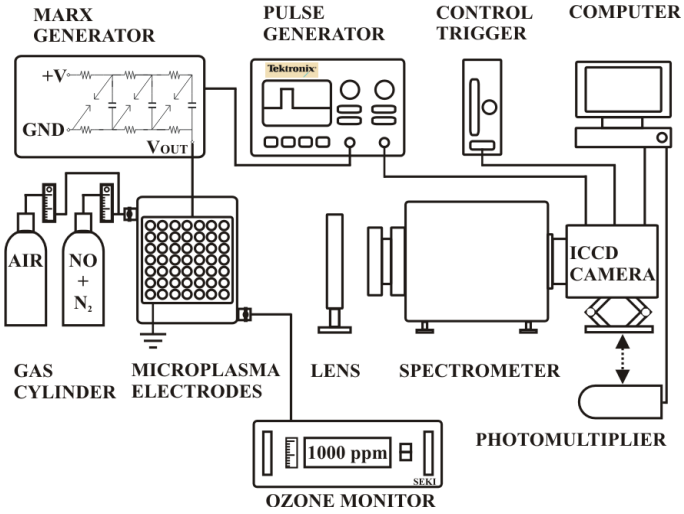

Fig. 3. An experimental setup for observing emission from microplasma electrode.

Fig. 4 shows the waveform of discharge voltage, discharge current and Gate pulse for an ICCD camera. An ICCD camera was turned on 1 µs, when gate signal voltage inputted.

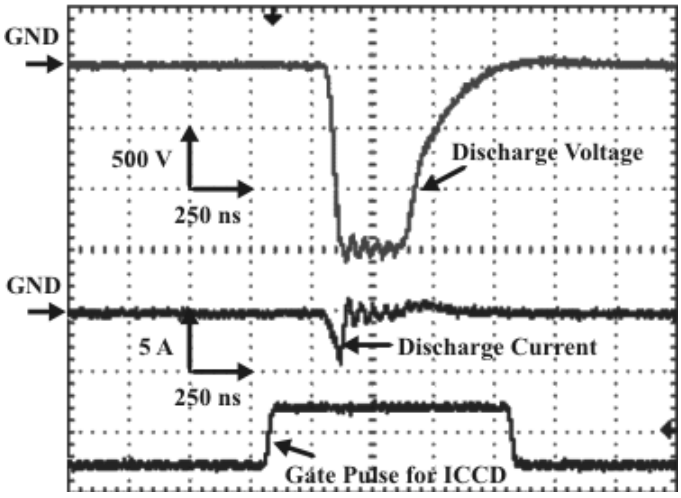

Fig. 4. An example of discharge voltage, its corresponding discharge current and Gate pulse for an ICCD camera (250 ns/div).

V. Characteristics of Microplasma

Fig. 5 shows the characteristics of discharge voltage versus discharge current of an experimental Marx generator for various frequency from 4 to 24 kHz. The measured discharge current contains capacitive current. Discharge currents increases with increase of discharge voltages for all the frequencies. Discharge current does not depend on frequency. It was observed that almost same discharge currents are obtained with same discharge voltage.

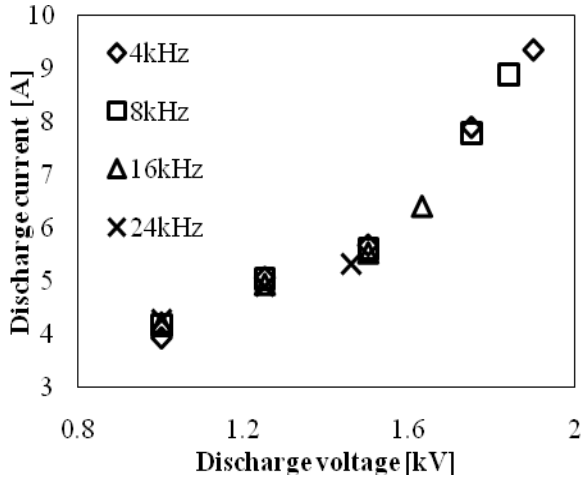

Fig. 5. Characteristics of discharge voltage versus discharge current of an experimental Marx generator.

Fig. 6 shows the characteristics of discharge voltage versus discharge power of an experimental Marx generator. Discharge power was calculated from the measured energy represented by the area of discharge voltage multiplied with discharge current. Discharge power increased with increase of frequency. The highest discharge power of 3.5 W was obtained at 16 kHz.

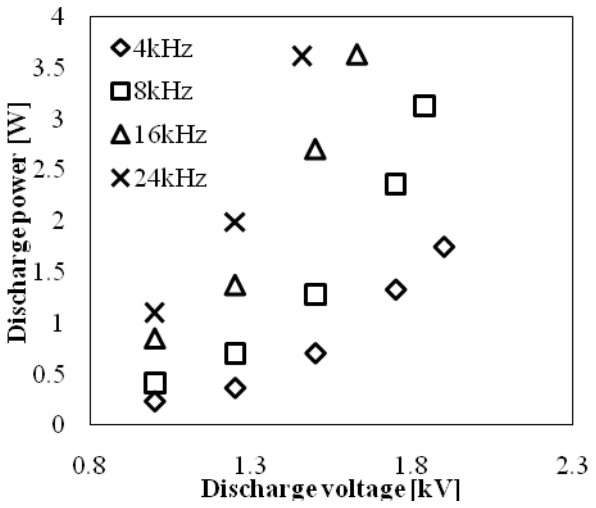

Fig. 6. Characteristics of discharge voltage versus discharge power of an experimental Marx generator.

VI. Ozone and NO_x Generation by Marx Generator

Fig. 7 shows the characteristics of ozone generation by using an experimental Marx generator. The air flow rate was set to 5 L/min. Ozone generation was observed, when the discharge voltage was higher than -1.2 kV. Characteristics of ozone generation lowers as the frequency goes up. Maximum ozone generation was 51 ppm at 8 kHz

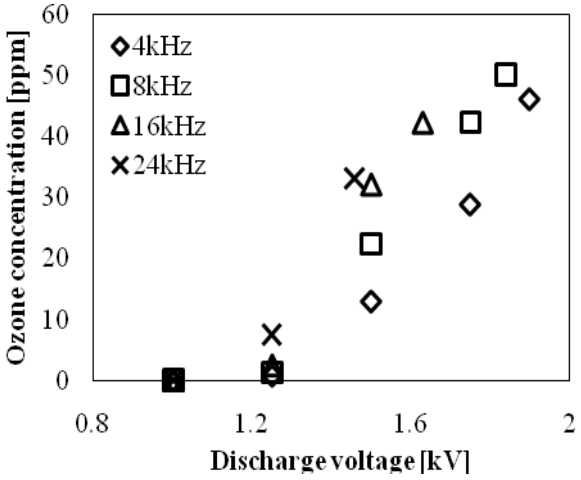

Fig. 7. Characteristics of ozone generation versus discharge voltage.

Fig. 8 shows the comparison of ozone generation between an experimental Marx generator and a neon transformer. Frequency of a neon transformer is 25 kHz. When frequency of discharge voltage was low, increase of ozone concentration was observed almost lineally. Generation of ozone has peaks at certain discharge power. In this condition (size of microplasma electrode, gas flow rate etc.), maximum ozone concentration was about 50ppm for an experimental Marx generator, and that of AC power source was less than 20ppm.

From this result, a Marx generator has higher efficiency for generating ozone. When AC voltage applied for discharge, capacitive current flow that could resulted to loss of energy.

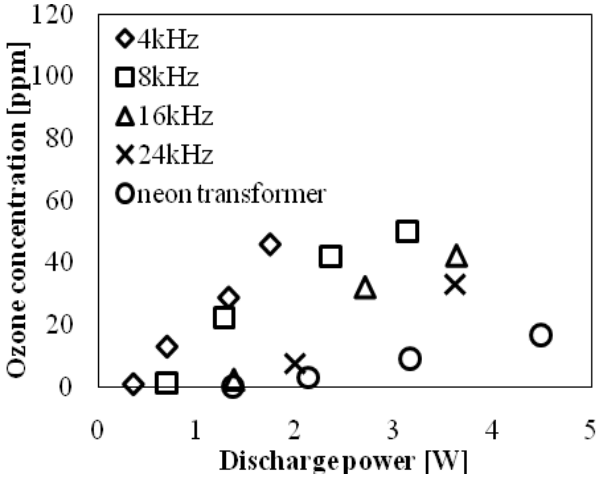

Fig. 8. Characteristics of ozone generation versus discharge power. AC neontransformer (25 kHz) was used to compare the efficiency of generating ozone.

Fig. 9 shows characteristics of NO_X generation versus discharge voltage by a Marx generator and a neon transformer.

NO_X generation was observed at 700 V, when the neon transformer was used and at 1.25 kV for the Marx Generator. NOx generation of 10 ppm for the neon transformer and 5 ppm for the Marx Generator were obtained at 1.1 kV and at 1.7 kV, 16 kHz, respectively.

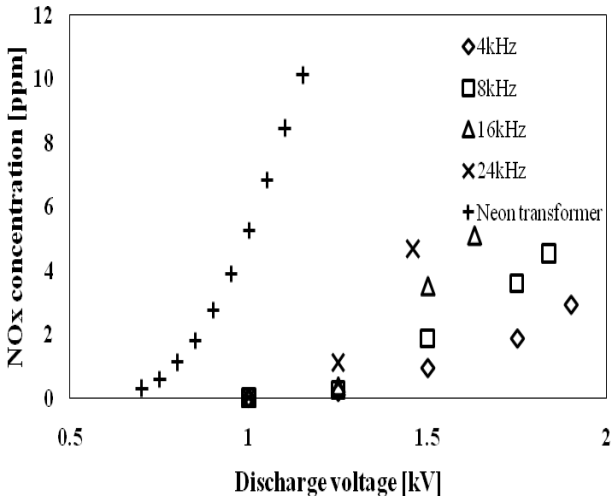

Fig. 9. Characteristics of NO_X generation versus discharge power. AC neontransformer (25 kHz) was used to compare generation NO_X.

VII. Emission Spectroscopy in Nitrogen

Fig. 10 shows the emission spectra of microplasma in nitrogen gas. N_2 second positive band and N_2 first negative band appeared in this spectra (Table. 1 [12]). The experiments were performed at -1.6 kV (negative pulse, rise time 80ns, width 530 ns) and a corresponding discharge current of -4.6 A. ICCD trigger pulse was set to 1 μs.

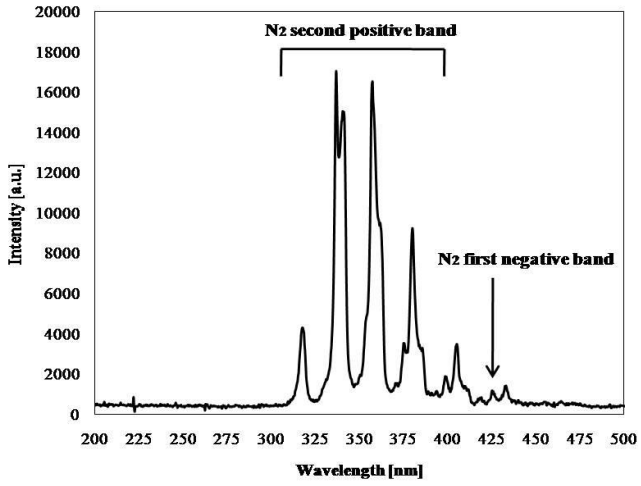

Fig. 10. Emission spectrum of pure nitrogen (V_D=-1.76 kV, I_D=-4.6 A, frequency 1 kHz, trigger pulse 1 μs).

Table. 1. List of detected peaks by emission spectrometry.

Species (system)	Transition	Peak Position (nm)
N_2 second positive	$C^3\Pi \rightarrow B^3\Pi$	296; 315; 337; 358; 376; 381; 400
N_2 first negative	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	391; 428

N_2 second positive band peaks originated from the following electron collisions [12]:

$$e + N_2(X^1\Sigma g^+) \rightarrow N_2(C^3\Pi_u) + e \quad (1)$$

$$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi g) + h\nu \text{ (second positive)} \quad (2)$$

Electron collisions energy at second positive band is at least 11 eV (Table. 2). So these electrons in microplasma has energy level over 11 eV.

Table. 2 Rate constant of N_2 second positive band [13]

Reaction	Rate constant
$e + N_2(X^1\Sigma g^+) \rightarrow N_2(C^3\Pi_u) + e$ E_0=11 eV	f (E/N)
$N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g) + h\nu$	$3\times10^7 s^{-1}$ [14]

Fig. 11 shows time evolution of N_2 second positive band. Emission appeared at the rising and falling part of discharge voltage. Emission time was about 50 ns. Emission of N_2 second positive band was observed by electron collisions. And N_2 (C) lifetime is estimated about 37 ns [15].

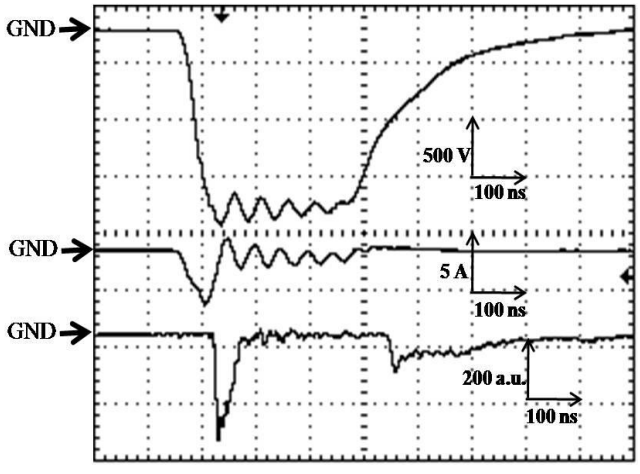

Fig. 11. Waveforms of discharge voltage, discharge current, and emission signal of microplasma (N_2 second positive band).

VIII. Emission Spectroscopy in NO/ N_2 Mixture

Fig. 12 shows an example of emission spectra in NO/N_2 mixture. NO-γ band, N_2 second positive band and N_2 first negative band were detected (Table 3) [14]. The experiments were performed at -1.6 kV (negative pulse, rise time 80ns, width 530 ns) and a corresponding discharge current of -4.6 A. ICCD trigger pulse was set to 1μs.

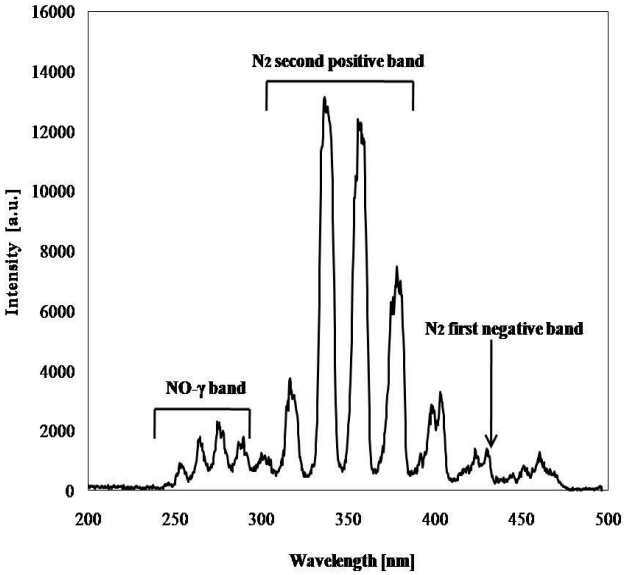

Fig. 12. Emission spectrum of NO/ N_2 mixture (V_D=-1.76 kV, I_D=-4.6 A, frequency 1 kHz, trigger pulse 1 μs).

Table 3. List of detected peaks by emission spectrometry.

Species (system)	Transition	Peak Position (nm)
N_2 second positive	$C^3\Pi \rightarrow B^3\Pi$	296; 315; 337.7; 357.7; 375.5; 380.5; 400
N_2 first negative	$B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$	427.8
NO-γ band	$A^2\Sigma^+ \rightarrow X^2\Pi$	226.9; 237.0; 247.9; 259.6; 271.5; 285.0

NO-γ band originated from the following collisions of the N_2 metastable state [16]:

$$N_2(A) + NO(X) \rightarrow N_2(X) + NO(A) \quad (3)$$
$$NO(A) \rightarrow NO(X) + h\nu(\text{NO-}\gamma\text{ band}) \quad (4)$$

Table. 4 Rate constant of NO-γ band.

Reaction	Rate constant
$N_2(A) + NO(X) \rightarrow N_2(X) + NO(A)$	$(6.5\text{-}7.8)\times10^{-11}$ $cm^3\ s^{-1}$
$NO(A) \rightarrow NO(X) + h\nu$(NO-γ band)	$5\times10^6\ s^{-1}$ [17]

Fig. 13 shows time evolution of NO-γ band. Emission appeared when discharge voltage rises and fall. Emission time was observed about 2 μs. Because of this phenomenon, NO-γ band causes collisions of the N_2 metastable state. N_2 metastable state lifetime is relatively long with 1.9 s[15].

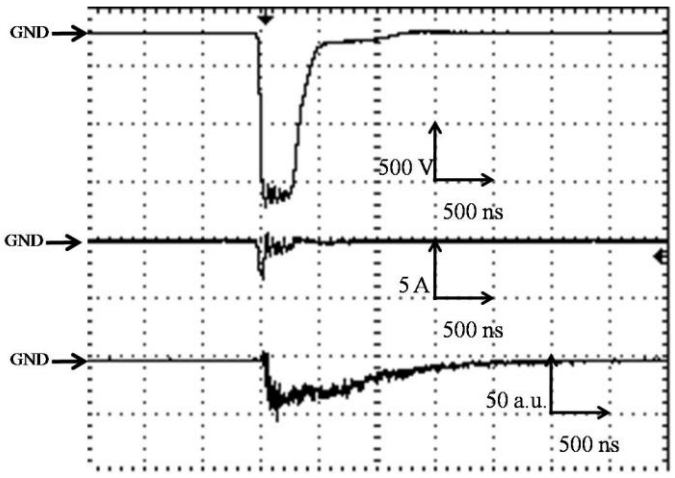

Fig. 13. Waveforms of discharge voltage, discharge current, and emission signal of microplasma (NO-γ band).

IX. Gas Temperature of Microplasma

Plasma temperature was estimated from measured emission spectra [18]. Comparison between the calculated curve and measured value are shown in fig. 14. By comparing the measured spectrum to the simulated spectrum of the nitrogen 2nd positive band system, it could be possible to estimate the rotational and vibrational temperatures. Since experiments are carried out under atmospheric pressure, rotational temperature could be closed to the actual gas temperature.

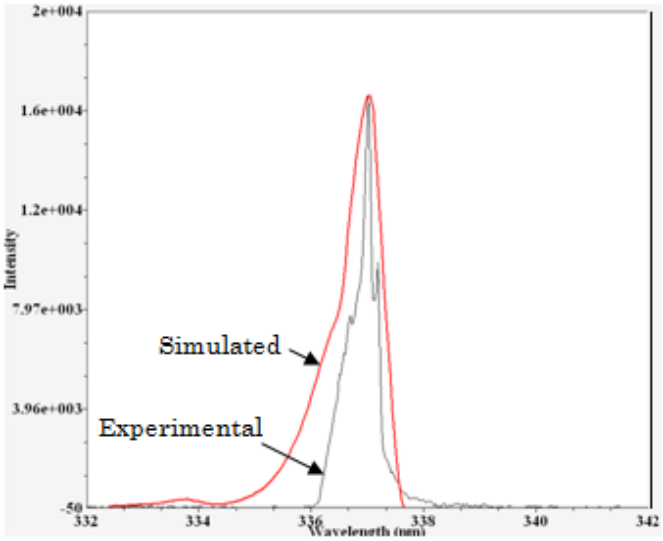

Fig. 14. Measured and simulated optical emission spectra of the nitrogen 2nd positive band system.

Table 5 shows calculated temperatures. Estimated rotational temperature and vibrational temperature show that microplasma could be one of non-thermal plasma[19].

Table 5. Estimated temperatures of microplasma in pure nitrogen at atmospheric pressure.

Temperature	Value (k)
Electron temperature	8200
Rotational temperature	360
Vibrational temperature	3100

CONCLUSION

The analysis of emission spectrum of the microplasma in NO/N_2 mixture was performed.

1) Marx generator as a pulsed power supply was generated a negative pulse. The voltage was -1.6kV peak, rise time 80ns, 530ns width. Discharge current was -4.6A peak, and it was observed within 100ns.
2) Ozone generation by Marx generator was 51 ppm at 8 kHz. Marx generator was more efficient as a result of comparing the neon transformer from the point of the discharge power. Generated NO_X values were lower when the Marx Generator was used. The maximal values of 10 ppm for neon transformer and 5 ppm for Marx Generator were obtained at 1.1 kV and 1.7 kV, 16 kHz respectively.
3) This negative pulse was applied to microplasma electrode. Emission spectrum from microplasma was observed by ICCD camera and spectrometer. N_2 second positive band peaks (337.1nm, 315nm, 357.7nm, 375.5nm) and NO-γ band peaks (247.9nm, 257.6nm) were observed. Also N_2 first negative band peak was confirmed at 427.8nm.
4) N_2 second positive band appeared 50 ns. Because of N_2 second positive band emitted by electron collisions. NO-γ band peaks appeared 2 μs. NO-γ band originated from the following the collisions of the N_2 metastable state.
5) By comparing the measured spectrum to the simulated spectrum of the nitrogen 2nd positive band system, it could be possible to estimate the rotational and vibrational temperatures. Estimated rotational temperature (360 K) and vibrational temperature (3100 K) show that microplasma could be one of non-thermal plasma.

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He has been part of the research team which examines the application and fundamental aspects of microplasma for environmental protection and microplasma generation by pulsed power. Currently is with Ricoh Co., Japan.

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Marius Blajan (Non-member) was born in Cluj-Napoca, Romania, in 1974. He received his B. S. and M. S. degrees in electrical engineering from Technical University of Cluj-Napoca in 1997 and 2000 respectively and the Ph. D. degree in electrical engineering jointly from Technical University of Cluj-Napoca, Romania, and University of Poitiers, France, in 2006.

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