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Dissociation fraction in low-pressure inductively coupled N_2–Ar and O_2–Ar plasmas

Young Wook Lee, Hye-lan Lee, T.H. Chung*

Department of Physics, Dong-A University, 840 Hadan-dong, Saha-Gu, Busan 604-714, Republic of Korea

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ABSTRACT

Experiments with a Langmuir probe and optical emission spectroscopy (OES) combined with actinometry were performed in inductively coupled rf 13.56 MHz N_2–Ar and O_2–Ar discharges under the pressure range of 1–30 mTorr and the power range of 400–600 W. The Ar contents in the gas mixture were varied from 5% to 80%. The effect of the Ar content on the variation of the emission line intensities from various species was investigated. The dissociation fraction of nitrogen and oxygen molecules was obtained from the measured intensity peaks of light emission by using the OES actinometry. The dissociation fraction of N_2 molecules has a peak value at a specific pressure (11 mTorr). The electron density and the electron temperature were obtained by using a Langmuir probe to investigate the effects of the plasma parameters on the dissociation fraction. The electron density was observed to increase with the power while the electron temperature to decrease with the pressure and power.

1. Introduction

In plasma processing, molecular and mixture gases are used in practice in order to achieve the desired selectivity and to improve the etch rate. Oxygen discharges are widely used for industrial-materials processing, such as dry etching of a photoresist, formation of an oxide film, and ashing of samples. Oxygen with a mixture of rare gases is usually used as the primary gas for oxidization, formation of passivation layer, or other plasma technologies applied to the production of integrated circuits. The etching of SiO_2 and Si typically involves mixtures of Ar and O_2 with the addition of a fluorocarbon [1]. Nitrogen discharge has also widespread applications in plasma process. The atomic nitrogen and oxygen play a key role in the processes such as etching and synthesis of nitrides and oxides, thus making the concentration of atomic species in the molecular gas plasma a significant concern. The determination of the N and O atom densities as a function of power and pressure is essential in the understanding and optimization of the plasma process for micro-electronics materials.

One of the promising ways to enhance the dissociation of molecular gas is to introduce another gas such as hydrogen and argon in the plasma [2]. The dissociation fraction of nitrogen and oxygen molecules have been obtained from the measured intensity peaks of light emission by using OES actinometry [3,4]. The emission intensity ratio is proportional to the ratio of the populations of the emitting state. This ratio is very sensitive to the electron temperature. The electron density and electron temperature (T_e) play an important role in the dissociation process. Generally, the dissociation reaction increases with the electron density and decreases with the electron temperature. However, in reality, the dissociation fraction depends on the electron energy distribution function and the surface recombination of neutrals at the wall in a complicated way. In this study, N_2–Ar and O_2–Ar plasmas are produced with inductively coupled plasma (ICP) sources. The purpose of this work is to optimize operational parameters of inductively coupled N_2–Ar and O_2–Ar discharges for maximum dissociation rates. The change of the emission line intensities from various species with control parameters (power, pressure and Ar content) is explored. This can provide the variations of the species populations in the discharge and they can be compared with the modeling study [5]. We are mainly interested in maximizing the atomization of N_2 and O_2 in low-pressure discharges where the main control parameters are gas pressure, gas composition, and applied power. In this work, the dissociation fractions of nitrogen and oxygen molecules are obtained by using OES actinometry. The electron density and electron temperature are obtained by using an rf-compensated Langmuir probe to investigate the effects of the plasma parameters on the dissociation. The discussions are mainly focused on the pressure and power dependence of dissociation fraction and the effects of the plasma parameters on this.

* Corresponding author.
E-mail address: thchung@dau.ac.kr (T.H. Chung).

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2. Experimental setup

The details of the experimental setup with the diagnostics system (OES and Langmuir probe) was described in Ref. [4]. The plasma chamber consists of a stainless-steel cylinder with a 28-cm diameter and a 34-cm length. A 1.9-cm-thick by 27-cm-diameter tempered glass plate mounted on one end separates the planar one-turn induction coil from the plasma. The induction coil is made of copper (with water-cooling) and is connected to an L-type capacitive matching network and an rf power generator. The plasma chamber is evacuated by using a diffusion pump backed by rotary pump giving a base pressure of 5×10^{-6} Torr. A 13.56 MHz generator (ENI OEM 12) drives an rf current in a flat one-turn coil through the matching network. To the nitrogen discharges generated, the argon was introduced as either an actinometer or as an adding gas. The argon content was varied in the range of 5–80% at the constant total pressure. A diagnostics study of low-pressure planar inductively coupled plasmas (for applications in etching and deposition of thin films) using the nitrogen–argon mixture gas was performed by using optical emission spectroscopy (OES) and Langmuir probes. Both diagnostics complement one another to determine plasma parameters [6]. The experiments were conducted under the conditions of pressures in the range of 1–30 mTorr (with plasma on) and the applied powers in the range of 400–600 W (all experiments performed in H-mode of ICP). The plasma density and electron temperature were obtained by using an rf-compensated single Langmuir probe (Wise Probe, P&A Solutions). The probe tip made of tungsten with a diameter of 0.1 mm and a length of 10 mm is located on the axis of the cylinder at 14 cm below the tempered glass plate. To measure the plasma parameters, the harmonic technique, which exploits the generation of harmonics resulting from excitation of the nonlinearity of the single Langmuir probe characteristic, combined with Druyvesteyn method was used [7,8].

Light collection was made by the optical fiber (0.1 mm slit diameter) attached to the CaF_2 window (5 mm thickness, 50.8 mm diameter). The light intensities of emissive molecules and radicals in the plasma were focused by means of optical fiber into entrance slit of 0.75 m monochromator (SPEX 1702), equipped with a grating of 1200 grooves per millimeter and slit width of 100 μm. The detection system had to be calibrated in intensity between 250 and 850 nm using a quartz halogen lamp with a known spectral radiance. Fig. 1 represents optical emission spectra from (a) N_2–Ar ICP discharges at $p = 1.4$ mTorr and $P = 400$ W and (b) O_2–Ar discharges at $p = 5$ mTorr and $P = 500$ W. In N_2–Ar plasmas, the intensity variations of spectral lines and bands from N_2 (337.1 nm, (C, 0) → (B, 0)), N_2^+ (391.4 nm, (B, 0) → (X, 0)), N (746.8 nm, $3p\ ^4S^0 \rightarrow 3s\ ^4P$), Ar (750.4 nm, $2p_1 \rightarrow 1s_2$), and Ar (811.5 nm, $2p_9 \rightarrow 1s_5$) are observed. For O_2–Ar plasmas, O (844.6 nm, $3p\ ^3P \rightarrow 3s\ ^3S$), O (777.4 nm, $3p\ ^5P \rightarrow 3s\ ^5S$), O_2^+ (550–565 nm, $b\ ^4\Sigma_g^- \rightarrow a\ ^4\prod_u$) with many Ar lines (black labels) and O lines (blue labels) are observed. The $Ar^*\ 2p_1$ level is very efficiently populated by electron-impact excitation from the ground-state, whereas its population due to the excitation from metastable states (Ar^m) is very inefficient [9]. There are two metastable Ar states, $1s_3$ ($^3P_0$) and $1s_5$ ($^3P_2$). The Ar^m ($^3P_2$) is effectively excited to the $2p_9$ state [10,11]. Therefore the $2p_9 \rightarrow 1s_5$ emission line (811.5 nm) provides useful information on the electron energy distribution in the plasma [10]. It should be noted that there appear Ar $3p \rightarrow 1s$ lines at 420.7 and 425.9 nm (red labels) in O_2–Ar plasmas.

If two spectral line 750.4 and 746.8 nm are chosen for the OES actinometry, the dissociation fraction can be determined by calculating the ratio [12],

$$\frac{\left[N\left(2p\ ^4S^0\right)\right]}{[N_2]} = \frac{R_{750}}{R_{746}}\frac{\nu_{750}}{\nu_{746}}\frac{A_{750}}{A_{746}}\frac{k_{Ar}^{dir}}{k_N^{dir}}\frac{\tau_{Ar}}{\tau_N}\frac{[Ar]}{[N_2(X)]}\frac{I_{746}}{I_{750}} \quad (1)$$

Here R is the spectral response of the system, A is the emission probabilities, ν is the frequency of the light emission, τ is the life time which is the inverse of the sum of the emission probabilities for all the radiative de-excitation processes, k_{Ar}^{dir} is the rate coefficient for electron-impact direct excitation to Ar^* ($2p_1$) from the ground-state Ar, k_N^{dir} is the rate coefficient for electron-impact direct excitation to N^* ($3p\ ^4S^0$) from the ground-state N ($2p\ ^4S^0$), and I is the emission line intensity. Quenching is negligible in low-pressure plasmas considered in this work. If two spectral line 337.1 and 746.8 nm are chosen for the OES actinometry, the dissociation fraction can be determined by calculating the ratio [13],

$$\frac{\left[N\left(2p\ ^4S^0\right)\right]}{[N_2]} = \frac{R_{337}}{R_{746}}\frac{\nu_{337}}{\nu_{746}}\frac{A_{337}}{A_{746}}\frac{k_{N_2}^{dir}}{k_N^{dir}}\frac{\tau_{337}}{\tau_{746}}\frac{I_{746}}{I_{337}}, \quad (2)$$

where $k_{N_2}^{dir}$ is the rate coefficient for electron-impact direct excitation to $N_2(C)$ from the ground-state $N_2(X)$.

In a similar fashion, for O_2–Ar plasmas, the intensity ratio of two lines O (844 nm) and Ar (750 nm) can be written as [14]

$$\frac{I_{844}}{I_{750}} = \frac{R_{844}}{R_{750}}\frac{\nu_{844}}{\nu_{750}}\frac{A_{844}}{A_{750}}\frac{\tau_O}{\tau_{Ar}}\frac{k_e^{3P}[O] + k_{de}^{3P}[O_2]}{k_{Ar}^{dir}[Ar]} \quad (3)$$

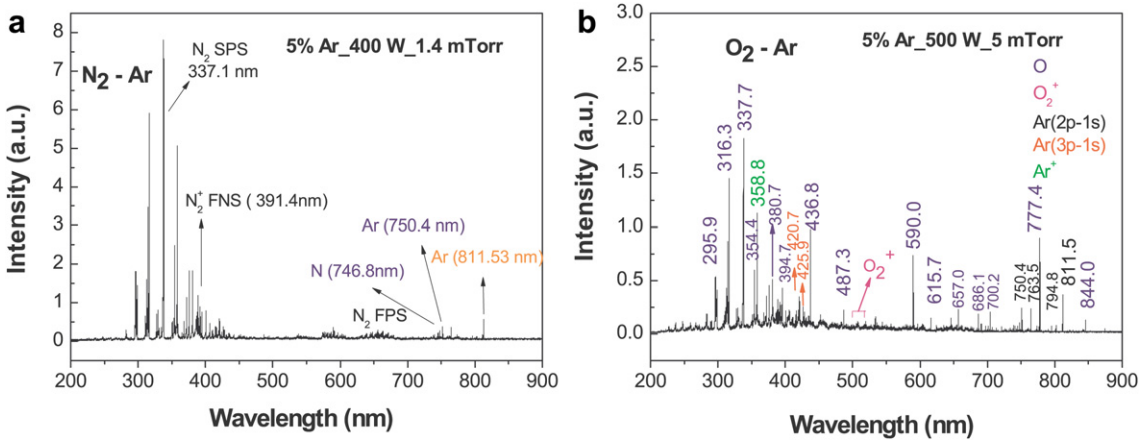

Fig. 1. Representative optical emission spectra from ICP (a) N_2-5%Ar discharges at $p = 1.4$ mTorr and $P = 400$ W and (b) O_2-5%Ar discharges at $p = 5$ mTorr and $P = 500$ W.

Here k_e^{3P} is the rate coefficient for electron-impact direct excitation to $O^*(^3P)$ from the ground-state O and k_{de}^{3P} is the rate coefficient for electron-impact dissociative excitation to $O^*(^3P)$ from the ground-state O_2. Therefore, the dissociation fraction can be formulated as

$$\frac{[O]}{[O_2]} = \frac{R_{750}}{R_{844}}\frac{\nu_{750}}{\nu_{844}}\frac{A_{750}}{A_{844}}\frac{\tau_{Ar}}{\tau_O}\frac{k_{Ar}^{dir}}{k_e^{3P}}\frac{[Ar]}{[O_2]}\frac{I_{844}}{I_{750}} - \frac{k_{de}^{3P}}{k_e^{3P}} \quad (4)$$

It should be noted that the rate coefficient for electron-impact dissociative excitation to N^* from the ground-state N_2 is very small and can be neglected in Eq. (1) [13].

3. Results and discussion

Fig. 2(a) shows the changes of the intensity ratios of the chosen spectral lines versus the Ar content for N_2–Ar discharge. The population of $Ar^*(2p_1)$ is increased larger than that of $N^*(3p\ ^4S^0)$ with increasing the Ar content. Thus the ratio I_N/I_{Ar750} is decreased with the Ar content. As the Ar content increases, the generation of $N_2^+(X)$ and its excitation to $N_2^+(B)$ increases. Although T_e decreases slightly (thus causing a direct electron-impact excitation to decrease), the production of Ar^m increases with the Ar content. This promotes the Penning excitation $Ar^m + N_2^+(X) \rightarrow N_2^+(B) + Ar$. Therefore the transition $N_2^+(B) \rightarrow N_2^+(X) + h\nu(391.4\ nm)$ becomes frequent thus making I_{N2}^+ intense. On the other hand, the transition N ($3p\ ^4S \rightarrow 3s\ ^4P$) is not much influenced by the Ar^m since the rate coefficient of the reaction $Ar^m + N \rightarrow N^* + Ar$ is very small. Therefore, the ratio I_N/I_{N2}^+ decreases with the Ar content. But this trend is relatively suppressed in Ar-dominating region (above Ar-60%). The transition $N_2(X) \rightarrow N_2(C)$ is increased with an increase of Ar^m due to the reaction $Ar^m + N_2(X) \rightarrow N_2(C) + Ar$. This is followed by the light emission $N_2(C) \rightarrow N_2(B) + h\nu(337.1\ nm)$. However, the increase in $N_2(C)$ results in the excitation of N^m to N($3p\ ^4S$) through the reaction $N^m + N_2(C) \rightarrow N(3p\ ^4S) + N_2$. Therefore, as the Ar content increases, the ratio of I_N/I_{N_2} remains almost unchanged. The population of Ar^m is increased with the Ar content more rapidly than that of Ar^* ($2p_1$) [15,16], thus I_{811}/I_{750} is increased with the Ar content except a small hump at Ar 20%. This is also related to a decrease in the electron temperature with increasing Ar content. The I_{811}/I_{750} line intensity ratio is an indicator of the EEDF changes and depends on the electron temperature (T_e). Although not shown in the figure, as the power increases, the ratio increases slightly because that although both the populations of the Ar^m and the resonant state $Ar^*(2p_1)$ are increased with power, Ar^m population is increased more rapidly [13]. Fig. 2(b) shows the variations of the intensity ratios of the chosen spectral lines with the Ar content for O_2–Ar discharge. Similar to the N_2–Ar discharge, the ratio $I_{O_{844}}/I_{Ar_{750}}$ is decreased with the Ar content. The ratio $I_O/I_{O_2^+}$ increases slowly up to the Ar content of 20% and remains not much changed afterward. This indicates that Penning excitations of O due to Ar^m increase with the Ar content [17]. But the Penning excitation of O_2^+ is also enhanced at higher Ar contents.

Fig. 2(c) represents the changes of the intensity ratios of the chosen spectral lines with pressure for N_2-5%Ar discharge. As pressure increases, the Penning ionization of N_2 and the charge transfer to N_2^+ are enhanced, therefore, the ratio $I_N/I_{N_2^+}$ decreases with the pressure. The ratio $I_N/I_{Ar_{750}}$ increases slightly at $p = 11$ mTorr, but not much changed. Fig. 2(d) shows the changes of the intensity ratios of the chosen spectral lines with pressure for O_2-5%Ar discharge. As shown in Fig. 2(d), both the ratios $I_{844}/I_{Ar_{750}}$ and $I_{844}/I_{O_2^+}$ increase slightly with pressure. This can be explained by that a decrease in T_e due to an increase of pressure causes the ratios k_e^{3P}/k_{Ar}^{dir} and $k_e^{3P}/k_{O_2^+}^{dir}$ to increase [14].

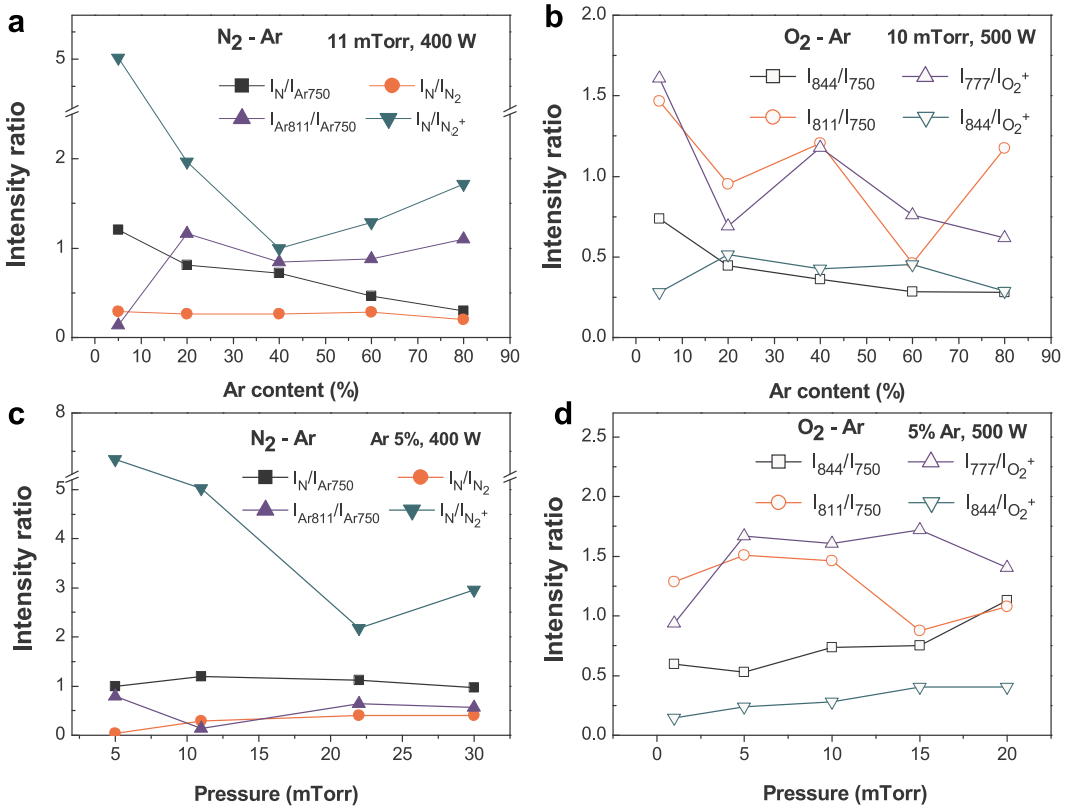

Fig. 2. Intensity ratios of the chosen spectral lines versus the Ar content in the mixture for (a) N_2-Ar discharges at $p = 11$ mTorr and $P = 400$ W, and (b) O_2-Ar discharges at $p = 5$ mTorr and $P = 500$ W. Changes of the intensity ratios as a function of the pressure for (c) N_2-5%Ar discharges at $P = 400$ W and (d) O_2-5%Ar discharges at $P = 500$ W.

Fig. 3(a) and (b) shows the plasma density and electron temperature for N_2-5%Ar discharge as a function of pressure obtained by a single Langmuir probe, respectively. The plasma density is found to increase with pressure up to 11 mTorr, and then decreases slightly, while the electron temperature decreases with it. The electron density and electron temperature play an important role in the dissociation process. Especially the electron density could be a dominant factor in some circumstance [2].

Fig. 4(a) represents the ratio of rate coefficients $k_{N_2}^{dir}/k_N^{dir}$, k_{Ar}^{dir}/k_N^{dir}, k_{Ar}^{dir}/k_e^{3P}, and k_{de}^{3P}/k_e^{3P}. The values of the electron-impact excitation cross sections are obtained from the literature [14,19–22]. In calculating the rate coefficient, Maxwell–Boltzmann energy distribution of electrons was assumed [14]. In Fig. 4(b), the dissociation fractions of nitrogen molecules in N_2-5%Ar discharges evaluated based on Eq. (1) were represented as a function of pressure. The dissociation fraction has a peak values at a specific pressure about 11 mTorr. The dissociation fractions in the ICP were lower than that (about 10%) of microwave-excited N_2-5%Ar plasmas [12], but much higher than those of capacitively coupled discharges [18]. Eq. (2) can also provide the dissociation fraction. Due to a large difference (thus causing an inaccuracy) in the value of the spectral response, the ratio $k_{N_2}^{dir}I_{746}/k_N^{dir}I_{337}$ is shown as an arbitrary value. The two plots give a little difference. The dissociation fraction given by Eq. (2) has a peak value at a specific pressure about 22 mTorr. The amount of dissociation reaction is proportional to the electron density, but the rate coefficient itself depends on T_e. Since the T_e decreases with pressure, the dissociation fraction has a maximum at a specific pressure. On the other hand, in O_2-5%Ar discharges

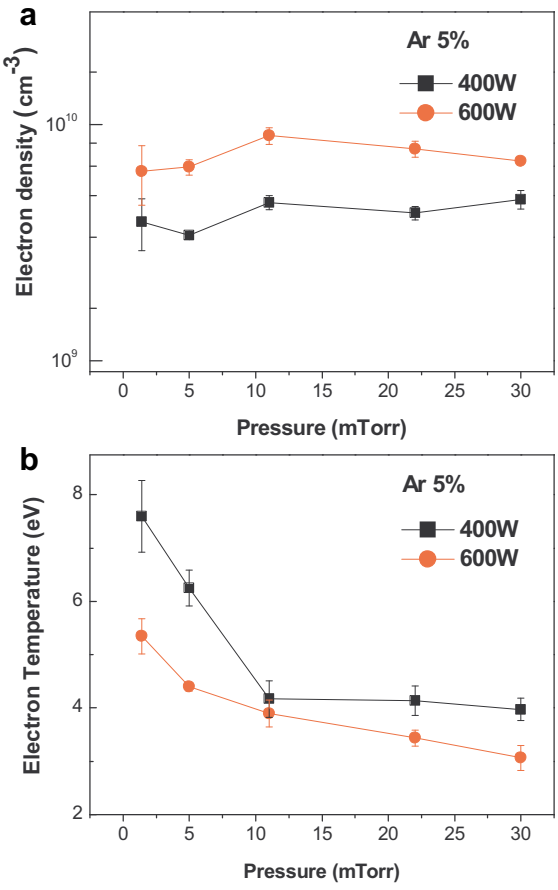

Fig. 3. Langmuir probe measurement of (a) the plasma density and (b) the electron temperature as a function of pressure in N_2-5%Ar discharges. The gas pressure is varied from 1.4 mTorr to 30 mTorr at the powers 400 W and 600 W.

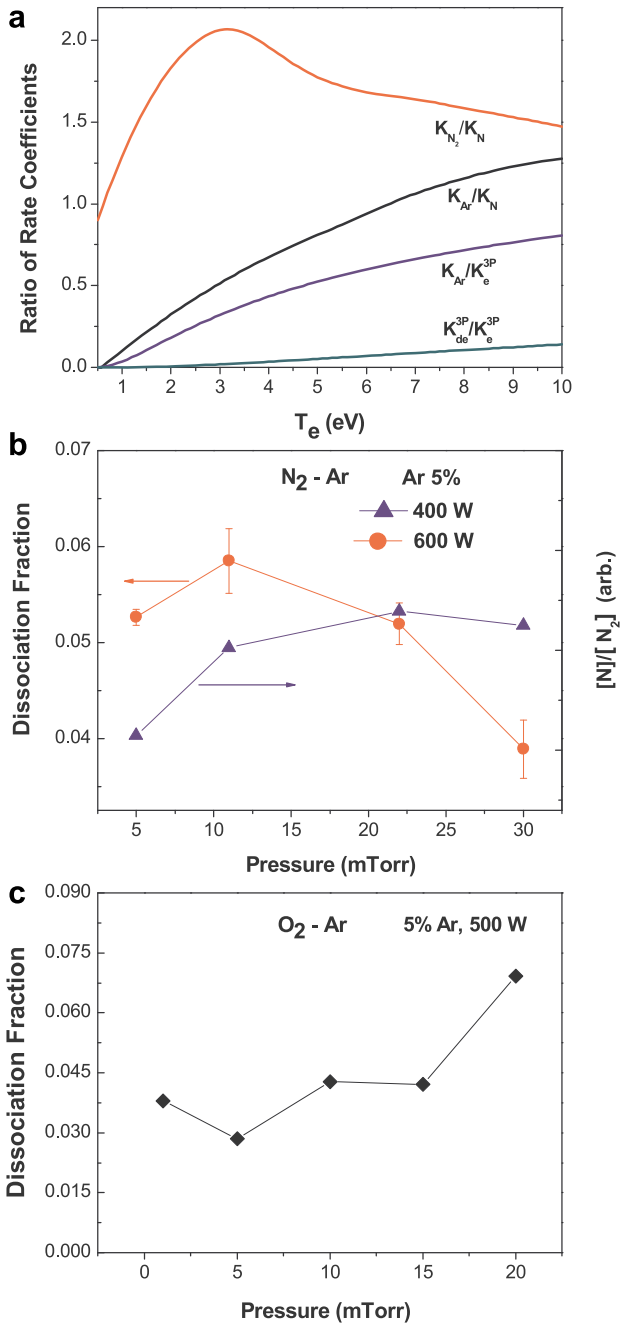

Fig. 4. (a) Ratio of the rate coefficients $k_{N_2}^{dir}/k_N^{dir}$, k_{Ar}^{dir}/k_N^{dir}, k_{Ar}^{dir}/k_e^{3P}, and k_{de}^{3P}/k_e^{3P}. Dissociation fraction as a function of pressure for (b) N_2-5%Ar discharges at $P = 600$ W (and at 400 W) and (c) O_2-5%Ar discharges at $P = 500$ W.

Table 1
Spectral responses and spectroscopy data for the transitions used in this study.

R	λ (nm)	Transition	τ (ns)	A ($\times 10^7$ s^{-1})
0.0260	746.8	N ($3p\ ^4S^0 \rightarrow 3s\ ^4P$)	26.3	1.9
0.0223	750.4	Ar ($2p_1 \rightarrow 1s_2$)	21.3	4.45
0.0068	811.5	Ar ($2p_9 \rightarrow 1s_5$)	30.2	3.31
0.479	337.1	N_2 (C, 0) → (B, 0)	37.0	1.41
0.448	391.4	N_2^+ (B, 0) → (X, 0)	60.0	1.2
0.0061	844.6	O ($3p\ ^3P \rightarrow 3s\ ^3S$)	22.7	3.22

(Fig. 4(c)), the dissociation fraction evaluated by Eq. (4) increases slightly with pressure up to 30 mTorr. The estimated dissociation fraction of ICP O_2 discharges was lower than that of DC O_2 flowing glow discharges for pressures ranging from 0.36 to 2 Torr and discharge currents ranging from 5 to 80 mA in Pyrex tubes of several millimeter diameters [14], a little lower than that (just below 10%) of a helicon discharge [23], but much higher than that of capacitively coupled discharges [8]. The spectral responses and spectroscopic data of the selected transitions used in Eqs. (1)–(4) are listed in table 1.

4. Conclusion

Experiments with a Langmuir probe and optical emission spectroscopy combined with actinometry were carried out in inductively coupled rf 13.56 MHz discharges at total pressures of 1–30 mTorr and the applied rf powers in the range of 400–600 W in the Ar content ranging from 5% to 80%. For actinometry, spectral lines from N (746.8 nm), N_2 (337.1 nm), O (844.6 nm), and Ar (750.4) were chosen. The dissociation fractions of nitrogen and oxygen molecules were obtained from the measured intensity peaks of light emission by using OES actinometry. In addition, the electron density and the electron temperature were obtained by using an rf-compensated Langmuir probe to investigate the effects of the plasma parameters on the dissociation. The change of the intensities of various spectral lines mentioned above was also explored. The dissociation fraction of N_2 molecules has a peak value at a specific pressure of 11 mTorr. This may be related to the behaviors of the electron density and electron temperature with varying pressure.

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