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Experimental Study of Temperatures of Atmospheric-Pressure Nonequilibrium Ar/N_2 Plasma Jets and Poly(ethylene terephtalate)-Surface Processing

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To understand the mechanism of surface processing using atmospheric-pressure nonequilibrium plasma jets, we measured the vibrational and rotational temperatures in the plasmas by optical emission spectroscopy. Plasma was excited using a high-frequency pulsed power supply, using a gas mixture of Ar (20 L/min) and N_2 (0.1 to 0.5 L/min) as the plasma gas, and changing the flow rate of N_2 gas at an input power of 100 W and plasma frequencies of 5 and 10 kHz. The measured vibrational and rotational temperatures in plasma were approximately 0.18 to 0.26 eV and 0.21 to 0.28 eV, respectively. We also carried out a plasma surface processing of polyethylene terephtalate film to measure the changes in water contact angle before and after the processing. We found a monotonic decrease in the contact angle of the processed poly(ethylene terephtalate) (PET) film as plasma rotational temperature increased. It is concluded that the hydrophilicity of the PET surface increases with plasma rotational temperature. [DOI: 10.1143/JJAP.46.795]

KEYWORDS: atmospheric-pressure nonequilibrium plasma, Ar/N_2 gas mixture discharge, optical emission spectroscopy, rotational temperature, vibrational temperature, PET film contact angle

1. Introduction

Concerning surface processing technology using atmospheric-pressure nonequilibrium plasma, several drawbacks have been discussed regarding the mechanisms by which we generate atmospheric non-equilibrium plasmas. At the same time, many practical and industrial examples have been reported in which this technology has been applied to various processes, such as the surface modification of polymer materials or the surface cleaning of semiconductor materials, because we can easily generate plasma under atmospheric pressure at a low cost.[1–4)]

Plasma gas temperature, and the densities of vibrationally excited states and radical species are important factors for surface-processing technologys. Therefore, to establish the optimal conditions of plasma for surface-processing, it is essential to obtain plasma parameters, such as the densities of vibrational levels and radical species, or the vibrational and rotational temperatures of plasma.[5)] The gas temperature of atmospheric-pressure nonequilibrium plasma, however, is much lower than the electron temperature of such plasma. The difference between the gas temperature and the electron temperature makes it difficult to understand some plasma parameters such as electron temperature, electron density, or density of radical species in plasma. For this reason, there is a need for a method of measuring these parameters easily.

We can estimate the relative density of vibrationally excited levels by optical emission spectroscopy (OES), from which we can determine vibrational temperature under the assumptions that vibrational levels are in the Boltzmann distribution. As for plasma with high collision frequencies such as atmospheric-pressure plasma, it is assumed that the rotational temperature gives an approximate of the gas translational temperature[5)] of neutral particles due to collisional relaxation.

In this study, we fabricated an atmospheric-pressure plasma jet apparatus and measured vibrational and rotational temperatures as basic properties of plasma to understand the surface processing mechanisms of various materials using an atmospheric-pressure plasma jet excited by a high-frequency pulsed power supply.[6)] Accurate measurements of the properties of atmospheric-pressure plasma of this type, for example, vibrational and rotational temperatures, have not been performed to date. For example, Somekawa *et al.* reported only the observation of this type of plasma jet with a high-speed camera; they did not report the spectroscopic characteristics of the plasma.[6)] Therefore, we decided to measure the vibrational and rotational temperatures of such plasma by optical emission spectroscopy to understand its characteristics. This is one of the most important objectives of this study. The second objective of the present study is to examine the changes in material surface characteristics before and after the plasma treatment using the plasma source described above. Although various studies have been reported with respect to such characteristic variation, most of them are mainly limited to the examinations of the correlations between surface characteristics and substrate temperature. In this study, we would like to examine the correlations between the changes in materials and those in plasma characteristics from the fundamental viewpoint of plasma surface treatment.

2. Experimental Procedure

Figure 1 shows a schematic diagram of the present experimental setup of the atmospheric-pressure plasma jet apparatus (Haiden Laboratory, PJ-6K). We used a high-frequency pulsed power supply at a pulse frequency of 10 kHz and an input power of 100 W. For the plasma gas, we used a gas mixture of Ar and N_2, keeping the flow rate of Ar constant (20 L/min) and changing that of N_2 appropriately.

The plasma torch consisted of a titanium rod (OD: 4 mm, length: 10 mm) at the center and an SUS pipe (OD: 36 mm,

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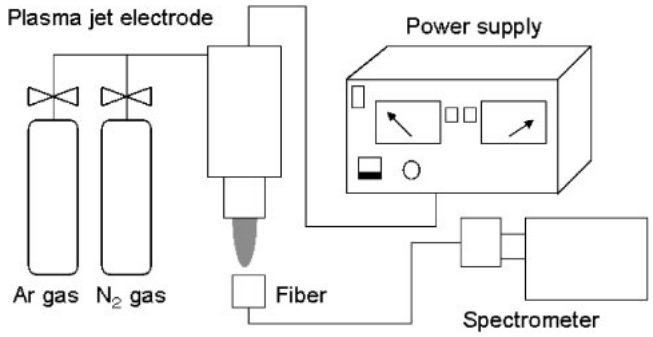

Fig. 1. Schematic of experimental setup.

ID: 30 mm, length: 87 mm) surrounding the rod. In the upper part of the torch, a quartz tube (OD: 26 mm, ID: 24 mm, length: 87 mm) was placed between the titanium rod and the SUS pipe, generating dielectric barrier discharges to produce reactive species. The ID and length of the plasma torch nozzle were 10 and 20 mm, respectively. In the lower part of the torch where no dielectrics were introduced, arc discharges were generated. By using the electromagnetic pumping effect, the reactive species generated in the upper part of the torch were effectively emitted from the nozzle.

In OES, we used a monochromator (Horiba, HR320) with an optical fiber as a light guide from the plasma. The slit width of the monochromator was set at 125 μm at the entrance port and to 175 μm at the exit port. The slit height was set at 100 μm at both the entrance port and the exit port. The wavelength resolution was 0.1 nm. A photomultiplier was used as a detector. OES was conducted using a monochromator with a scanning mechanism, after plasma was generated stationarily under stable conditions. The optical fiber head was placed 35 mm in the axial direction from the plasma jet nozzle, and a quartz plate was set between the fiber head and the torch nozzle to avoid thermal damage. Figure 2 shows an example of the emission spectra when the plasma gas was a mixture of argon (20 L/min) and nitrogen (0.5 L/min) in the wavelength range of 300–900 nm. We could obtain an emission spectrum of a second positive system due to the transition from the C $^3\Pi_u$ state to

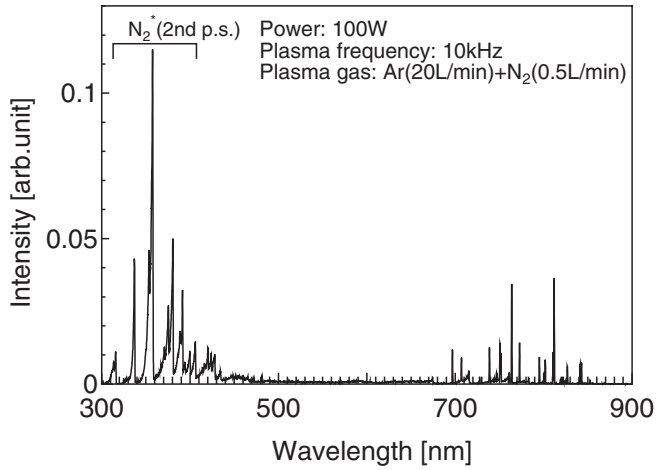

Fig. 2. The emission spectrum at 300–900 nm of Ar (20 L/min) + N_2 (0.5 L/min) in metastable state at 100 W and 10 kHz.

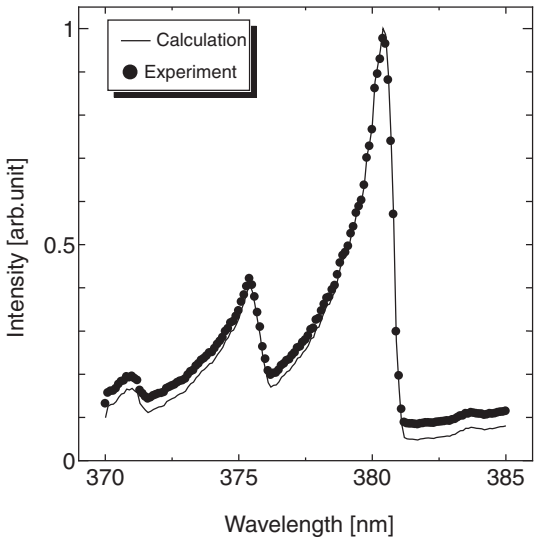

Fig. 3. Example of comparison between that spectrum of N_2 second positive system calculated theoretically and measured experimentally.

the B $^3\Pi_g$ state with sufficient intensity. To determine the state of vibrational kinetics in nitrogen and understand vibrational temperature, we measured the relative population density of the vibrational excited states of N_2 C $^3\Pi_u$ with a vibrational quantum number $v = 0-4$ by spectroscopy examination. The gas translational temperature of nitrogen plasma can be well approximated from the rotational temperature of a nitrogen molecule under atmospheric-pressure discharge.[7] We determine rotational temperature from the observed spectrum of the second positive system. Rotational temperature is obtained from a comparison of the second positive spectra observed experimentally with the calculated ones.[8] As described in ref. 9 in detail, vibrational and rotational temperatures can be obtained by calibrating the sensitivity of the spectra, fitting them by theoretical calculation using vibrational and rotational temperatures as parameters, and applying them as best-fit parameters. Figure 3 shows an example of the comparison. The gas temperature of plasma can be approximated from the rotational temperature. Let us discuss the effect of some broadening mechanism. Doppler broadening level can be estimated from the ratio of the thermal velocity v_{th} to the light velocity c using

$$\frac{\Delta\lambda_D}{\lambda} = \frac{v_{th}}{c}, \tag{1}$$

where $\Delta\lambda_D$ is the Doppler width. Equation (1) leads to a Doppler broadening level of about $10^{-6}\lambda$, which is much smaller than the instrumental resolution. We may have to consider a Doppler blue shift because we measure the properties of the plasma from the downstream direction. However, the effect of the Doppler blue shift is also imperceptible, because the flow velocity of the present plasma jet is much smaller than the sound velocity, and consequently, it is also negligible.

Meanwhile, the pressure broadening level $\Delta\lambda_P$ is estimated using the following equation since neutral–neutral collision is the predominant process for the excited nitrogen molecule under the present conditions.

$$\frac{\Delta\lambda_P}{\lambda} = \frac{\nu_{col}}{\nu} = \frac{N\sigma v_{th}}{\nu}, \quad (2)$$

Here N is the number density of neutral molecules, σ is the neutral–neutral collision cross sectional area, and ν is the frequency of emitted light. Equation (2) shows that $\Delta\lambda_P$ becomes about $10^{-7}\lambda$, which is also much smaller than the present experimental resolution. Thus, the spectral resolution of the present detection system is determined from the equipment's width, and estimated to be about 0.1 nm. In this way, we can fit the emission spectrum of the second positive system obtained experimentally by a theoretical calculation with sufficient accuracy.

To examine the changes in the surface characteristics before and after the plasma treatment, we measured the dampness of the surface of a poly(ethylene terephtalate) (PET) film (Teijin Dupont Films, Q51) after plasma processing. The PET film specimen was $10 \times 10\,mm^2$ in area and 51 μm in thickness. The PET film was exposed to plasma at 35 mm from on electrode for 5 s. Dampness analysis was conducted 24 h after the plasma surface processing. We measured contact angle by dropping 3.4 mg of water onto what using a contact-angle meter (Kyowa Interface Science, Type CA-D).

3. Results and Discussion

Figure 4 shows relationship between the temperature and the flow rate of N_2, keeping the flow rate of Ar constant (20 L/min) and that of N_2 in the range from 0.1 to 0.5 L/min, in which the input power was 100 W, and the pulse frequencies were 5 and 10 kHz. The function of the light-receiving devices almost determines the accuracy of the measured rotational temperature. By making the correlation coefficient maximum in the fitting procedure, we can maintain the error in the vibrational and rotation temperatures to be less than ±0.001 eV. This figure shows that vibrational and rotational temperatures increase as the flow rate of nitrogen increases. In addition, it is found that these temperatures increase as pulse frequency increases.

The reason for these phenomena can be considered as follows: the increase in the flow rate of nitrogen gas leads to an increase in the nitrogen molecule density in the discharge region. This increases the collision frequency between electrons and neutrals, and, as a result, more vibrationally excited states are generated. Then, collisional relaxation becomes more frequent between vibrationally excited states, that is, the VV energy transfer,[9] which finally leads to an increase in vibrational temperature. Vibrational energy is eventually converted to rotational or translational motion energy also due to collisions (e.g., VT relaxation[10]), and results in an increase in rotational or translational temperature.

We measured the vibrational and a rotational temperatures of atmospheric plasma jets with an input power of 100 W and a plasma frequency of 5 kHz. We found that the vibrational and rotational temperatures were 0.18–0.24 and 0.2–0.26 eV, respectively. When the plasma frequency was 10 kHz, the vibrational and rotational temperatures became approximately 0.2 to 0.26 eV and 0.23 to 0.28 eV, respectively.

Figure 5 shows the relationship between the rotational temperature and the water contact angle of a PET film processed using plasma, when a mixture of Ar and N_2 was used as the plasma, keeping the flow rate of Ar constant (20 L/min) and that of N_2 in the range from 0.1 to 0.5 L/min, in which the input power was 100 W and the pulse frequencies were 5 and 10 kHz. The PET film was exposed to plasma at 35 mm from the electrode for 5 s. The contact angle of an unprocessed PET film was 70°. As previously mentioned, the instrument function of light-receiving devices do not have a significant effect on the measurement of temperature. When the pulse frequency was 5 kHz and the rotational temperature was in the range from 0.21 to 0.26 eV, hydrophilicity improved, so that the contact angle decreased to 34–45°. Similarly, when the plasma frequency was 10 kHz and the rotational temperature was in the range from 0.23 to 0.28 eV, hydrophilicity improved so that the contact angle decreased to 31–43°. We can obviously verify

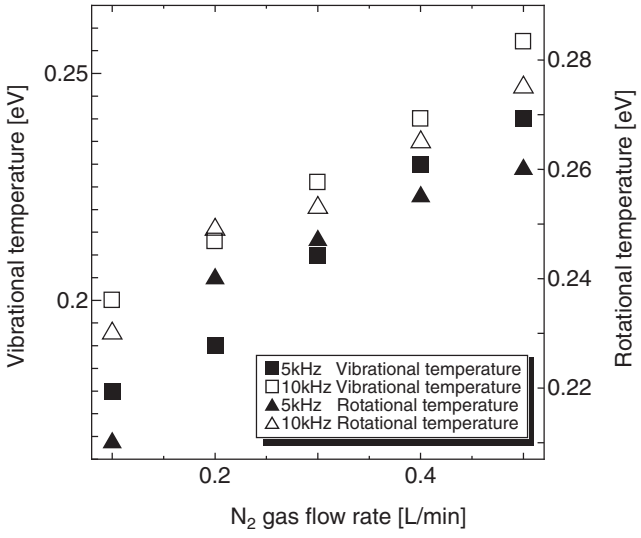

Fig. 4. Relationships of nitrogen gas flow rate with vibrational and rotational temperatures in atmospheric-pressure argon and nitrogen plasma measured by optical emission spectroscopy.

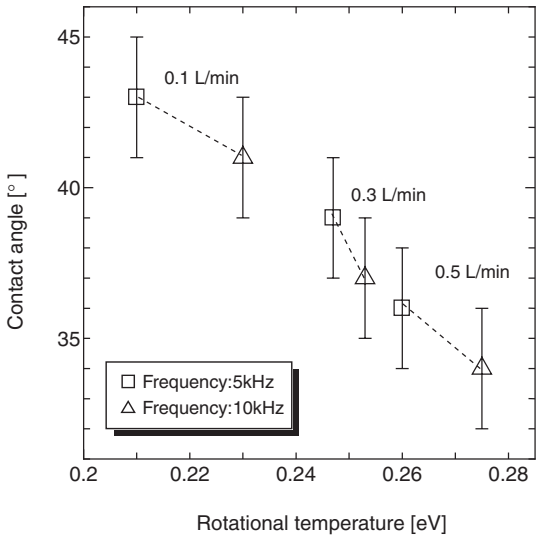

Fig. 5. Water contact angle of PET film plotted against rotational temperature of atmospheric-pressure argon and nitrogen plasma.

that an increase in rotational temperature results in an improvement of the contact angle of a PET film. Taking the rotational temperature as an approximate of the gas temperature, it can be considered that atmospheric-pressure plasmas of 0.21 to 0.28 eV (2400 to 3200 K) is to be irradiated. We found a monotonic decrease in the contact angle of the processed PET film as plasma rotational temperature increased. It is concluded that the hydrophilicity of a PET surface is further improved as plasma rotational temperature increases.

4. Conclusions

To examine the characteristics of atmospheric-pressure plasma jets excited by a high-frequency pulsed power supply, we experimentally measured the vibrational and rotational temperatures in plasma. We confirmed that the vibrational and rotational temperatures in plasma increase as plasma frequency and the flow rate of nitrogen gas increase. In addition, we found that vibrational and rotational temperatures in plasma of atmospheric-pressure plasma jets are 0.21 to 0.28 eV.

When the plasma frequency was 5 or 10 kHz and the rotational temperature was in the range of 0.21 to 0.28 eV, the hydrophilicity of the PET film used improved so that the contact angle decreased to 31–45°.

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