Properties of atmospheric pressure plasmas with microwave excitations for plasma processing

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Atmospheric pressure plasmas with microwave excitations were successfully produced in dielectric barrier micro plasmas employing N_2, Ar, or He gas. N_2 optical emissions of the second positive system were measured for evaluating the gas temperature. The gas temperatures of the plasmas could be much less than 1000 K. Blackbody emissions were measured by Fourier transform infrared spectrometer for evaluating the electrode temperature. Temperatures of both the gas and electrode were evaluated by fitting the experimental results with calculations. The gas temperature in the N_2 plasma was notably increased with the discharge time as compared with those in Ar and He plasmas. It was found that the pulsed discharge and the water-cooled electrode were effective for reducing the gas temperature. The pulsed discharge decreased the gas temperature from 900 to 600 K, and the water-cooled electrode decreased the gas temperature by more than 200 K. Controlling the temperature of the electrodes was the most effective technique to reduce the gas temperature, because the gas temperature was in equilibrium with the electrode temperature. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1851539]

I. INTRODUCTION

Plasma processing is a most attractive industrial technology because an etching, deposition, or synthesis processing of materials is able to be performed at a low temperature. Recently, the industrial demand has focused on not only the synthesis of functional materials, but also high-speed plasma processing. So far, plasma processing has been performed by using low-pressure and high-density plasmas, such as capacitively coupled plasma, inductively coupled plasma, surface-wave excited plasma, and so on. In these processes, the vacuum operation is viewed as a necessary requirement. Atmospheric pressure plasmas can have a useful advantage over conventional low pressure plasmas, because they can be used without the need for a vacuum system. Therefore, the use of atmospheric pressure plasmas will greatly expand the application not only in conventional, but also in new industrial fields.

Recently, various kinds of atmospheric pressure plasma sources such as a dc excitation[1–4] and high frequency (kHz–MHz)[5–9] have been developed. Kono *et al.* reported a generation of a high-density nonequilibrium plasma at an atmospheric pressure using a microwave excitation.[10] To realize the high-density atmospheric pressure plasma with a low gas temperature, the applications of atmospheric pressure plasma spread further. Recently, we developed the nonequilibrium atmospheric pressure plasma with microwave excitations for the abatement of perfluorinated compound (PFC) gases, where the PFC gases were polymerized to the particles in the gas phase. In the atmospheric pressure, the dissociation and the subsequent three body reactions could occur more often than in a low pressure. Realization of high-density plasmas with a low gas temperature enables us not only to dissociate PFCs but also to polymerize them without gas emissions.

In this article, we have developed atmospheric pressure microdischarges using dielectric-barrier electrodes with microwave excitations. The plasma enables us to generate the stable atmospheric plasmas employing N_2, Ar, and He gases. The temperature of both the gas and electrode was measured by fitting the experimental results with the calculation of the N_2 optical emission and blackbody emission, respectively. It was found that the pulsed discharge and the water-cooled electrode were effective for reducing the gas temperature. In particular, controlling the electrode temperature was one of the most important techniques to reduce the gas temperature. This is because the gas temperature was almost in equilibrium with the electrode temperature.

II. EXPERIMENT

Figure 1 shows a schematic diagram of an atmospheric pressure microdischarge system using dielectric-barrier electrodes with microwave excitations. The microwave (2.45 GHz) was converted to a coaxial mode through a rectangular-coaxial transducer, and then propagated along a water-cooled coaxial line to a ring microgap electrode, that was coated by dielectric materials. Aluminum oxide (Al_2O_3) was used as a dielectric material. The gap distance between the outer and inner electrodes was 0.1 mm (16 mm in diameter). The ring plasma was generated between the two electrodes. The gases (N_2, Ar, or He) were introduced into the gap from the upper side of the electrode and then dissociated in the microplasma generated between the electrodes. The quartz or KBr window was set in the bottom of the chamber in order to collect UV and IR radiations, respectively. To minimize impurities in the discharge, the processes chamber

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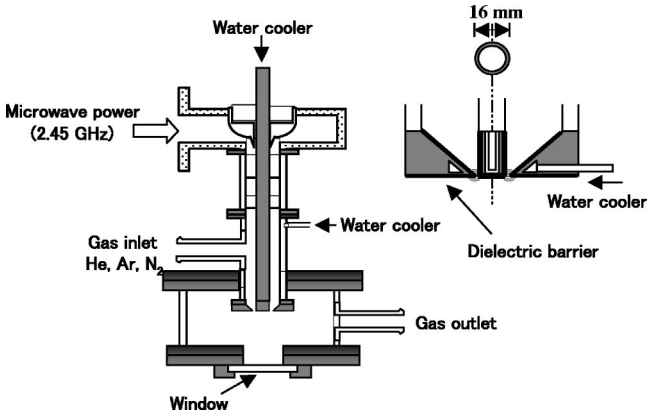

FIG. 1. Atmospheric pressure microdischarge system using dielectric-barrier electrodes with microwave excitations.

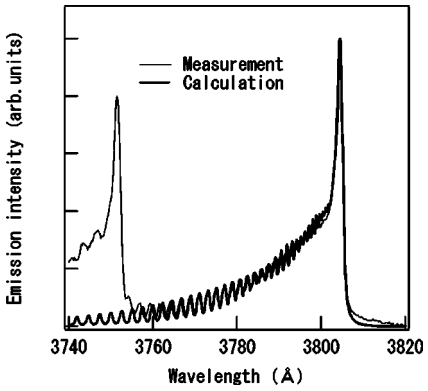

FIG. 3. Typical example of the emission intensity and the calculated intensity of the N_2 second positive system.

was evacuated by a rotary pump before injections of gases. Although uniform plasmas in the atmosphere were successfully produced along the slit of metals,[10] unless He gas was used we were not able to produce uniform plasmas along the coaxial gap of metals. In this study, we have developed the atmospheric pressure microplasma using the electrodes of dielectrics. The plasma enabled us to generate uniform atmospheric pressure plasmas with even N_2 and Ar gases. It was reported that memory effects based on electrons contribute to a dielectric-barrier glow discharge.[7] Therefore, it is considered that the electrode of dielectrics used in the microplasma led to stored charges as compared with the metal electrode and so produced the uniform plasmas along the electrodes, even in the N_2 plasma.

Figure 2 shows the He and Ar atmospheric pressure plasma. In the case of the N_2 plasma, the discharge was produced along the ring electrode at a diameter of 16 mm. However, much of the Ar discharge was produced over the electrode gap and along the dielectric surface. The electron density of the Ar discharge became larger than the N_2 discharge because the Ar gas had a large dissociation cross section and threshold energy, as compared with the N_2 gas. The high electron density in the Ar plasma caused the discharge areas to expand over the electrode gap.

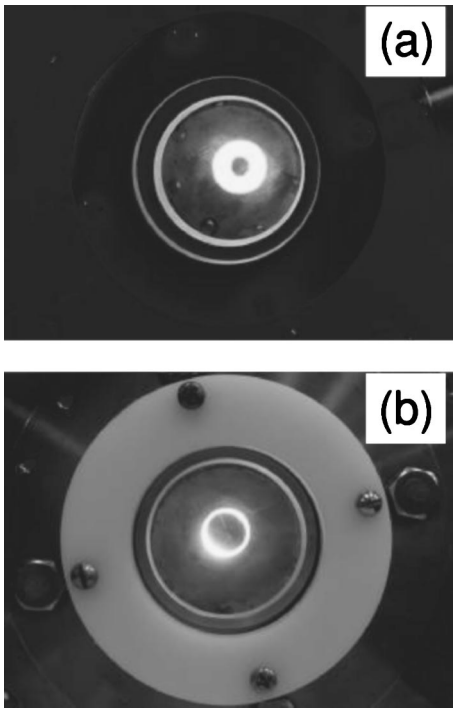

FIG. 2. Pictures of (a) N_2 and (b) Ar atmospheric pressure plasmas.

Optical emission spectroscopy measurements were performed using an Intensified charge-coupled device (ICCD) spectrometer (model PI-MAX1300RB-25-FG, focal length 750 mm, grating 1200 lines/mm, Rober). At a high pressure, a rotational temperature tends to equilibrate with a kinetic temperature due to abundant collisions between neutral and excited molecules. The rotational temperature of the N_2 molecule was used to determine the kinetics of gas temperature. The rotational temperature was evaluated by measuring the emission on the (0–2) band in the N_2 second positive system ($C\,^3\Pi_u$–$B\,^3\Pi_g$). The ICCD detector was used to carry out the time evolution of the rotational temperature by μsec order.

The rotational temperatures were determined by comparing results between an experimental and a theoretical spectrum on the (0–2) band of the N_2 second positive system ($C\,^3\Pi_u$–$B\,^3\Pi_g$). The calculation was carried out by the determination of the transition wavelengths and the line strengths of the rotational levels, which are the component in terms of three quantum numbers (J', J'', and Ω) where J', J'', and Ω represent the rotational quantum number of the upper level, quantum number of the lower level, and the multiplicity, respectively. The rotational constant used was found as a reference.[11] In this study, Honl–London factors were used as the intensity distribution and Hund's case (a) was assumed. Each rotational line was represented by an expression of the instrumental line shape.[12]

A small amount of N_2 (0.05%) was added to Ar and He gases in order to evaluate the gas temperature in Ar and He plasma. The N_2 addition technique to evaluate the gas temperature in the N_2 noncontamination plasma was reported elsewhere.[13,14] Figure 3 shows the typical example of the emission intensity and the calculated intensity of the N_2 sec-

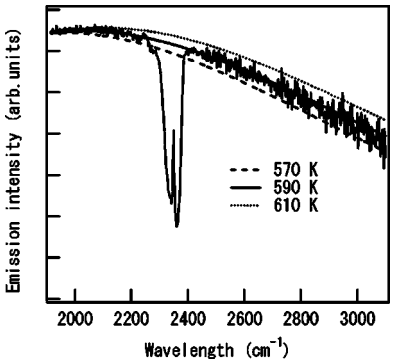

FIG. 4. Comparison of a measurement spectrum and blackbody emission spectra for temperatures 570, 590, and 610 K.

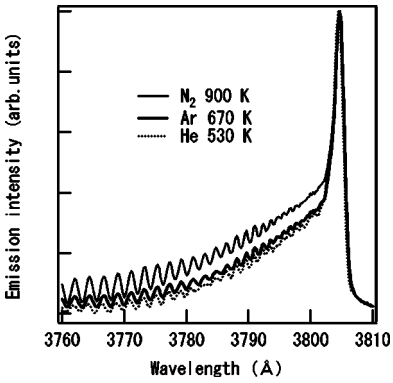

FIG. 5. Comparison of spectra in cw N_2, Ar, and He atmospheric plasma.

ond positive system. The rotational temperature was evaluated by fitting the measured spectrum with a numerical calculated one and the temperature was 800 K. The emission peak at 375.54 nm was derived from the (1–3) band of the N_2 second positive system.

In order to measure the temperature of the electrode, Fourier transform infrared spectroscopy (FTIR) measurements were performed. IR radiations from the electrode at which the plasma were generated were collected through the ZnSe lens and passed into a Michelson interferometer and detected with an infrared detector. The spectrum was corrected for the dependence of the sensitivity of the instrumental detection on wavelength. The continuing radiation can be modeled by using the emission from a blackbody. The energy density per unit volume, ρ, emitted from a blackbody at a temperature, T, as a function of wavelength, λ can be expressed as[15]

$$\rho \propto \frac{8\pi hc}{\lambda^5}\frac{1}{\exp(ch/k_B\lambda T)-1}.$$

Blackbody emission spectra at various temperatures were calculated and the measurement spectra emitted from the electrode were fitted by the calculated blackbody emission spectra. Figure 4 shows the measurement spectrum and blackbody emission spectra for temperatures of 570, 590, and 610 K. For comparison, the blackbody intensity was normalized to the measurement spectrum at the short wave number of the spectrum. The large absorption at 2350 cm^{-1} was due to CO_2 in the atmosphere. The electrode temperature was evaluated to be 590 ± 10 K.

III. RESULTS AND DISCUSSIONS

A. Measurement of gas temperature at cw and pulsed discharge in N_2, Ar, and He atmospheric pressure plasmas with microwave excitations

The atmospheric pressure plasmas with microwave excitations were successfully generated in N_2, Ar, or He gas using the dielectric barrier microplasma. Figure 5 shows the comparison of spectra in N_2, Ar, and He atmospheric plasmas on the condition at a microwave power of 200 W, a pressure of 1 atm, and a gas flow rate of 2000 sccm. The spectra in He and Ar plasmas including 0.05% N_2 gas mixed those of pure He and Ar plasmas. The gas temperature was 900, 670, and 530 K for N_2, Ar, and He gases, respectively. It was reported that the electron temperature was 1.3 eV in the microwave-excited microdischarge in the atmosphere.[10] The gas temperature was much lower than the electron temperature, so that nonequilibrium plasmas were produced with a dielectric barrier microdischarge with microwave excitation employing all of the N_2, Ar, and He gases.

The wiggles in the spectra are due to the band structures by the triplet splitting of the *P*, *Q*, and *R* branches. In particular, the wiggles in the short wavelength are due to high rotational levels *J*, where the relative positions of the components become wider than those in low rotational levels. Therefore, the wiggles could obviously be seen in the region of the short wavelength. The distribution of the intensities depends on the rotational temperatures. The relative intensities in the short wavelength with a bandhead of 380.5 nm increased with increasing rotational temperatures.

Figure 6 shows the time evolution of rotational temperatures in N_2, Ar, and He atmospheric pressure plasmas in the condition of a microwave peak power of 300 W, a pressure of 1 atm, and a gas flow rate of 2000 sccm. The plasma was modulated at 50 μm s on, and 50 μm s off. The rotational temperature in N_2 plasma was increased abruptly from 740 to 1250 K. In the case of the Ar and He plasma, the temperatures were increased by about 100 K. At the high pressure,

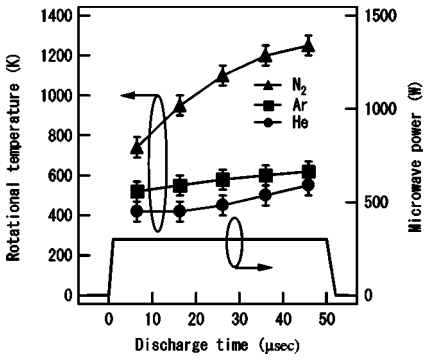

FIG. 6. Time evolution of rotational temperatures in N_2, Ar, and He atmospheric plasma.

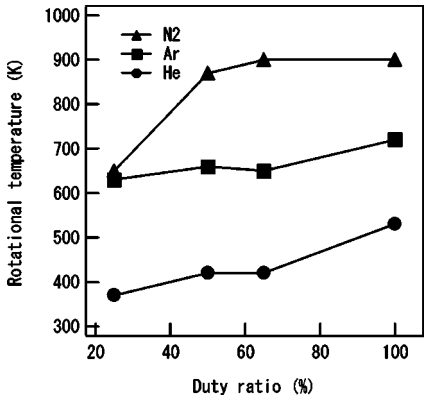

FIG. 7. Rotational temperatures in N_2, Ar, and He atmospheric pressure plasmas as a function of the duty ratio of microwave pulse power.

the gas was usually heated due to the collisional momentum transfer between the electrons and the neutrals.[16] Average energy heated by the elastic collision between a molecule and an electron was calculated to be 5.1×10^{-5}, 3.6×10^{-5}, and 3.6×10^{-4} eV for N_2, Ar, and He molecules, respectively, using the electron temperature of 1.3 eV. The N_2 molecule was heated not only by the elastic collision, but also by the vibrational and rotational excitations with electrons, as compared with Ar and He. The energy heated due to vibrational and rotational excitations can be much larger than the energy calculated by the elastic collision. So, the rotational temperature in N_2 plasma might be increased rapidly, as compared with temperatures in Ar and He plasma. It is considered that the gas temperatures in Ar and He plasmas were effectively cooled by losing a kinetic energy with the diffusion to the electrode and/or out of the plasma region. The pulsed discharge reduced the gas temperature efficiently in the N_2 plasma.

Figure 7 shows the rotational temperature in N_2, Ar, and He atmospheric pressure plasma as a function of the duty ratio of the microwave power in the condition of an average power of 200 W, a pressure of 1 atm, and a gas flow rate of 2000 sccm. As the duty ratio was decreased from 100%, that is a continuous wave, to 25%, the gas temperature in the N_2 plasma was decreased dominantly from 900 to 600 K, as compared with temperatures in Ar and He plasma. These results indicate that the short pulsed modulation of microwave power was effective for reducing the gas temperature in N_2 plasma.

B. Influence of the electrode temperature on the gas temperature

The gas temperature is a very important plasma parameter for controlling processes of the atmospheric pressure plasma. At the high pressures, the plasma tends to be in a thermal equilibrium due to frequent collisions between electrons and gas molecules. The excess high gas temperature causes the evaporation of electrodes for producing the plasma and the melting of materials irradiated by the plasma. The technique of generating nonequilibrium plasmas at the atmospheric pressure is a key factor for the application of atmospheric

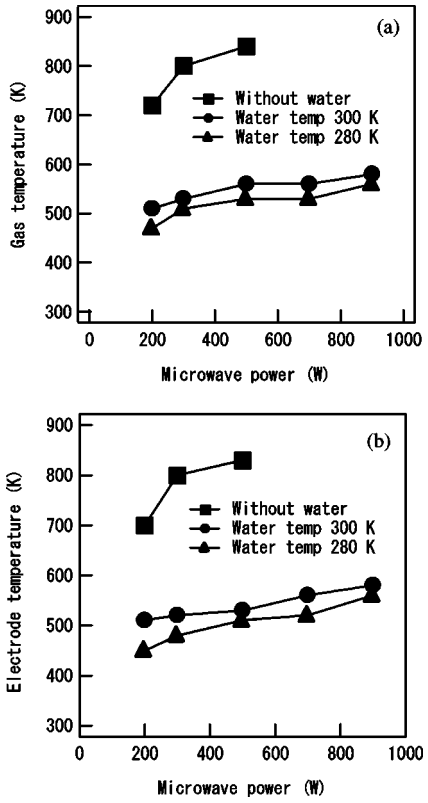

FIG. 8. Gas temperature and electrode temperature as a function of the microwave power on the condition of a different water-cooled temperature.

pressure plasma to the material processes. One of the mechanisms for generating the nonequilibrium plasma is that an energy for a gas heated by an elastic collision with electrons was lost at once by a collision with a cold electrode.[10] Therefore, the gas temperature could be in equilibrium with the electrode temperature. Controlling the electrode temperatures heated by the plasma could be a key parameter to reduce the gas temperature.

We have investigated the influence of the electrode temperature on the gas temperature at the atmospheric pressure plasma. The experiment was carried out in the condition of a He 1 atm without gas flow. Figure 8 shows the gas temperature and the electrode temperature as a function of the microwave power on the condition of a different water-cooled temperature. The plasma was not successfully generated between electrodes at microwave powers over 500 W without water cooling. Al_2O_3 seemed not to disintegrate even with noncooled electrodes. The high gas temperature at microwave powers over 500 W might lead to reduced gas density among the electrodes in the condition without flowing. It was found that the electrode temperature was almost in equilibrium with the gas temperature, as shown in Figs. 8(a) and 8(b). The result indicates that the collisions between the gas and the cold electrode were a very important factor for producing the nonequilibrium plasma. The gas temperature was decreased below 200 K by cooling the electrode by water flow. The water-cooled electrodes reduced the gas temperature efficiency as well as the short pulse modulation of mi-

crowave power as shown in Fig. 7. FTIR is very useful for measuring the electrode temperature very accurately and giving us important information for controlling the electrode temperature heated by plasma. The effective cooling of the electrode heated by plasmas was very useful for reducing the gas temperature at the almost atmospheric pressure plasma, where the kinetic energy was lost in the collisions with the electrode because the gas temperature tends to be in equilibrium with the electrode temperature.

IV. CONCLUSION

The atmospheric pressure plasmas with microwave excitations were successfully generated in N_2, Ar, or He gas using dielectric barrier microplasma. We demonstrated controlling the gas temperature by the pulsed modulations and cooled electrodes. The gas temperature in N_2 plasma was notably increased with the discharge time, as compared with temperatures in Ar and He plasmas. The pulsed discharge decreased the gas temperature from 900 to 600 K. The water-cooled electrode decreased more than 200 K. The evaluation of the electrode temperature enabled us to give important information for efficiency making the gas temperature low, because the gas temperature tends to be in equilibrium with the electrodes temperature.

ACKNOWLEDGMENT

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