Optical and Langmuir Probe Diagnostics of Low-pressure Inductively Coupled Nitrogen-Argon Plasmas

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Abstract: Low-pressure inductively coupled discharge in a N₂-Ar has been studied to investigate the discharge structure under different operation conditions. By means of optical emission and probe diagnostic techniques, the concentrations of species of interest, electron temperature, and their variations with different conditions have been investigated. Dissociation fraction, rotational and vibrational temperatures of nitrogen molecules are obtained for various discharge conditions.

Keywords: inductively coupled nitrogen-Ar plasma, optical emission, Langmuir probe.

1. Introduction

Due to the wide applications of plasma processes involving nitrogen, much effort has been devoted to study the nitrogen plasma. Since the atomic nitrogen plays a key role in the synthesis of nitrides, the concentration of atomic nitrogen in the nitrogen plasma is the significant concern [1]. Electric discharges produced either by microwaves, helicon waves or radio frequency (rf) power are commonly used for generating nitrogen atoms [1, 2]. Recently, there has been a steadily growing interest in the application of inductively coupled plasma (ICP) sources for numerous plasma-enhanced materials processing.

One of the promising ways to enhance the dissociation of molecular nitrogen is to introduce another gas such as hydrogen and argon in the plasma [1]. The determination of the N atom density as a function of applied rf power and pressure is essential in the understanding and optimization of the plasma process for micro-electronics materials. The purpose of this work is to optimize operational parameters of inductively coupled N₂/Ar discharges for maximum dissociation rates [3]. In view of all plasma processes involving nitrogen, it is therefore of importance to develop accurate and reliable diagnostic techniques to monitor the properties of N₂/Ar discharges [3, 4]. By means of optical emission and probe diagnostic techniques, the plasma parameters and the concentrations of species of interest are obtained. Their variations with pressure, rf power, and Ar content have been investigated. Dissociation fraction, rotational and vibrational temperatures of nitrogen molecules are obtained for various discharge conditions.

2. Experiment

A schematic diagram of the experimental setup with the diagnostics system (optical emission spectroscopy (OES)), and Langmuir probe) is shown in Fig. 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. A 13.56 MHz generator (ENI OEM 12) drives an rf current in a flat one-turn coil through the rf power generator and matching network. To the nitrogen discharges generated, the argon was mixed as either an actinometer or as an adding gas. The percentage of argon flow was varied in the range of 5 ~70 % 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 probe. Both diagnostics complement one another to determine
plasma parameters [5]. The experiments were conducted under the conditions of pressures in the range of 1-30 mTorr and the applied rf powers in the range of 200 - 500 W.

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 light was collimated at the exit slit where a photomultiplier tube converted photons into an electric signal. We obtain the dissociation fraction using the integrated intensity of peaks of the emission spectra. And we obtain the electron density, the electron temperature and the electron energy probability function (EEPF) via Langmuir probe.

3. Results and Discussion

A representative optical emission spectrum from the ICP nitrogen-argon plasma is shown in Fig 2. Most of the peaks and bands originate from the transition \( \text{N}_2 (C) \rightarrow \text{N}_2 (B) \), namely the second positive system. The varieties of lines and band structures originate in the numerous rotational and vibrational levels between which transitions can occur. Two other features are present. They are transition at 391.4 nm (the first negative system, \( \text{N}_2 (B) \rightarrow \text{N}_2 ^+ (X) \)) and the appearance of the first positive system (the transition between \( \text{N}_2 (B) \) and \( \text{N}_2 (A) \)).

For optical emission actinometry, spectral lines and bands from \( \text{N}_2 (337.1 \text{ nm}, (C,0) \rightarrow (B,0)), \text{N}_2 ^+ (391.4 \text{ nm}, (B,0) \rightarrow (X,0)), \text{N} (746.8 \text{ nm}, 3p^5 3s^2 3p^4 1s^2 3p^6 \rightarrow 3s^2 3p^6), \text{Ar} (750.4 \text{ nm}, 2p^5 1s^2), \) and \( \text{Ar} (811.53 \text{ nm}, 2p^5 1s^2) \) are chosen. The effects of Ar percentage, rf input power, and gas pressure on the emission intensity of the spectral lines are investigated. The effect of the percentage of argon flow was examined in the range of 5 \( \sim \) 70 % in the OES experiment. Figure 3 shows the effects of Ar percentage, rf input power, and gas pressure on the emission intensity of the spectral lines.

The assumption that the discharge is in a corona balance has allowed us to use a modified Boltzmann plot method to determine the values of \( T_e \) as a function of different processing parameters of interest such as the discharge pressure, initial argon content and the applied rf power [8, 9]. Figure 3(a) represents the variations of \( T_e \) as a function of the power at 1.4 mTorr and (b) shows \( T_e \) as a function of the pressure in plasmas excited with 350W both with an initial 5% of argon in the incoming flow.

The electron temperature obtained by a single Langmuir probe has a similar trend of variation to \( T_e \) measured by OES.

Fig. 2: A representative optical emission spectrum from ICP \( \text{N}_2/\text{Ar} \) discharges (the Ar content 5 %).

Fig. 3: Electron temperature measured by OES (a) as a function of power and (b) as a function of pressure.
The gas temperature ($T_g$) is an important parameter since it must be known to determine neutral densities and ion-neutral mean free path. The gas temperature of the N$_2$/Ar discharge can be deduced from the rotational temperature ($T_{rot}$) of N$_2^+$, which is expected to be in equilibrium with $T_g$. The rotational temperature of a molecule can be obtained by comparing the synthetic diatomic molecular spectrum with measured one [10, 11]. The N$_2^+$ first negative system band from 390 nm and 392 nm for the 391.44 nm line is fitted to obtain N$_2^+$ rotational temperature.

To obtain the best fit between the experimental and the synthetic spectral bands, a least-square procedure is used. A typical fitting of the measured first negative (0,0) band spectrum with the synthetic spectrum is shown in Fig. 4. Good agreement between the measured spectrum and the synthetic suggests reasonable evaluation of $T_{rot}$. In Fig. 5, rotational temperature within 95% N$_2$ - 5%Ar discharge are plotted. As expected, the gas temperature shows an increase as both the applied power and the pressure are increased.

The variations of the vibrational temperature of nitrogen molecules with the applied power and gas pressure are also investigated. As shown in Fig. , the vibrational temperature increases with pressure and rf power. This can be accounted for from the observation that N$_2$ molecules in the plasma have considerable populations in the excited vibrational levels [10, 12]. As the Ar content is increased, an impact of metastable Ar leads to a higher density of vibrationally excited N$_2$ molecules. This effect plays a more important role if the collision rate is increased by higher pressure.

The characteristics of inductively coupled N$_2$/Ar plasma were investigated by using double Langmuir probe (DLP) under the conditions of pressure kept at 1.4 mTorr and applied powers in the range of 200 – 500 W. The effect of the percentage of argon flow was examined in the range of 0 – 100 % in the Langmuir probe experiment. The electron density, the ion density and the electron temperature were obtained by using double Langmuir probe in order to investigate the influence of the plasma parameters on the dissociation fraction. The electron and ion density were found to increase with increasing applied rf power and the argon fraction. The electron temperature decreased with the increasing applied rf power and the argon fraction. The ion density had values ranging from $3.52 \times 10^9$ to $1.12 \times 10^{11}$/cm$^3$ and the electron temperature had values ranging from 4.47 to 5.37 eV.

![Fig. 4: Rotational temperature as a function of (a) power and (b) pressure.](image)

![Fig. 5: Vibrational temperature as a function of (a) pressure, (b) power, and (c) Ar content.](image)

![Fig. 6: Double Langmuir probe measurement of (a) the ion density and (b) the electron temperature as a function of Ar content. The gas pressure is fixed at 1.4 mTorr and the power is varied from 200 W to 500 W.](image)
The dissociation fraction was measured by using OES actinometry (5 % Ar) [7].

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\frac{[N]}{[N_2]} = \frac{R_{750} \nu_{250} A_{250} k_{Ar} \tau_{Ar} [Ar]}{R_{746} \nu_{246} A_{246} k_N \tau_N [N_2]} I_{750}
\]

Here R is the spectral response of the system, A is the emission probabilities, \( \nu \) is the frequency of the transition, \( \tau \) is the life time which is the inverse of the sum of the emission probabilities for all the radiative de-excitation processes, k is the excitation coefficient, and I is the line intensity. The pressure was varied from 1.4 to 30 mTorr and the power was fixed at 500 W. The dissociation fraction (\([N (2p \ ^{4}S_0)] / [N_2]\)) was found to have values ranging from 7.9 to 10.8 % measured by the OES actinometry.

Fig. 7: Dissociation fraction as a function of pressure.

Although not shown in figure, it was found that the dissociation fraction increased with increasing applied rf power and the Ar gas fraction up to 20 % while it increased firstly with increasing pressure and then decreased. For discharges with higher Ar contents, the density of the metastable Ar may become important and, as a consequence, the Ar (2p) state is created from the metastables by electronic collisions, and the actinometry may become invalid [13]. However, the metastables of argon are efficiently quenched by N\(_2\) and N, and the production of these states in the low-pressure discharge is not significant except for a case of very high Ar content. The contribution to excited states of Ar (2p) and N (3p \(^{4}S_0\)) from other route than from the ground state should be considered to fully exploit the actinometry techniques. If the correction factor (to \( k_{Ar} \) and \( k_N \)) is cleverly utilized, it is possible to estimate the dissociation fraction for higher Ar content by actinometry.

4. Conclusion

This study reports measurement of the dissociation fraction, the electron temperature, the rotational and vibrational temperature by optical emission spectroscopy. Along with these, Langmuir probe measurement was also performed. The electron and ion density were found to increase with increasing applied rf power and the argon fraction. The electron temperature decreased with the increasing applied rf power and the argon fraction. The electron temperature obtained by a single Langmuir probe has a similar trend of variation to \( T_e \) measured by OES. The gas temperature shows an increase as both the applied power and the pressure are increased. The vibrational temperature of N\(_2\) increases with the pressure and the rf power. For the pressure range of 1.4 - 30 mTorr, the dissociation fraction first increased and had a peak at 11 mTorr, thereafter, slightly decreased or saturated. The estimation of dissociation fraction for a discharge with higher Ar content by OES actinometry is our next task.

References