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Control and analysis of ion species in inductively coupled nitration plasma using a grid system

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We control the ion density ratio of $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ with the voltage-biased grid system in inductively coupled nitration plasma. The ion density ratio is controlled from 0.39 to 0.04 with decreasing grid-biased voltage. We try to analyze the variation of the ion density ratio using the measured plasma parameters and particle balance equation. The important factor determining the ion ratio is the plasma potential difference between the source region—where plasma is generated—and the diffusion region—where the electron temperature is controlled. When the plasma potential is higher in the source region than in diffusion region, the ion density ratio is determined by the electron temperature in Region I. Inversely, the ion density ratio is determined by the electron temperature in Region II, when the plasma potential is higher in Region II than in Region I. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2056595]

Plasma is widely used for semiconductor device processing, and as the design rule becomes smaller and smaller, fine control of processing becomes very important. The processing results are affected by the radical or ion density and their ratio which strongly depends on the plasma parameter, such as the electron density, self-bias voltage, and electron temperature. Among them, the electron temperature is the most important parameter determining the density ratio of radical and ion. For example, the radical density ratio of CF_2 to F, which is a key factor determining the SiO_2 etching selectivity to Si is inversely proportional to the electron temperature.[1] The ion density ratio of N^+ to N_2^+ is ($[\mathrm{N}^+]/[\mathrm{N}_2^+]$) also a strong function of the electron temperature.[2] So, controlling the electron temperature is very important for fine control of processing. Generally, the electron density increases with the input power, so it is easy to control and we can obtain a various range of the electron density at any condition. On the contrary, controlling the electron temperature is very difficult, because it is a strong function of the operating pressure, so changing the electron temperature at fixed pressure is very difficult. There are a few methods to control the electron temperature: Ashida *et al.*[3] decreased the electron temperature using pulse-modulated input power. Bai *et al.*[4] controlled the electron temperature in inductively coupled plasma (ICP) with mixing inert gases (He, Ar, and Xe). They have tried to analyze the electron temperature variation as a function of the inert gas mixing ratio using the two-ion-species global model.[4] Another method of controlling the electron temperature is using a grid which is inserted in a chamber and biased with dc voltage.[5–7] Interestingly, there are many results about the electron temperature control using the grid, but there are no results which report the ion density ratio control using the grid method, which raises some questions about whether the grid method can be used for controlling the ion or radical density ratio. In this letter, we try to control the ion density ratio with the grid method in a N_2/Ar mixture inductively coupled nitration plasma. We also try to analyze the ion density ratio variation with the measured plasma parameters and particle balance equation.

The ICP reactor used in this experiment is described in a previous paper.[7] There is a dc-biased grid (noted as ϕ_g) in the middle of the chamber to divide the chamber into the source region (Region I) and the diffusion region (Region II). The plasma is generated in Region I and diffuse to Region II, where the electron temperature and ion density ratio are controlled with the biased grid. Another grid (noted as ϕ_s) is set up on the bottom of the chamber to control the plasma potential in Region II. Additionally, we set up a quadrupole mass spectrometer (QMS) (Hiden EQP) on the side wall of the chamber in the Region II to measure the ion density. We measure the ion energy distribution functions using the QMS and integrate it to obtain the ion density. Electron energy probability functions are measured using radio-frequency-compensated Langmuir probe to measure the effective electron temperatures ($T_{\mathrm{eff}}=2/3\langle\varepsilon\rangle$), electron densities [$n_e=\int f(\epsilon)d\epsilon$], and plasma potentials in each regions. The probe consists of the measurement probe of 4 mm long, floating-loop reference probe with a resonant filters.[8] We use the ac measurement technique[9,4,6] with a lock-in amplifier, because it has the advantage of low output noise. All of the experiments in this letter are done in a N_2/Ar mixture of 10 mTorr plasma, and their partial pressure is 2 mTorr and 8 mTorr, respectively. The input power is fixed at 600 W and ϕ_s is fixed at 35 V.

Figure 1 shows the ion density ratio ($[\mathrm{N}^+]/[\mathrm{N}_2^+]$) and electron temperature (T_{II}) variations as a function of the grid bias voltage (ϕ_g) in Region II, which shows that we can control the ion density ratio of ($[\mathrm{N}^+]/[\mathrm{N}_2^+]$) using the grid method. We can divide $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ variation profile into three regimes as denoted in the Fig. 1. In Regime 1, $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ has an almost constant value of 0.25. In Regime 2, it increases dramatically with decreasing ϕ_g and has the maximum value of 0.39 at $\phi_g=-10$ V. In Regime 3, $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ decreases sharply and reaches a minimum value of 0.039 with decreasing ϕ_g. The variation profile of T_{II} is almost similar to that of

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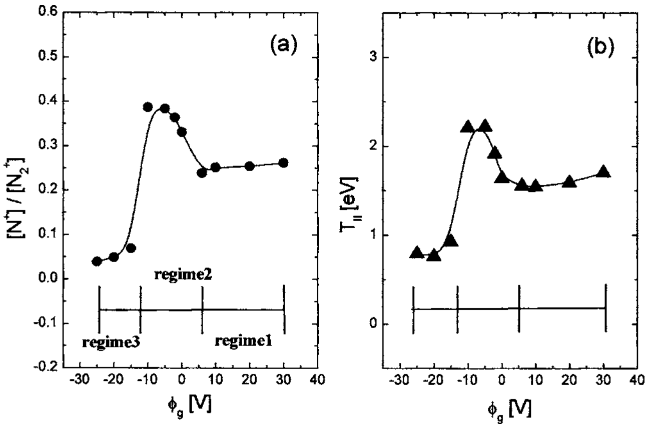

FIG. 1. The measured ion density ratio of N^+ to N_2^+ and electron temperature T_{II} in Region II as a function of grid bias voltage ϕ_g.

$[N^+]/[N_2^+]$. Bai *et al.*[4] reported that $[N^+]/[N_2^+]$ is a function of the electron temperature as follows:

$$\ln[N^+]/[N_2^+] = -8.7 \times \frac{1}{T_e} + C, \tag{1}$$

where C is a constant which depends on the ionization cross section, mass, and the mean-free path of the two ions. So, the similar variation profiles of $[N^+]/[N_2^+]$ and T_{II} look reasonable. However, we should be more careful to analyze $[N^+]/[N_2^+]$ in Region II, because there are two kinds of ions in Region II: One is ions coming from Region I and the other is ions generated in Region II. So, the ion density ratio cannot be explained simply by Eq. (1) alone. Actually, the ion density ratio is too large compared with the values in Ref. 2 in Regime 1 ($\phi_s \geqslant 6$ V)$:[N^+]/[N_2^+]$ is about 0.25 at $T_{\text{II}} = 1.6$ eV, but in Ref. 2, T_e should be higher than 2.5 eV to obtain the ion density ratio of 0.25. So, more analysis is necessary to explain the variation of the ion density ratio.

When there is a grid, sheath is generated around the grid wires, and the interface between Regions I and II can be divided into three regions: sheath-free region, sheath region, and grid region. $\alpha_i, i=0,1,2$ note their area ratio to the area of the interface between Regions I and II, respectively, and ions in Region I can diffuse to Region II only through the sheath-free region with their sound speed.[5] So, the ion production rate in Region II ($P_{\text{II},x}$) is the sum of the ion flux from Region I (Γ_{I}) and ionization rate in Region II, which can be expressed as follows:

$$P_{\text{II},x} = S_g \alpha_0 \Gamma_{\text{I},x} + \Omega_{\text{II}} n_g n_{\text{II}} K_{\text{II},x},$$

$$= S_g \alpha_0 a_{\text{I}} n_{\text{I},x} \sqrt{\frac{T_{\text{I}}}{M_x}} + \Omega_{\text{II}} n_g n_{\text{II}} K_{\text{II},x}, \tag{2}$$

where S_g is the area of the interface between Regions I and II, Ω_{II} is the volume of region II, n_g is the neutral number density of N_2, and $K_{\text{II},x}$ is the ionization coefficient of Region II. In this letter, $x=1,2$ for N^+ and N_2^+, respectively. $a_{\text{I}} = 0.61$ at the grid sheath boundary is given from the Boltzmann relation.[10] We assume that all ions directed to α_1 or α_2 cannot go into Region II, but they are collected to grid.[5] By the particle balance equation,

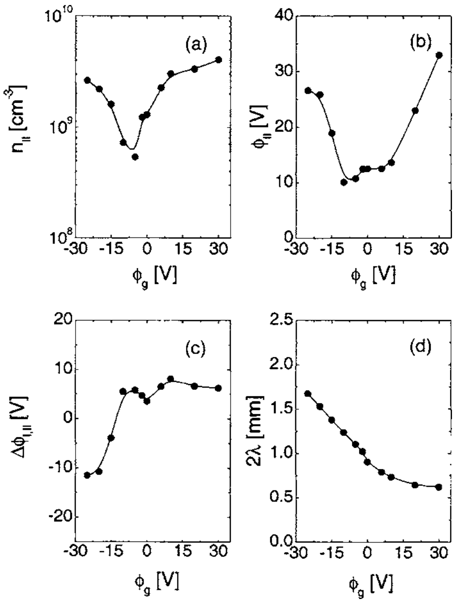

FIG. 2. The measured plasma parameters in Region II as a function of the grid bias voltage: (a) electron density n_{II} (b) plasma potential in Region II ϕ_{II}, (c) potential difference between the Regions I and II ($\Delta\phi_{\text{I,II}} = \phi_{\text{I}} - \phi_{\text{II}}$), and (d) sheath length (2λ) around grid wires as a function of ϕ_g.

$$[S_g + S_{\text{I}}] a_{\text{I}} n_{\text{I},x} \sqrt{\frac{T_{\text{I}}}{M_x}} = \Omega_{\text{I}} n_g n_{\text{I}} K_{\text{I},x}, \tag{3}$$

where S_{I} is the surface area of Region I except the grid area. In our experiment, $S_{\text{I}} = 5.3 S_g$, insert this condition in Eq. (3), we can obtain the ion flux diffusing into Region II as follows:

$$S_g \alpha_0 a_{\text{I}} n_{\text{I},x} \sqrt{\frac{T_{\text{I}}}{M_x}} = \frac{1}{6.3} \alpha_0 \Omega_{\text{I}} n_g n_{\text{I}} K_{\text{I},x}. \tag{4}$$

Inserting Eq. (4) into Eq. (2), Eq. (2) is deduced as follows:

$$P_{\text{II},x} = \frac{1}{6.3} \alpha_0 \Omega_{\text{I}} n_g n_{\text{I}} K_{\text{I},x} + \Omega_{\text{II}} n_g n_{\text{II}} K_{\text{II},x}. \tag{5}$$

In Eq. (5), the first term in on the right-hand side is the ion production rate in Region II caused from the flux diffusing from Region I, and the second term is the ion production by the ionization in Region II. We can calculate their ratio (R_x, $x=1$, 2 for N^+ and N_2^+, respectively) from Eq. (5) as follows:

$$R_x = \frac{\alpha_0 \Omega_{\text{I}} n_{\text{I}} K_{\text{I},x}}{6.3 \Omega_{\text{II}} n_{\text{II}} K_{\text{II},x}},$$

$$= \frac{\alpha_0 n_{\text{I}}}{18.5 n_{\text{II}}} \sqrt{\frac{T_{\text{I}}}{T_{\text{II}}}} \cdot e^{\varepsilon_{iz,x}(T_{\text{I}} - T_{\text{II}})/T_{\text{I}} T_{\text{II}}}, \tag{6}$$

where we insert $\Omega_{\text{I}} = 5921$ cm^3 and $\Omega_{\text{II}} = 17404$ cm^3, and $K_x = \sigma_0 (8eT/\pi m)^{1/2} e^{-(1+2T/\varepsilon_{iz,x})} \simeq \sigma_0 (8eT/\pi m)^{1/2} e^{-\varepsilon_{iz,x}/T}$. $\sigma_0 = \pi(e/4\pi\epsilon_0 \varepsilon_{iz,x})^2$. m and e are the electron mass and charge, respectively. $\varepsilon_{iz,x}$ is the ionization threshold energy.

We can calculate R_x, using the measured plasma parameters which are shown in Fig. 2. The electron density and temperature in Region I have an almost constant value of 3.2×10^{10} cm^{-3} and 3.2 eV, respectively. In the Regime 1 ($\phi_g \geqslant 6$ V), R_x is larger than 7.0 as shown in Fig. 3, which

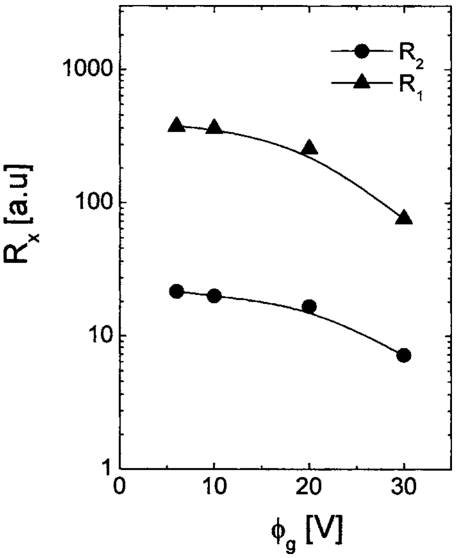

FIG. 3. The ion production ratio of the ion flux diffusing from Region I to the ionization rate in Region II (R_x) as function of ϕ_g in Regime 2.

means that the second term in Eq. (5) or Eq. (2) is negligible. In other words, most ions in Region II come from Region I, and contribution by the ionization in the Region II is negligible. Thus, Eq. (2) can be deduced as follows:

$$P_{\mathrm{II},x} \simeq S_g \alpha_0 a_{\mathrm{I}} n_{\mathrm{I},x} \sqrt{\frac{T_{\mathrm{I}}}{M_x}}. \tag{7}$$

The ion density of each ion is proportional to its production rate and inversely proportional to loss rate, and the main loss process is the diffusion to the chamber wall in our experiment due to low pressure.[2] Thus, we can obtain the ion density ratio of $[\mathrm{N}^+]$ to $[\mathrm{N}_2^+]$ as follows:

$$\frac{[\mathrm{N}^+]}{[\mathrm{N}_2^+]} = \frac{P_{\mathrm{II},1} u_{B,2}}{P_{\mathrm{II},2} u_{B,1}} \simeq \frac{S_g \alpha_0 a_{\mathrm{I}} n_{\mathrm{I},1} \sqrt{\dfrac{T_{\mathrm{I}}}{M_1}}}{S_g \alpha_0 a_{\mathrm{I}} n_{\mathrm{I},2} \sqrt{\dfrac{T_{\mathrm{I}}}{M_2}}} \cdot \frac{\sqrt{\dfrac{T_{\mathrm{II}}}{M_2}}}{\sqrt{\dfrac{T_{\mathrm{II}}}{M_1}}},$$

$$= \frac{n_{\mathrm{I},1}}{n_{\mathrm{I},2}}. \tag{8}$$

So, in Regime 1, the ion density ratio $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ in Region II has the same value as that of Region I, and is determined by the electron temperature in Region I not in Region II. Though we cannot measure the ion density ratio in Region I due to its complex geometry, we can guess their values from our previous paper of Ref. 2. At the same discharge conditions (pressure, power, and Ar mixing ratio) except for the absence of the grid, $[\mathrm{N}^+]/[\mathrm{N}_2^+] \simeq 0.26$,[2] which is almost the same value when $\phi_g \geqslant 6$ V in the Region II with the grid system.

In the case of $\phi_g \leqslant -15$ V (Regime 3), $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ drops rapidly with decreasing ϕ_g, and is low ($\leqslant 0.07$). In Regime 3, the plasma potential in Region II is higher than in Region I, which prevents the ions in Region I from diffusing into Region II. So, the first term in Eq. (5) becomes 0, and the ion ratio of $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ is determined by Eq. (1) and the electron temperature in Region II, not in Region I. The low value of $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ in Regime 3 is due to the low electron temperature in Region II.

In Regime 2 ($-15 \text{ V} < \phi_g < 6$ V), both the ion density ratio and the electron temperature in Region II (T_{II}) increase with decreasing ϕ_g. In this regime, $\Delta\phi_{\mathrm{I,II}}$ ($\phi_{\mathrm{I}} - \phi_{\mathrm{II}}$) is still positive and the ions can diffuse from Region I to Region II. The difference between Regimes 1 and 2 is that the sheath length increases almost linearly with decreasing ϕ_g in Regime 2. We assumed that all ions entering the sheath region or grid region cannot go into Region II, but they are collected to the grid. Actually some portion of the ions can diffuse into Region II, and the portion of the ions diffusing into Region II is determined by the ion mass, electric field profile in the sheath, and the initial velocity of the ions when they entered the sheath. So, the ion flux entering Region II can be changed by their mass or the increasing sheath, and we guess that the expanding sheath can be the reason for the increase in the ion density ratio. However, we cannot explain the increase in the ion density ratio exactly, and more study is necessary.

We can control the ion density ratio of $[\mathrm{N}^+]/[\mathrm{N}_2^+]$ from 0.39 to 0.04 as well as the electron temperature using the grid method in inductively coupled nitration plasma. The important factor determining the ion density ratio in Region II is the plasma potential difference between Regions I and II ($\Delta\phi_{\mathrm{I,II}}$), as well as the electron temperature in Regions I and II. When $\Delta\phi_{\mathrm{I,II}} > 0$, the ion density ratio in Region II is determined by the electron temperature in Region I, not in Region II. To decrease the ion density ratio, the plasma potential should be higher in Region II than in Region I, thus the ions in Region I must not diffuse to Region II. The ion density ratio increases to a higher value than that of Region I in spite of the lower electron temperature in Region II, and the expanding sheath can be the reason for that. However, more study is necessary to explain the increase in the ion ratio.

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