AIP Applied Physics Letters

Control and analysis of ion species in N2 inductively coupled plasma with inert gas mixing

K. H. Bai, D. S. Lee, H. Y. Chang, and H. S. Uhm

Citation: Appl. Phys. Lett. **80**, 3907 (2002); doi: 10.1063/1.1479452
View online: http://dx.doi.org/10.1063/1.1479452
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v80/i21
Published by the American Institute of Physics.

APPLIED PHYSICS LETTERS VOLUME 80, NUMBER 21 27 MAY 2002

Control and analysis of ion species in N_2 inductively coupled plasma with inert gas mixing

K. H. Bai,[a] D. S. Lee, and H. Y. Chang
Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701, South Korea

H. S. Uhm
Department of Molecular Science and Technology, Ajou University, Suwon 442-749, South Korea

(Received 4 February 2002; accepted for publication 20 March 2002)

We control the ion density ratio of $[N^+]/[N_2^+]$ and investigate the relation between the ion ratio and the plasma parameters in inductively coupled plasma. We measure the electron energy distribution functions and the ion ratio in a N_2/He, Ar, Xe mixture system as a function of mixing ratio. We can control the ion ratio from 0.002 to 1.4, and the ion ratio is a strong function of electron temperature. We can calculate the ion ratio using a simple model, and the obtained results agree well with the measured values in N_2/He, Ar, but there is a large discrepancy in the N_2/Xe discharge. The non-Maxwellian structure of the electron energy distribution functions may be the reason for the discrepancy. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1479452]

The inductively coupled plasma (ICP)[1–4] has attracted much interest due to its ability to produce high density plasma in low pressure, and there have been numerous investigations of ions in ICP.[5–7] Recently, there has been great interest in the N_2 discharge due to its use in the synthesis of GaN and TiN film. In a pure N_2 ICP, the dissociation rate is small due to strong N–N bond strength,[8] and Ar is mixed to increase the dissociation rate.[9] The ion density ratio of N_2^+ to N^+ is also small in pure N_2 discharge, and Y. Wang *et al.* and Petrov *et al.* have reported that the ion ratio increases when Ar is mixed.[10,11] The reactions of Ar metastable species (Ar*) with N_2^+ and N^+ are considered to be the cause of the increase in the ion ratio. However, N_2^+ is still a dominant ion like for the capacitively coupled plasma.

The ion ratio in the plasma is a function of the plasma parameters. However, there have been few analysis, without using simulation, on the relation between the plasma parameters and the ion ratio in the mixture of N_2 and inert gases.

In this paper, we mix various inert gases (He, Ar, Xe) in a N_2 plasma to control the plasma parameters. We measure the electron energy distribution functions (EEDFs) to obtain plasma parameters and measure ion species (N_2^+, and N^+) using a commercial quadrupole mass spectrometer (Hiden EQP) to analyze the relation between the plasma parameters as a function of mixing ratio. We also calculate the ion ratio using a simple model.

The ICP reactor used in this study is similar to that in Ref. 12. However, we modified the system slightly: We removed the grid and stainless steel cylinder which holds the grid, and we set up a quadrupole mass spectrometer (QMS, Hiden EQP) on the side wall of the chamber. We set an rf-compensated Langmuir probe[13] at $z=16$ cm and QMS at $z=5$ cm, where $z=0$ at the substrate, and measured the EEDFs $[f(\epsilon)]$, effective electron temperatures $[T_{\mathrm{eff}}=\frac{2}{3}\langle\epsilon\rangle]$, electron densities $[n_e=\int f(\epsilon)d\epsilon]$, and plasma potentials, where ϵ is the electron energy. In this experiment, we fix the total pressure at 10 mTorr in all cases. 13.56 MHz rf power is coupled to a single-turn copper coil around the pyrex cylinder, and a matching network is used to eliminate the reflected power. We use the ac measurement technique[14–17] with a lock-in amplifier, because it has the advantage of low output noise. Ions enter the QMS after passing through the orifice, which is 100 μm in diameter. We measure the ion energy distributions (IEDs) using a QMS and obtain ion density by integrating the IEDs.

Figure 1 shows the measured plasma parameters and the ion density ratio of $[N^+]/[N_2^+]$ as a function of He mixing ratio. The electron density is almost constant, but the electron temperature increases from 2.2 eV to 8 eV when He is mixed. Generally, the electron temperature is inversely proportional to the ionization cross-section of discharge gas. The increase in the electron temperature with He mixing is due to the small cross-section of He. The electron temperature is almost constant near a He mixing ratio $\kappa=0$, and it increases rapidly near $\kappa=1$, where $\kappa=P_{\mathrm{He}}/P_{\mathrm{N_2+He}}$ is the mixing ration of He in N_2. The electron temperature increases in a similar way when He is mixed to Ar plasma.[12] Compared to N_2, He has a high ionization threshold energy, small ionization cross-section, and small mass. Hence, when the He mixing ratio is small, He is not ionized efficiently and the discharge shows almost N_2 plasma characteristics. The electron temperature decreases more effectively when the mixed gas has a high ionization threshold energy, large ionization cross-section and large mass due to its high ionization rate and slow Bohm velocity, and vice versa.[12] Thus the electron temperature does not increase effectively by slight He mixing. On the contrary, slight N_2 mixing to He plasma results in a large decrease in the electron temperature.

The plasma potential and the ion ratio of $[N^+]/[N_2^+]$ increase in a similar way to the electron temperature. The ion ratio of $[N^+]/[N_2^+]$ increases from about 0.1 to 1.4.

Figure 2 shows the results when Ar is mixed. Conversely to the He mixed case, the electron density shows a large increase (from about 7×10^9 to 4×10^{10}), but the electron temperature increases slightly (from 2.2 to 2.8 eV) with Ar mixing. The ion ratio of $[N^+]/[N_2^+]$ increases with the Ar

---

[a] Electronic mail: bazarofe@kaist.ac.kr

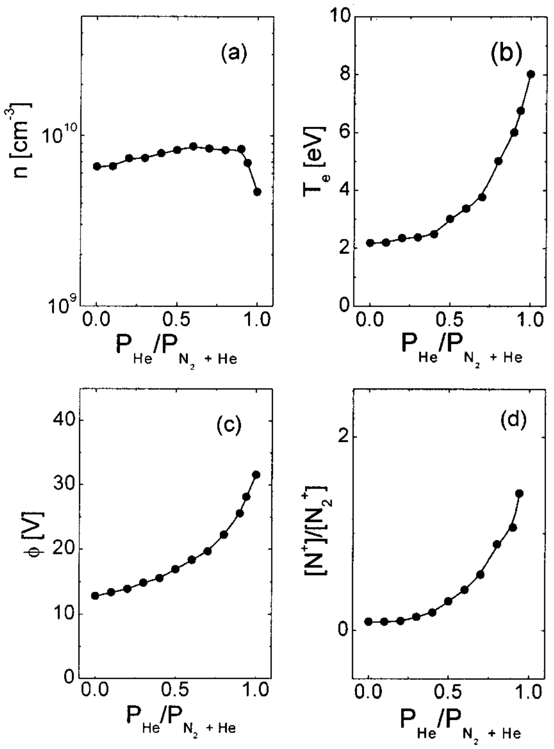

FIG. 1. The measured plasma parameters. (a) electron density, (b) electron temperature, (c) plasma potential, and (d) ion ratio of $[N^+]/[N_2^+]$ as a function of He mixing ratio.

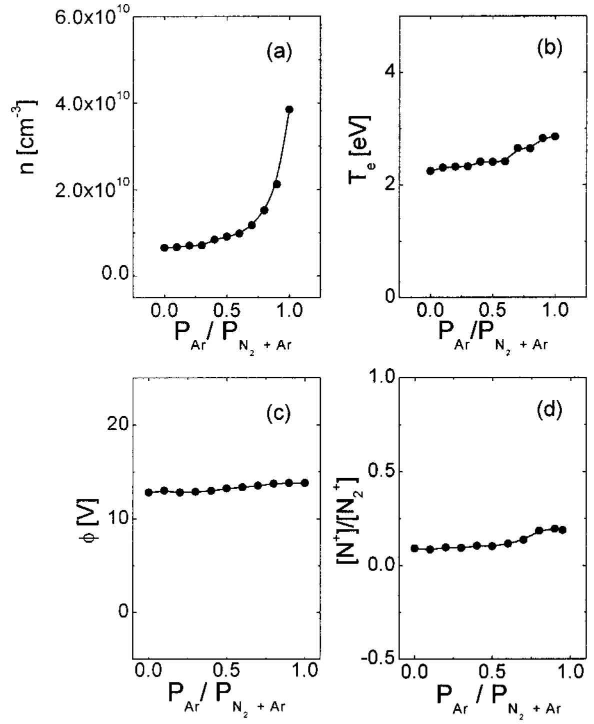

FIG. 2. The measured plasma parameters. (a) electron density, (b) electron temperature, (c) plasma potential, and (d) ion ratio of $[N^+]/[N_2^+]$ as a function of Ar mixing ratio.

mixing ratio. Similar results were reported in Ref. 10. In spite of the large increase of the electron density, the increase rate of $[N^+]/[N_2^+]$ is small, which suggests that $[N^+]/[N_2^+]$ is a strong function of the electron temperature rather than the electron density in our experimental conditions.

Figure 3 shows the variation of the plasma parameters and $[N^+]/[N_2^+]$ as a function of Xe mixing ratio. The electron density increases in a similar trend to the Ar mixed case. However, the increase rate is larger than in the N_2/Ar mixture due to the larger ionization cross section of Xe. The electron temperature decreases abruptly near a Xe mixing ratio of 0, but the decrease rate is small when the mixing ratio is large. As phenomenon is also shown in the Ar/Xe mixture, which results from the large ionization cross section and large mass of Xe.[12] The ion ratio of $[N^+]/[N_2^+]$ shows a similar trend to that of the electron temperature. Unfortunately, we can not measure the $[N^+]/[N_2^+]$ when the Xe mixing ratio is larger than 0.6 due to the small signal of $[N^+]$.

The ion density is proportional to the creation rate and inversely proportional to the loss rate of the ion. We assume that $N_2+e\rightarrow N_2^+ +2e$:15.6 eV, and $N_2+e\rightarrow N^+ + N + 2e$:24.3 eV[18] are the dominant creation processes of N_2^+, N^+. N_2 metastable species (N_2^*) also contributes to the creations of N_2^+, N^+; however, the ratio of $[N_2^*]/[N_2]$ is usually small, and the above assumption is reasonable. Another assumption is that the dominant loss process of ions is diffusion to the chamber wall. Actually, there are many loss reactions of N_2^+ and N^+: for N_2^+, $N_2^+ + e\rightarrow N+N$, $N_2^+ + e \rightarrow N_2$; for N^+, $N^+ + e\rightarrow N$, $N_2^+ + N\rightarrow N^+ + N_2$. But, their loss rate is smaller than wall loss rate by at least one order.[19] We can express the each ion density as

$$[N_2^+]\propto \frac{K_{N_2^+}}{u_{N_2^+}}, \quad \text{and} \quad [N^+]\propto \frac{K_{N^+}}{u_{N^+}}, \tag{1}$$

where subscript N_2^+ and N^+ denote the values of N_2^+ and N^+; K and u are the ionization rate constant and the Bohm velocity, respectively.

We can describe the ionization rate constant of each ion as

$$K_{N_2^+} = K_{0,N_2^+}\cdot e^{-15.6/T_e}, \quad \text{and} \quad K_{N^+} = K_{0,N^+}\cdot e^{-24.3/T_e}, \tag{2}$$

where K_0 is a constant which is a function of a cross section. From Eq. (1) and Eq. (2), we can express the ion density ratio of $[N^+]/[N_2^+]$ as

$$\begin{aligned} [N^+]/[N_2^+] &= Ce^{-8.7/T_e}, \\ \ln[N^+]/[N_2^+] &= -8.7\frac{1}{T_e}+C, \end{aligned} \tag{3}$$

where C is a constant and is a function of the mass ratio of N_2^+ to N^+, K_0, and effective plasma size.[20] Figure 4 shows that Eq. (3) agrees well with the experimental results in the He and Ar mixture cases, but there is a large discrepancy in the N_2/Xe mixture. Generally, the EEDF shows a two-temperature structure in inert gas discharge because inelastic collisions occur only in the high energy range; but in molecular discharge, inelastic collisions occur in the entire energy range and the EEDF shows a near-Maxwellian structure. In the mixture of a molecular and inert gases, the EEDF develops from a Maxwellian to two-temperature structure with inert gas mixing ratios.[21] Thus in N_2/Xe discharge, the EEDF is a two-temperature structure and the tail temperature (electron temperature in the high energy range) is lower than the bulk temperature (electron temperature in the low energy range). When we calculate $1/T_e$ in Fig. 4, we use the effec-

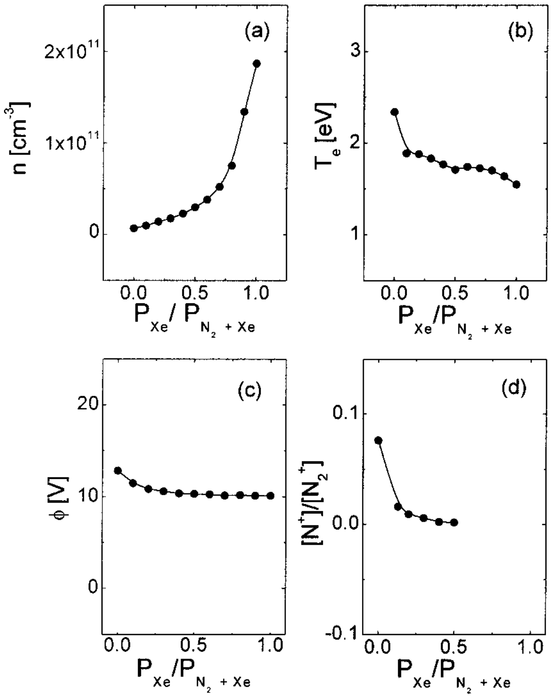

FIG. 3. The measured plasma parameters. (a) electron density, (b) electron temperature, (c) plasma potential, and (d) ion ratio of $[N^+]/[N_2^+]$ as a function of Xe mixing ratio.

tive electron temperature ($T_{\rm eff}=2/3\langle\epsilon\rangle$) which is similar to the bulk temperature, but the ionization reactions of N_2^+ and N^+ occur in the high energy range. So, in N_2/Xe mixture, $1/T_e$ in Fig. 4 is underestimated and, we believe, this can explain the more rapid decrease in the $[N^+]/[N_2^+]$ value. In the N_2/Ar mixture, the EEDF is also a two-temperature structure; however, compared to Xe, the inelastic cross section of Ar is small and the EEDFs may be more Maxwellian and the discrepancy between the measured and calculated values of $[N^+]/[N_2^+]$ is insignificant. Reactions between Xe and two ion species also can be the reason for the rapid decrease in $[N^+]/[N_2^+]$; however, we do not know the information about the reactions and more study is necessary.

We measured the EEDFs and the ion density ratio of $[N^+]/[N_2^+]$ in N_2/He,Ar,Xe mixture discharge as a function of mixing ratio to study the relations between the plasma parameters and the ion density ratio. $[N^+]/[N_2^+]$ is a strong function of the electron temperature, and the effect of the electron density is almost negligible in our experimental conditions. When He is mixed, the electron temperature increases from 2.2 to 8 eV and the $[N^+]/[N_2^+]$ increases from 0.1 to 1.4, but the electron density is almost constant. In N_2/Ar mixture, the increase rate in the electron temperature is small. Though the electron density increases by a factor of 5, $[N^+]/[N_2^+]$ increases by a factor of 2. The electron temperature and $[N^+]/[N_2^+]$ decrease, but the electron density increases by about 30 times when Xe is mixed. We propose a simple model to calculate $[N^+]/[N_2^+]$ as a function of the electron temperature, and the calculated values agree well with the measured values in the He and Ar mixture cases, but there is a large discrepancy in the N_2/Xe mixture discharge. The non-Maxwellian EEDF structure in N_2/Xe mixture may be the reason for the discrepancy. Reactions between Xe and ion species may be another reason, but more study is necessary. The agreement in He and Ar mixture provides potential support for the assumption that the EEDF is Maxwellian in this mixture system, which significantly simplifies models in discharge modeling. We think that the simple model suggested in this paper to calculate $[N^+]/[N_2^+]$ is useful in controlling $[N^+]/[N_2^+]$ in actual processing.

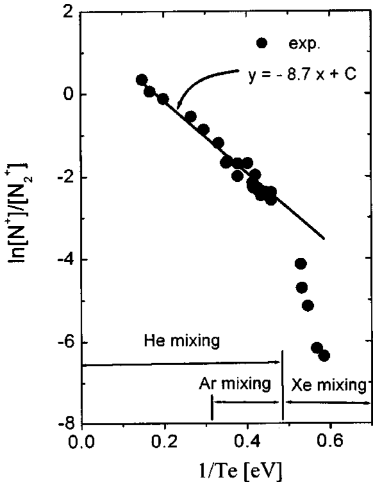

FIG. 4. Ion ratio of $[N^+]/[N_2^+]$ as a function of $1/T_e$ in various mixtures.

This work was sponsored in part by the Ministry of Science and Technology (MOST) and the Industry of Commerce, Industry and Energy (MOCIE). This work was also supported in part by National Research Laboratory Project of Korea. One of the authors is grateful to S. S. Kim in Korea Basic Science Institute for his help.

[1] J. Hopwood, Plasma Sources Sci. Technol. **1**, 109 (1992).
[2] J. H. Keller, J. C. Forster, and M. S. Barnes, J. Vac. Sci. Technol. A **11**, 2487 (1993).
[3] P. C. G. Ventzek, T. T. Sommerer, R. J. Hoekstra, and M. J. Kushner, J. Vac. Sci. Technol. B **13**, 461 (1994).
[4] R. B. Piejak, V. A. Godyak, and B. M. Alexandrovich, Plasma Sources Sci. Technol. **3**, 169 (1994).
[5] U. Kortshagen and M. Zethoff, Plasma Sources Sci. Technol. **4**, 541 (1995).
[6] J. R. Woodworth, M. E. Riley, D. C. Meister, B. P. Aragon, M. S. Le, and H. H. Sawin, J. Appl. Phys. **80**, 1304 (1996).
[7] J. R. Woodworth, M. E. Riley, P. A. Miller, G. A. Nichols, and T. W. Hamilton, J. Vac. Sci. Technol. A **15**, 3015 (1997).
[8] Y. Wang, R. J. Van Brunt, and J. Olthoff, J. Appl. Phys. **83**, 703 (1998).
[9] M. Tabbl, M. Kazopoulo, T. Christidis, and S. Isber, Appl. Phys. Lett. **78**, 2131 (2001).
[10] Y. Wang and J. Olthoff, J. Appl. Phys. **85**, 6358 (1999).
[11] I. Petrov, A. Myers, J. E. Greene, and J. R. Abelson, J. Vac. Sci. Technol. A **12**, 2846 (1994).
[12] K. H. Bai, H. Y. Chang, and H. S. Uhm, Appl. Phys. Lett. **79**, 1596 (2001).
[13] V. A. Godyak, R. B. Piejak, and B. M. Alexandrovich, Plasma Sources Sci. Technol. **1**, 36 (1992).
[14] G. R. Branner, E. M. Friar, and G. Medicus, Rev. Sci. Instrum. **34**, 231 (1963).
[15] K. H. Bai, J. I. Hong, C. W. Chung, S. S. Kim, and H. Y. Chang, Phys. Plasmas **8**, 3498 (2001).
[16] K. H. Bai, J. I. Hong, S. J. You, and H. Y. Chang, Phys. Plasmas **8**, 4246 (2001).
[17] U. Kortshagen, I. Pukropski, and M. Zethoff, J. Appl. Phys. **76**, 2048 (1994).
[18] S. Tang, W. Wang, J. Liu, and X. Yang, J. Vac. Sci. Technol. A **18**, 2213 (2000).
[19] O. Eichwald, M. Yousfi, A. Hennad, and M. D. Benabdessadok, J. Appl. Phys. **82**, 4781 (1997).
[20] Michael A. Lieberman, and Allan J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (Wiley, New York, 1994).
[21] H. Singh and D. Graves, J. Appl. Phys. **87**, 4098 (1994).