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Quantitative evaluation of the densities of active species of N_2 in the afterglow of Ar-embedded N_2 RF plasma

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The N_2 and Ar-20%N_2 RF plasmas and afterglows have been generated in a quartz tube under a flowing condition maintained at 6–8 Torr and a flow rate of 0.5–0.6 slm. The detailed emission characteristics of active species have been analyzed by emission spectroscopy. Under such conditions, the plasma rotational temperature increases from 400 to 800 K with increasing RF powers from 50 to 130 W, while the characteristic vibrational temperature remains at about 10^4 K. The densities of active species (N, N_2(A), N_2(X, v > 13) and N_2^+) in the afterglow are measured to be in the order of ~10^{15}, ~10^{11}, ~10^{14} and ~10^{10} cm^{-3}, respectively. In addition, the following characteristics of the afterglows are noted: First, the same densities of the active species can be obtained at lower RF powers (20–50 W) for Ar-20%N_2 than for pure N_2 which requires higher RF powers (50–100 W). Second, the ionization degree of N_2^+/N_2 in the plasma increases readily to a saturation value at a lower RF power of 50 W for Ar-20%N_2, whereas in the afterglow, the absolute density of N_2^+ is further reduced below 10^9 cm^{-3}.

1. Introduction

N_2 is an abundant, but inert molecule that does not react easily under ambient conditions. However, the reactions involving N species can be facilitated by employing excited or dissociated species of N_2 as in the plasmas of N_2 or N_2 mixtures as well as in their afterglows [1–4]. Application of such reactions involving atomic N or excited N_2 species can be useful in NO_x or O_3 removal from atmosphere [5], surface nitridation or nitrogen doping at lower temperatures [1,6,7] and plasma sterilization [8]. Previously, it has been demonstrated that dominant active species of N-atoms in the afterglows produced by N_2 microwave plasmas can be successfully used for sterilization [4,9].

Various excited states of N_2, N_2^+ and atomic N species are formed in N_2 plasmas and in the afterglows. Their lifetime can be as long as 2 s especially for the case of N_2(A) which can play a significant role in a subsequent reaction due to the high threshold energy of ~6.2 eV [10]. In addition, such a flowing condition can provide a chance of controlling the densities of the excited states of N_2 in the afterglow in a way that neutral active species such as N-atoms, N_2(X,v > 13) and N_2(A) metastable molecules are enriched over N_2^+ ions [11–13]. The controlled densities of active N_2 (or N) species in the afterglows can be potentially useful for a damage-free surface treatment.

Characterization of such excited states of N_2 can be readily performed by employing optical emission spectroscopy [14–16] due to a high sensitivity of the technique to radiative emission of N_2(B,C) and N_2^+(B) states produced by such excited species [10,17,18]. In addition, the measurement technique is relatively simple and can be directly applied for the diagnostics of various discharge conditions, where complicated excitation and de-excitation processes are balanced to produce steady-state equilibrium concentrations of different active species. This complexity may impose the interpretation difficult [19], but the control of the discharge condition [2,11,18,20] and the development of kinetic models [21–23] allow us to better characterize the plasma. For the determination of electron density and temperature in the plasma, line-ratio methods are frequently employed [24]. The line-ratio method is developed in the N_2 afterglows where radiative species are produced by kinetic reactions between metastable and ion species without electron collisions [12].

In this study, the N_2 and Ar–N_2 RF flowing plasmas and their afterglows are systematically characterized by optical emission spectroscopy. The densities of various excited states of N_2 can have

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a profound effect on the detailed characteristics of surface plasma treatments when it is used in such an application. High ratio of N_2^+/N_2 in the Ar–N_2 plasma is expected due to additional collisions between Ar^+ and N_2 in addition to electron collisions. This may lead to higher densities of excited N_2 species in the afterglow at lower RF powers when Ar is mixed with N_2. Here, the mixture of Ar-20%N_2 is chosen due to a detection limitation of N_2 exited states and is compared with pure N_2 as the RF power is varied. By employing well-established techniques [25], the N_2 rotational and vibrational temperatures and the N_2^+/N_2 intensity ratios are determined for the N_2 and Ar–N_2 RF plasmas generated with RF power of 20–130 W. At a flow rate of 0.5–0.6 slm and pressure of 6–8 Torr, well-defined afterglows are formed downstream; this allows a quantitative determination of the active species of N, $N_2(X,v > 13)$, $N_2(A)$ and N_2^+ in the early and late afterglows by the line-ratio method after calibration by NO titration.

The NO titration of N-atoms density involves two steps:

Step 1: Introducing NO (using an Ar-1.5%NO gas mixture) in the afterglow at a flow rate (Q(NO)) less than that of N (Q(N)) coming from the N_2 plasma, produces a violet emission by the following reactions:

$$N + NO \rightarrow N_2 + O \tag{R1}$$

$$N + O + N_2 \rightarrow NO(B) + N_2 \tag{R2}$$

with NO_β violet bands from NO(B).

Step 2: At higher NO flow rate, Q (NO) > Q(N), a green emission is observed as all the N atoms are consumed by NO to produce O atoms by R1. The O atoms further react with NO as follows:

$$O + NO + N_2 \rightarrow NO_2^* + N_2 \tag{R3}$$

with a green continuum emission from NO_2^*.

Thus, an equivalent point (that is, the point at which $Q(NO_{ext})$ equals to Q (N)) can be determined between the violet and green emissions and can be used to obtain the N atoms density [N] by the following equation:

$$[N]/[N2] = Q(N)/Q(N_2) = Q(NO_{ext})/Q(N_2) \tag{1}$$

In N_2 late afterglow (LA), the intensity of N_2 1st pos. (580 nm) is proportional to the square of the N-atom density. Then, the other band intensities (N_2 2nd pos., 316 nm), (N_2^+ 1st neg., 391.4 nm) are compared with that of N_2 1st pos. (580 nm) to obtain the $N_2(A)$ and N_2^+ densities from that of N-atoms.

This line-ratio method has been successfully used for the characterization of microwave [26–28] and RF [12,13] afterglows of N_2 [12,26], N_2–H_2 [13,27,28] and N_2–O_2 [26] mixtures.

2. Experiment

As shown in Fig. 1, all the experiments are performed in a quartz tube which consists of two parts of a discharge tube (O.D. = 10 mm, I.D. = 6 mm, length = 300 mm) and an afterglow tube (O.D. = 25 mm, I.D. = 21 mm, length = 300 mm). A RF plasma is generated between two Cu strips wrapped around the discharge tube with an interval of 20 mm by applying RF power (13.6 MHz) between the two Cu strips in a capacitive mode. An afterglow appears in the afterglow tube which is visible by naked eyes when the pressure and the flow rate are adjusted properly. In this experiment, we obtain clearly visible afterglows under a flowing condition with a flow rate of 0.5–0.6 slm maintained at a pressure of 6–8 Torr. The RF power transmitted to the flowing gas is varied from 20 to 130 W.

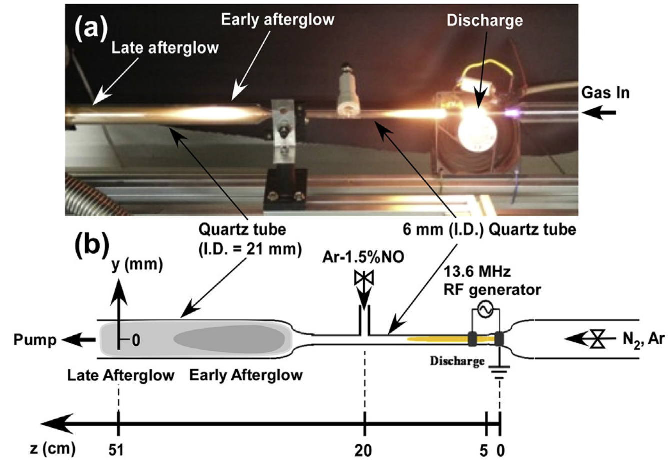

Fig. 1. A picture (a) and a schematic diagram (b) of our experimental setup for the generation of RF plasma of N_2 and Ar–N_2 and for the observation of the afterglows. The position of the measurement along the tube (z) is labeled with respect to the starting point (z = 0) of the RF plasma generation. The vertical position of the measurement (y, along the tube diameter) is set to the center (y = 0) of the tube.

For the determination of N-atom density (N-atom titration), an Ar-1.5% NO gas mixture is introduced at z = 20 cm in the discharge tube [12,13]. The emission spectra are obtained by measuring the emission from the afterglows (or from the plasma) by transferring the emission to a spectrometer (Monera 500, resolution = 0.2–0.8 nm) with a PMT (Hamamatsu R928) using an optical fiber [29].

3. Results and discussion

3.1. Characterization of the N_2 and Ar–N_2 RF plasmas

3.1.1. Rotational temperatures

The emission spectra from the RF plasma is recorded between 760 and 780 nm at a resolution of 0.2 nm by reducing the slits of the spectrometer to 20 μm. Fig. 2 shows the emission spectra of N_2 and Ar-20%N_2 plasmas at 760–780 nm. The series of peaks represent the sequence $\Delta v = 2$ of N_2 1st pos. emission $N_2(B \rightarrow A)$. Here, the intensity ratio (P1/P2) of the first two rotational sub-bands (labeled as P1 and P2) is related to the rotational temperature of the plasma which is usually between 300 and 1000 K with an uncertainty estimated to be about 20% [25,30].

It is an important characteristic parameter of the RF plasma of N_2 since it is directly related to the gas temperature due to the efficient rotational-translational energy transfer in the N_2 plasma [17,31,32].

From Fig. 2(a), we determine that for the N_2 plasma at 6 Torr and 0.6 slm, the P1/P2 ratio decreases from 1 to 0.75 as the RF power is raised from 50 to 130 W. The ratios correspond to gas temperatures of 400–800 K, respectively (Fig. 2)(b). For the case of Ar-20%N_2 at 6 Torr and 0.6 slm, the P1/P2 ratio decreases from 0.9 to 0.8 when the RF power changes from 50 to 100 W; this corresponds to a gas temperature of 500 and 690 K, respectively (Fig. 2)(c). The gas temperatures are about the same between the two N_2 and Ar-20% N_2 plasmas.

At the 8 Torr condition, the rotational temperature is also measured to be in the range of 390–780 K at 50–100 W for the N_2 plasmas, and 440–540 K at 20–50 W for Ar-20%N_2 plasmas. Thus, it can be concluded that very similar gas temperatures are achieved at lower RF powers by mixing N_2 with Ar. It is here mentioned that the Ar metastable atoms can excite the N_2 molecules [25] at low N_2