Journal of the Korean Physical Society, Vol. 53, No. 2, August 2008, pp. 617∼623

Measurement of the Degree of Dissociation in Inductively Coupled Nitrogen Discharges by Using Optical Emission Actinometry and Mass Spectrometry

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(Received 11 January 2008, in final form 28 March 2008)

The degree of dissociation is evaluated by using optical emission actinometry and mass spectrometry for inductively coupled nitrogen plasmas with pressures of 1 – 10 mTorr. The degree of dissociation is found to be between 1 % and 3.5 % and gradually increases with pressure and decreases slightly with power. The pressure dependence of the degree of dissociation measured by using optical emission actinometry and mass spectrometry exhibits a similar behavior. A physical explanation of these observations is given with a discussion of the particle balance and plasma properties, such as the electron density, the electron temperature and the electron energy probability function measured by using a Langmuir probe.

PACS numbers: 52.25.Rv, 52.70.Kz, 52.20.Hv
Keywords: Degree of dissociation, Inductively coupled nitrogen plasma, Optical emission actinometry, Mass spectrometry, Electron energy probabilty function

I. INTRODUCTION

Nitrogen atoms are of great importance in the field of material science. Electric discharges produced either by microwaves, helicon waves or radio frequency (rf) power are commonly used for generating nitrogen atoms [1–4]. It has been known for a long time that most of these plasma systems are characterized by high nitrogen atom content. Recently, there has been a steadily growing interest in the application of inductively coupled plasma (ICP) sources for numerous types of plasma-enhanced materials processing.

The determination of the neutral species density as functions of the radio frequency power and the pressure is essential in the understanding and the optimization of the plasma process for micro-electronics materials. The behavior of the degree of dissociation for the molecular discharge differs significantly with the plasma chemistry [5–7]. The degree of dissociation in an inductively coupled nitrogen plasma is important for understanding and improving the nitridation processes because the number density of N atoms is deducible from the degree of dissociation. Generally, it is difficult to achieve a high dissociation efficiency of N_2 due to its extremely high bonding energy [8].

The dissociation of N_2 molecules in nitrogen plasmas has been diagnosed by using several techniques, such as mass spectrometry [9,10] and optical emission spectroscopy [3,11,12]. In other articles, the degrees of dissociation were found to be 1 – 4.9 % [13], 0.58 – 4.4 % [8], 1 – 7 % [1] and 1 % or below [2,3,5].

Nakano *et al.* measured the dissociation degree of N_2 in an inductively coupled plasma by using vacuum ultraviolet emission spectroscopy [13]. The emissions of the NI line at 174.4 nm and the N_2 second positive system band at 337 nm were selected by using a 20-cm VUV monochromator. They observed that the degree of dissociation increased with the rf power when the N_2 pressure was kept at 4.98 mTorr, which was a consequence of the electron density increasing linearly with the rf power and that the electron energy distribution function at an electron energy high enough to dissociate N_2 did not seem to decrease strongly at higher rf powers [13]. This explanation is supported by the dependence of the electron temperature on the rf power being weaker than that on the N_2 pressure. In contrast, no large increase in the degree of N_2 dissociation with pressure was observed for a fixed rf power (1 kW), not even when the electron density increased sharply in the pressure range of 0.09 – 4.98 mTorr [13]. Here, the electron temperature decreased abruptly with increasing N_2 pressure, indicating that the ratio of the electrons that can dissociate N_2 molecules to the total number of electrons decreases significantly as the N_2 pressure is increased [8]. Czerwiec *et al.* measured the dissociation fraction for an ICP sustained in a long cylindrical tube with a small radius specially designed for radical beam generation. They obtained a dissociation fraction from 0.1 (evaluated by using optical emission actinometry) up to 0.7 (by using mass spectrometry) for N_2 discharges at 50 mTorr [9].

Langmuir probes and optical emission spectroscopy

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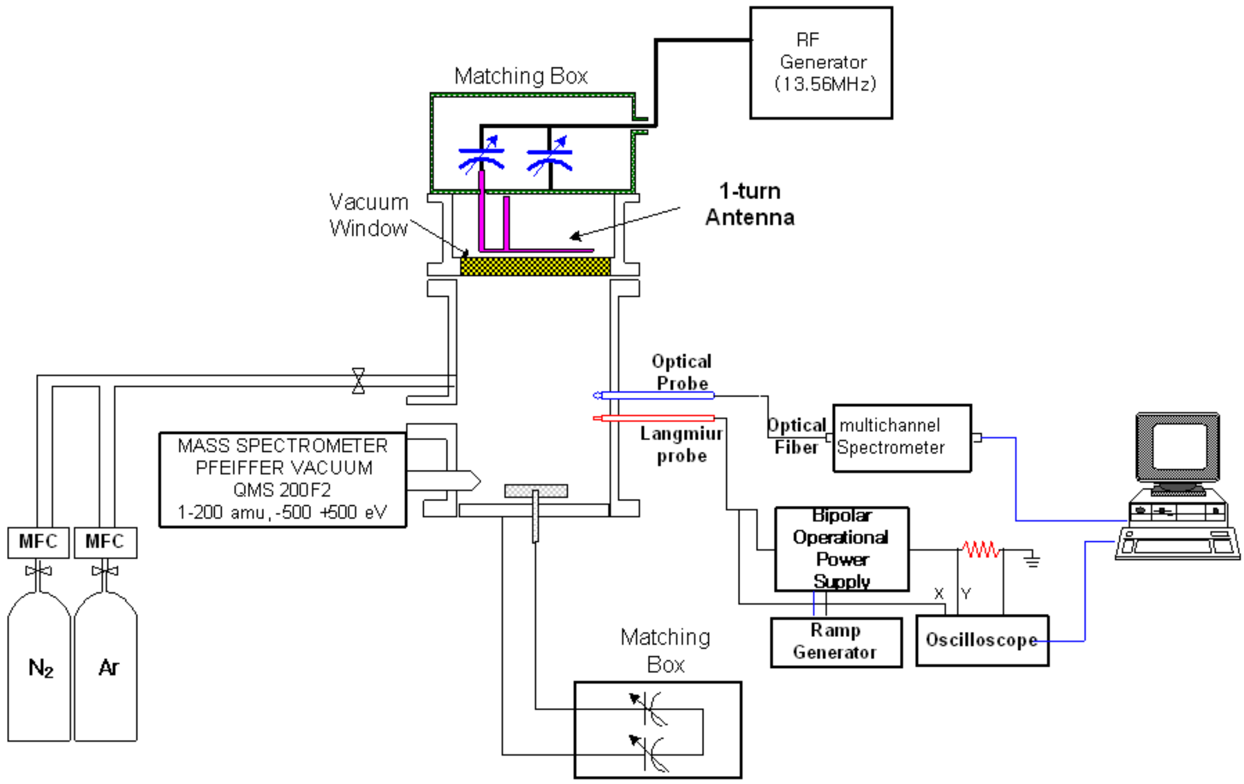

Fig. 1. Schematic diagram of the experimental setup and diagnostics system.

(OES) are the established diagnostic methods for determining the plasma parameters in processing plasmas. In this work, we measured most of the important plasma parameters, such as the densities of charged species, the electron temperature and the electron energy probability function by using a Langmuir probe. We obtained the degrees of dissociation by using OES actinometry and mass spectrometry. Specifically, we measured the degrees of dissociation at various powers (250 – 500 W) in the pressure range 1 – 10 mTorr, which is different from the range of similar studies [5, 8, 13]. A physical explanation of the variations of the degree of dissociation with pressure and power is given with a discussion of the particle balance and of plasma properties such as the electron density, the electron temperature and the electron energy probability function measured by using a Langmuir probe.

II. EXPERIMENT

A schematic diagram of the experimental setup with the diagnostics system (OES, quadrupole mass spectrometer (QMS) and Langmuir probe) is shown in Figure 1. 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 a rf power generator.

The plasma chamber is evacuated by using a diffusion pump backed by rotary pump giving a base pressure of 9×10^{-6} Torr. The equilibrium gas pressure in the chamber is monitored with a combination vacuum gauge (IMG 300). The operating gas pressure is controlled by adjusting the mass flow controller. The flow rate of the nitrogen gas is in the range of 50 – 80 sccm. The nitrogen gas pressure is varied in the range of 1.4 – 8.5 mTorr and a 13.56-MHz generator (ENI OEM 12) with a power output of 250 – 500 W drives an rf current in a flat one-turn coil through the rf power generator and matching network. The source gas is N_2 gas. We add 5 % Ar as an actinometer for all cases.

Although the electron density increases significantly with increasing Ar fraction, the 5 % Ar in the nitrogen gas having a total pressure of less than 10 mTorr, does not cause significant changes in the plasma parameters compared to the pure nitrogen case. It has been observed that Penning dissociation does not occur easily in an Ar/N_2 discharge [5,14]. We obtain the degree of dissociation by using the integrated intensities of the peaks of the OES and QMS. We obtained the electron density, the electron temperature and the electron energy probability function (EEPF) by using a Langmuir probe.

The light from emissive molecules and radicals in the plasma is collected by an optical fiber that is coupled to a multi-channel spectrometer (OPC-2000, Optel Precisions) in the wavelength range of 250 – 800 nm with a resolution of 1 nm. The dependence of the emission intensities on the plasma parameters is investigated. In plasma processing, the most useful and well developed technique is actinometry. In this method, a known concentration of an impurity is introduced and the intensities of two neighboring spectral lines, one from the known gas and one from the sample, are compared. Since both species are bombarded by the same electron distribution and the concentration of the actinometer is known, the density of the sample can be calculated. For the nitrogen plasma with the actinometer Ar, the degree of dissociation is defined by [9]

$$D_{OES} = 0.75 \left(\frac{I_N}{I_{Ar}}\right) \left(\frac{x_{Ar}}{x_{N_2}}\right), \quad (1)$$

where I_{Ar} and I_N are the intensities of emission line of Ar at 811.53 nm and the emission line of N at 746.68 nm and x_{Ar} and x_{N_2} are the percentages of argon and nitrogen in the gas mixture with the discharge off.

In these experiments, a QMS (QMS 200F2, Pfeiffer Vacuum) is mounted on the main chamber. A 100 μm diameter aperture connects the QMS analysis section with the main chamber. The degree of dissociation given by mass spectrometry is

$$D_{MS} = 1 - \frac{I^{plasma\ on}(N_2)}{I^{plasma\ off}(N_2)}, \quad (2)$$

where $I^{plasma\ on}$ and $I^{plasma\ off}$ are the intensities of the ion peak just before and just after the plasma is switched off. The intensities of the peaks are determined from the area of each mass peak, which is obtained by integrating the signal across the peak [11].

A rf-compensated, cylindrical, single Langmuir probe (SLP-2000, Plasmart) is mounted through one of the ports on the vacuum chamber. The probe tip made of tungsten with a diameter of 1 mm and a length of 3 mm is used to measure the plasma parameters. The second derivative of the measured probe current, I'', is related to the electron energy distribution function(EEDF), $f(\epsilon)$, as follow:

$$f(\epsilon) = \frac{2m}{e^2 S} \left(\frac{2eV}{m}\right)^{1/2} I'', \quad (3)$$

where e is the electron charge, S is the probe area, m is the mass of electron, V is the probe potential referenced to the plasma potential (space potential) and ϵ is measured in units of eV. The electron density and the effective electron temperature are calculated with the measured EEDF as follows:

$$n_e = \int_0^{\epsilon_{max}} f(\epsilon) d\epsilon, \qquad T_e = \frac{2}{3n_e} \int_0^{\epsilon_{max}} \epsilon f(\epsilon) d\epsilon, \quad (4)$$

where ϵ_{max} is determined by using the dynamic range of the EEDF measurement. The electron temperature can also be determined from the slope of the probe $\ln(I) - V$ curve in the exponential region (from the point where the probe current is zero to where the slope of the curve begins to decrease). We observe that both methods yield almost same values of the electron temperature. The EEDF integral method has been used to obtain plasma parameters for many processing plasmas utilizing molecular gases [15–18].

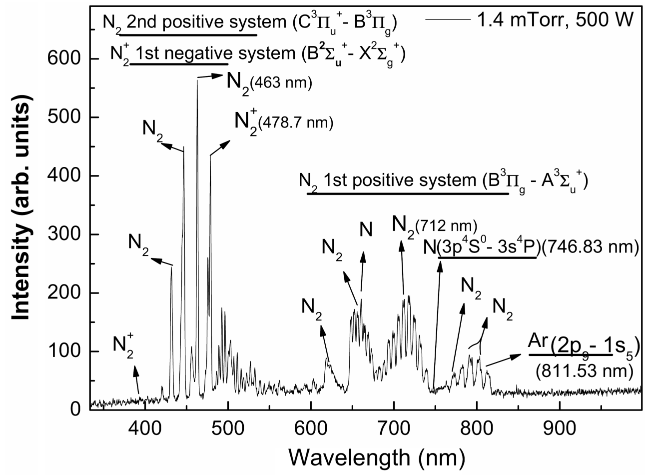

Fig. 2. Spectrum of the optical emission from an inductively coupled nitrogen discharge. the feed gas compositions is 5 % Ar and 95 % N_2.

In this experiment, we obtain the degree of dissociation for an inductively coupled nitrogen discharge as functions of the pressure (1 – 10 mTorr) and the input power (250 – 500 W). We try to find the behavior of the variation of the degree of dissociation with power and pressure. In order to better understand the effect of power and pressure on the degree of dissociation, we use EEPF (electron energy probability function), the electron density and the electron temperature measured by Langmuir probe.

III. RESULTS AND DISCUSSION

Figure 2 presents a typical optical emission spectrum of an ICP discharge containing a nitrogen plasma. The main emission peaks correspond to several transition lines of atomic nitrogen and of molecular nitrogen. The spectrum is characterized by the first positive band system ($B^3\Pi_g - A^3\Sigma_u^+$) and the second positive band system ($C^3\Pi_u - B^3\Pi_g$) of the N_2 molecule and by the first negative band system ($B^2\Sigma_u^+ - X^2\Sigma_g^+$) of the nitrogen molecular ion N_2^+. The spectrum is dominated by strong molecular features, which peak around 400 – 500 nm and 650 – 800 nm. The emission of the N line at 746.68 nm [$3p^4S_{3/2} \rightarrow 3s^4P_{5/2}$] is selected. Argon is chosen as the actinometer and the $2p_9 \rightarrow 1s_5$ transition at 811.53 nm is used because it is not sensitive to two-step excitation.

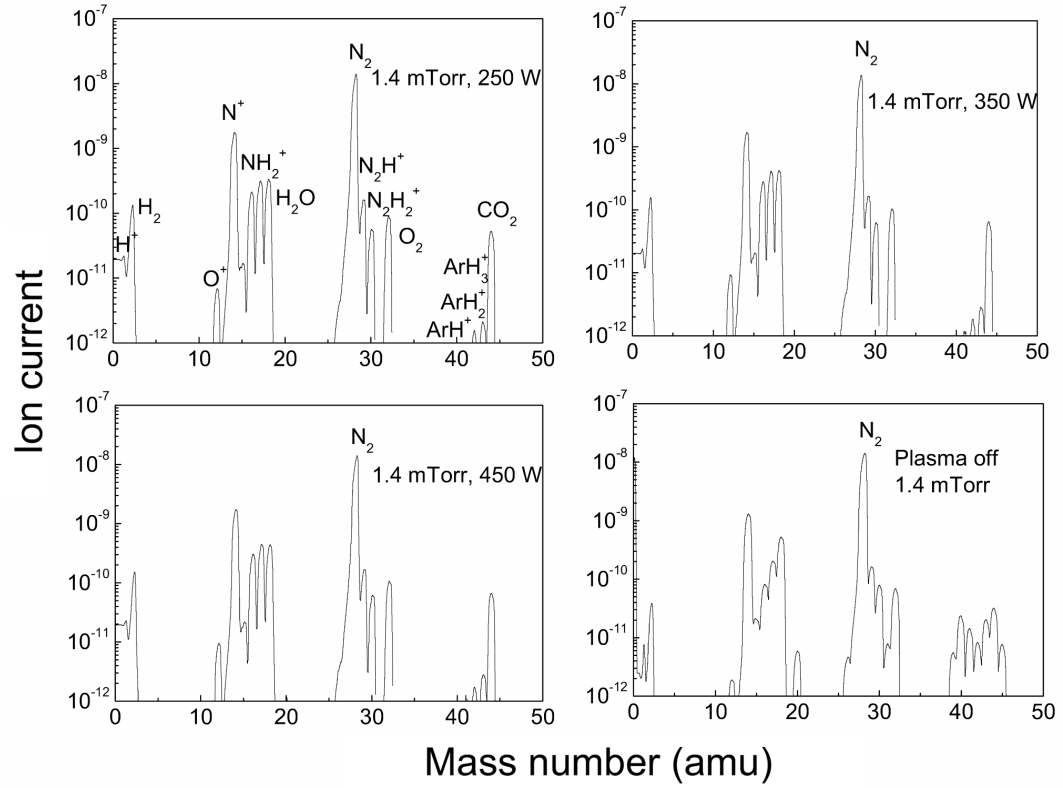

Fig. 3. Mass spectra for several discharge conditions (p = 1.4 mTorr, P = 0, 250, 350, 450 W).

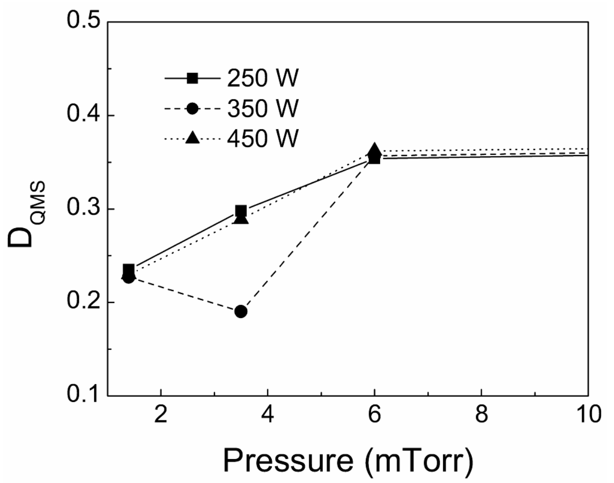

Fig. 4. Degree of dissociation measured by using mass spectrometry as a function of pressure at three different powers (P = 250, 350, 450 W).

The total intensity of the emission from state $C^3\Pi_u$ and state $B^3\Pi_g$ changes with the pressure and the power. By comparing the ratio of the emission intensity of the second positive band system to that of the first positive band system, one can obtain the electron temperature [19].

Figure 3 shows representative mass spectra for several parameter conditions. It is observed that the ion currents do not significantly vary with the pressure and the power. The values of the ion currents at mass 28 are monitored to give the degree of dissociation by using Eq. (2).

Figure 4 demonstrates the evolution of the degree of dissociation, D_{MS}, measured by using mass spectrometry as a function of pressure for three different input powers. As illustrated in Figure 4, the degree of dissociation increases with pressure. Although not shown in figures, we found that when the pressure was kept constant and the power was varied (250 – 500 W), the degree of dissociation obtained by using QMS did not change significantly. It should be noted that the degree of dissociation obtained by using mass spectrometry is always higher than that obtained by using OES actinometry. A possible explanation for this discrepancy is that the actinometry provides information on the nitrogen atom density inside of the ICP chamber while the QMS gives information on the nitrogen atom density in the processing chamber of the QMS.

These dissociation trends correlate well with the electron density and the electron energy probability function trends. Figure 5 shows the electron energy probability function (EEPF) for various values of the pressure and the power. The EEDF in nitrogen discharges was observed to be non-Maxwellian for the entire energy range [20]. In this work, the electron energy probability functions were observed to be Maxwellian in a rough manner

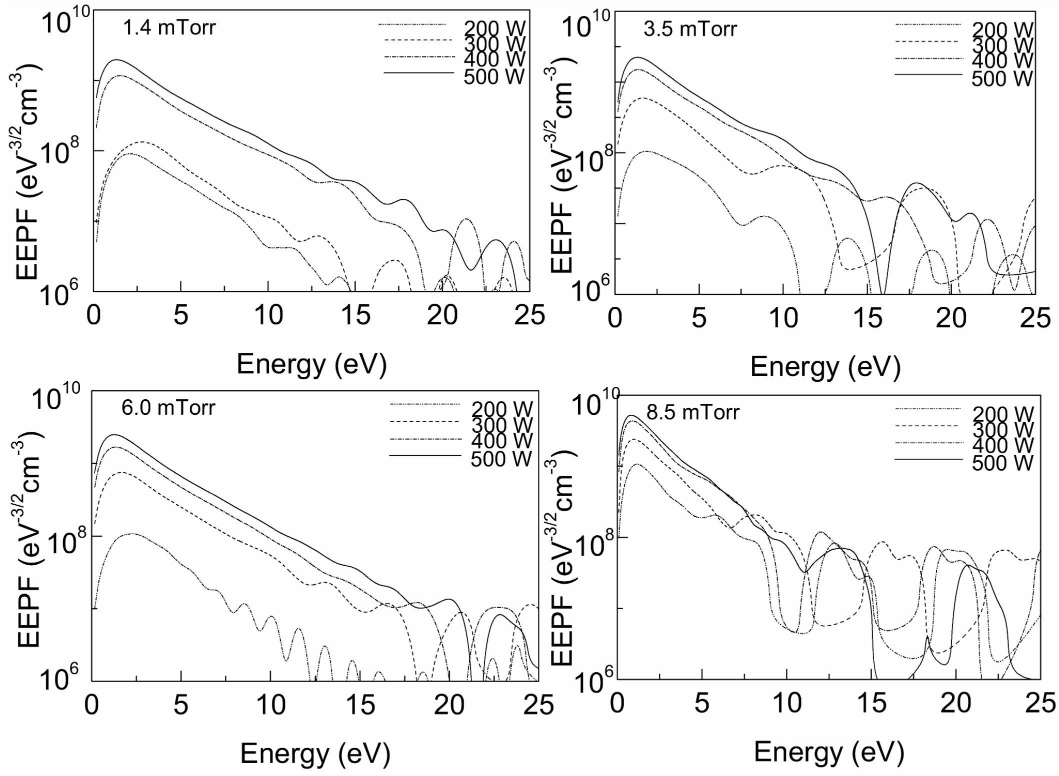

Fig. 5. Electron energy probability functions for various discharge conditions.

for low-pressure high-power plasmas. A low-energy and a high-energy electron groups occur as in most of radio-frequency discharges [21].

For nitrogen, the threshold for dissociation is at 9.8 eV; however, the cross section function does not rise significantly until after 15 eV. From there, it rises gradually to a value of 6.74×10^{-19}cm^2 at 20 eV. Because of the high threshold and the peak energy well above 20 eV, very little N_2 is dissociated and the very high energy region is probably not altered by a pressure in the 1 – 10 mTorr pressure range [5]. As the pressure is increased from 1.4 mTorr to 8.5 mTorr, the population of electrons with energy less than 15 eV is enhanced. On the other hand, the population of electrons with energy greater than 15 eV exhibits an unstable behavior, which might be caused by noise, while showing no significant enhancement with increasing pressure.

The number of electrons having an energy between 10 eV and 20 eV is observed to increase with increasing power at a pressure of 1.4 mTorr. These electrons contribute to increasing the electron-impact dissociation. However, at 8.5 mTorr, the population of electron energy high enough to dissociate N_2 does not seem to increase at higher input powers. In the 8.5-mTorr case, the higher energy (>10 eV) electrons were observed to be slightly decreased as the power was increased. This might be one cause of the decrease in the degree of dissociation with increasing power.

Figure 6 demonstrates the evolution of the electron density and the electron temperature for various input powers at different pressures. The electron density increases with increasing power and pressure. The electron temperature decreases with pressure and does not vary significantly (or decreases slightly) with power. The effective electron temperature has been observed to decrease with increasing rf voltage in a capacitively coupled rf discharges [21]. It should be noted that the variations of the electron density and the electron temperature with pressure and power depend on the operating region and on the specific reactor wall condition. The variations are restricted to inductively coupled nitrogen discharges with pressures in the range of 1 – 10 mTorr and powers in the range of 250 – 500 W.

The degree of dissociation, as determined by using OES actinometry, is shown as a function of input power in Figure 7. As the power is increased, the intensities of the optical emission peaks shown in Figure 2 are increased, respectively, but the degree of dissociation decreases. There are two reasons for this. In the first place, as the power is increased, although the electron density is increased, the number of electrons with higher energies is not changed, as shown in Figure 5. As the input power is increased, the number of electrons having enough energy to dissociate N_2 is slightly decreased and the electron temperature is decreased a little. Therefore, the electron-impact dissociation is decreased and this causes the degree of dissociation to decrease. However, this power dependence of the degree of dissociation

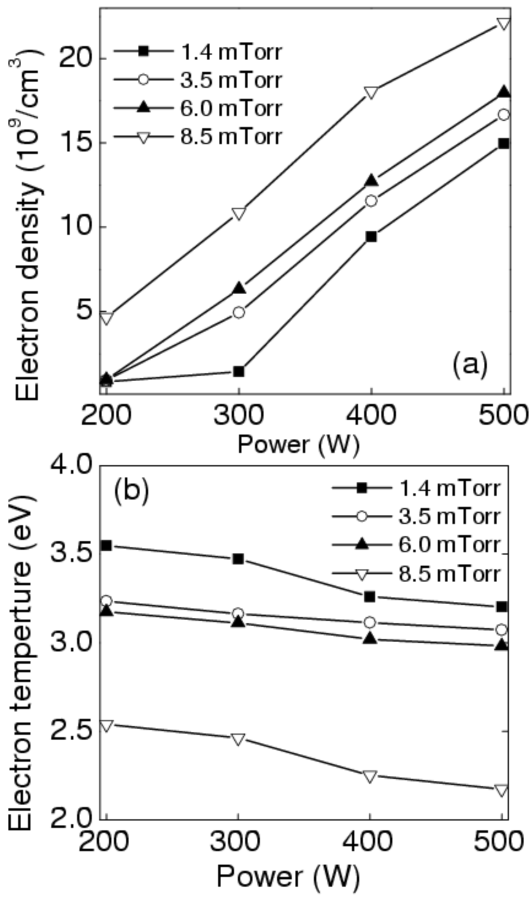

Fig. 6. The input power dependence of electron density and electron temperature for different pressures (p = 1,4, 3.5, 6.0, 8.5 mTorr).

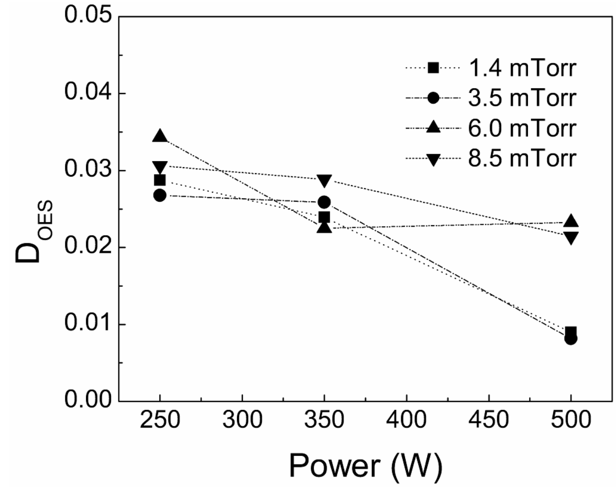

Fig. 7. Degree of dissociation measured by optical emission actinometry as a function of power for four different gas pressures (p = 1,4, 3.5, 6.0, 8.5 mTorr).

seems to be limited to the parameter region considered in this work. From the global balance of the discharge kinetics, the dissociated neutral atom density is expected to be proportional to the power for a larger power variation [22]. Figure 7 also shows the pressure dependence of the degree of dissociation. The degree of dissociation increases overall with N_2 pressure when the input powers are 250 W and 500 W.

Neutral nitrogen atoms are assumed to be generated mainly by electron-impact dissociation of N_2 and to be lost by diffusion to and recombination at the reactor wall and by the electron-impact ionization of N,

$$2K_{diss}n_e n^0_{N_2} = (K_d + K_{iz}n_e)n_N, \tag{5}$$

where K_{diss} is the rate coefficient for dissociation of N_2, $n^0_{N_2}$ is the initial density of N_2, K_d is the rate coefficient for the diffusion to and recombination at the reactor wall of N atoms, K_{iz} is the rate coefficient for the electron-impact ionization of N and n_N is the density of N atoms. The degree of dissociation is approximated by

$$D \approx \frac{n_N}{n^0_{N_2}} = \frac{2K_{diss}n_e}{K_d + K_{iz}n_e} \tag{6}$$

If K_{diss} and K_{iz} are assumed to have Arrhenius forms $K_{diss} = K_{diss0}e^{-\varepsilon_{diss}/T_e}, K_{iz} = K_{iz0}e^{-\varepsilon_{iz}/T_e}$ (ε_{diss} (=9.8 eV) and ε_{iz} (=15.5 eV) are the threshold energies for dissociation and ionization reactions), then K_{diss} and K_{iz} decrease with decreasing electron temperature (K_{iz} has a steeper variation).

Figure 6 shows that T_e remains unchanged or decreases slightly and that n_e increases as the power is increased. However, in Eq. (6), both $K_{iz}n_e$ and $K_{diss}n_e$ increase; therefore, the degree of dissociation is expected to remain unchanged with increasing power. The figure shows that T_e decreases whereas n_e increases as the pressure is increased. However, in Eq. (6), $K_{iz}n_e$ decreases dominantly over $K_{diss}n_e$; therefore, the degree of dissociation may increase with increasing pressure. In comparison with Figure 4, the D_{QMS} and the D_{OES} exhibit similar trends as functions of pressure. In general, higher power results in a higher electron density and, thus, a higher dissociated neutral atom density. However, in the parameter region of 1 – 10 mTorr and 250 – 500 W, the degrees of dissociation decrease slightly with power.

IV. CONCLUSION

By using OES actinometry, the degree of dissociation is evaluated to be between 1 % and 3.5 % for an inductively coupled nitrogen plasma with pressures of 1 – 10 mTorr. The degree of dissociation is found to gradually increase with pressure and to decrease slightly with power. The pressure dependences of the degree of dissociation measured by using OES and QMS show similar trends. As the pressure increases, the degrees of dissociation measured by using OES and QMS are increased. However, the power dependences of the degree of dissociation measured by using OES and QMS exhibit slightly different behaviors. As the power increases, the degree of dissociation given by using OES is slightly decreased whereas the degree of dissociation given by using QMS shows no appreciable changes. Although the electron density increases with power, the number of electrons with higher energy does not change (or is slightly decreased). The main cause of the decrease in the electron temperature with increasing power is that the high-energy electrons are depleted to the wall. Therefore, the electron-impact dissociation reaction is slightly decreased with power in the pressure region from 1 mTorr to 10 mTorr. The magnitude of the degree of dissociation measured by using the QMS is larger than that measured by using the OES actinometry. The degree of dissociation at various powers and pressures in this study seems reasonable when compared with other studies [5, 8,13].

ACKNOWLEDGMENTS

This work was supported by the research fund of Dong-A University.

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