Spectroscopic Analysis of Argon and Zinc Emission Lines in Argon–Nitrogen Mixed Gas Inductively Coupled Plasma

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The characteristics of an argon-matrix inductively coupled plasma (ICP) containing small amounts of nitrogen gas are considerably different from those of a pure argon ICP. The role of nitrogen in the mixed gas ICP is investigated from spectroscopic analyses of argon emission lines. The spectral widths of the argon and hydrogen lines increase with the amount of nitrogen gas added, which means that the electron number density of the plasma is raised. The emission intensities of the argon and zinc lines also increase, and the variation in these intensities corresponds to that in the spectral width of the argon and hydrogen lines when nitrogen is added in the plasma. These observations suggest that the nitrogen addition causes a great change in the region of the ICP from which the argon lines are dominantly emitted. Furthermore, the intensity of the NO band heads decreases in the argon–nitrogen mixed gas ICPs, implying that the increment in the plasma temperature contributes to the decomposition of NO radicals.

Keywords Inductively coupled plasma, argon–nitrogen mixed plasma gas, zinc line intensity, NO band heads intensity

Gases introduced into an inductively coupled plasma (ICP) play various roles: the plasma support as an intermediate gas, the plasma production as an outer gas, and the sample injection as a carrier gas. Accordingly, the kind of the gas employed is the most critical parameter in determining the fundamental characteristics of the ICP. Pure argon is usually employed in all the channels of the gas carried to the plasma, although nitrogen ICPs are employed particularly under high r.f. power conditions.[1,2]

Several researchers have reported a worthwhile modification of the plasma: to replace a part or all of the argon gas with other gases.[3–13] In most cases, argon–nitrogen mixture systems became an object of research because the running cost for operating the ICP could be reduced by using nitrogen, a cheaper gas. In addition, several spectroscopic analyses have revealed the enhanced properties of the argon–nitrogen ICP, in comparison to those of pure argon gas, indicating that an appropriate selection of the experimental parameters can lead to the utilization of the argon–nitrogen mixed gas plasma in the ICP emission spectrometry.[5–8]

Montaser *et al.* reported the effect of nitrogen gas in the outer gas flow on the emission intensities of the analytes and provided some interesting results regarding the analytical performance of the argon–nitrogen ICP.[9,10] Their papers concluded that the performance of the argon-matrix plasma containing about 5% nitrogen gas was superior to that of the pure argon plasma and that the optimum observation height was reduced compared to the conditions with pure argon gas. Spectroscopic features of the argon–nitrogen ICP were further investigated by Choot *et al.*[11–13] They indicated that the intensities of the ionic lines were uniquely enhanced relative to the neutral atomic line emission when nitrogen was added to the plasma. Their studies suggested that the mixed gas plasmas yield different excitation and ionization conditions when compared with the argon plasma.[12]

One observes a great many emission lines of argon over a wide wavelength range of the ICP spectrum. The emission intensities of the argon lines will be sensitive to changes in the properties of the plasma. Therefore, intensity measurements will give useful information on the mixed gas ICP when nitrogen is added to the argon plasma.

The spectral width of argon emission lines also reflects the plasma characteristics. A line broadening due to a strong Stark effect is observed in some argon atomic lines between 500 and 600 nm.[14] One can estimate a variation in the electron density of the plasma from the spectral broadening of these emission lines.[15] Further, the beta line of hydrogen atom (H I 486.1 nm) is very often used for the electron density measurement, because the contribution of the Stark effect yields most of the line profile.

In this paper, we investigated the effect of nitrogen addition on the excitation and ionization in the mixed gas plasmas primarily based on the analyses of the argon emission lines. These examinations could provide knowledge in the plasma region from which the argon lines are radiated. The induction zone of ICP[16], which surrounds the central channel of the plasma, is a predominant source for argon emission lines. Therefore, the state of the induction zone where electric energies are directly transmitted from the load coil is evaluated from the observation of the argon lines. On the other hand, the variation in the emission intensities of analyte species can be caused by the nitrogen addition at the portion of the central channel where sample solutions are injected. We will discuss the role of nitrogen gas by comparing the results obtained for the different zones of the ICP.

Experimental

Apparatus

Our plasma source unit consisted of a plasma torch, a matching box, and a radio frequency generator. No modification of the unit was carried out. A Fastie–Ebert mounting spectrograph, equipped with a photomultiplier tube, was employed. Table 1 describes all other instrumentation and the operating conditions in detail.

Reagent

Zinc was selected as an analyte element. A stock solution was made by dissolving 2.5 g of high purity zinc metals (more than 99.999%) in small amounts of heated hydrochloric acid (6 M) and by subsequent dilution to concentration of 10 mg/ml with distilled water. Sample solutions of the zinc concentration of 0.01 mg/ml were prepared by diluting the stock solution with the appropriate amounts of dilute hydrochloric acid. All the solutions contained *ca.* 0.02 M hydrochloric acid.

Analytical lines

Some argon atomic lines in the wavelength range between 400 and 450 nm were observed for the evaluation of their emission intensities. The literature was consulted on argon emission lines exhibiting the relatively strong Stark broadening.[15] The full widths at half maximum (FWHM)[14] of the Ar I 549.5 nm and the Ar I 555.9 nm lines, and, in comparison, those of the H I 486.1 nm (H_β) line were employed for the estimation of the electron number densities of the plasma.

The Zn I 213.86 nm, the Zr II 202.55 nm, and the Zr II 206.19 nm lines were selected as the analytical lines for zinc atom and ion, respectively. Both the atomic and the ionic lines have similar excitation energies. Therefore, the relative population of the zinc species can be deduced from the calculation of the ion-to-atom line ratio between these lines. The spectroscopic assignment for each emission line is summarized in Table 2.

Procedure

An argon–nitrogen mixed gas was introduced only as the outer gas flow of the ICP. For the intermediate and the carrier gas flow, pure argon was employed at fixed flow rates. The argon flow rate of the outer gas was kept at 16.0 l/min and relatively small amounts of nitrogen

Table 1 Instrumentation (a) and experimental conditions (b)

(a)	
Plasma source unit	ICPS-2H (Shimadzu Corp., Japan)
R.f. generator	frequency: 27.12 MHz
	nominal output power range: 0−2.7 kW (continuous rating)
Induction coil	two turns, 30 mm i.d., water cooled
Torch	Fassel-type, outer gas tube of 18 mm i.d.
Nebulizer	pneumatic
Spray chamber	Scott-type double pass
Spectrometer	GE-340 (Shimadzu Corp., Japan)
	focal length: 3.4 m
	grating: 1200 grooves/mm
	blaze wavelength: 300 nm
	slit width: 30 μm
	slit height: 3 mm
Photomultiplier	R-955 (Hamamatsu Photonics Corp., Japan)
Optics	fused-silica lens, focusing a 1:1 image of the plasma source on the entrance slit
Gas mixer	MX-3S (Crown Corp., Japan)
	Ar: 0−25 l/min
	N_2: 0−1.0 l/min
(b)	
Incident r.f. power	1.2−2.3 kW (as parameter)
Reflected power	less than 40 W, see text
Outer gas flow rate	Ar 16.0 l/min (fixed) and N_2 0 − 0.6 l/min (as parameter)
Intermediate gas flow rate	Ar 1.45 l/min (fixed)
Carrier gas flow rate	Ar 1.00 l/min (fixed)
Observation height	4−33 mm above load coil (as parameter)
Sample uptake rate	*ca.* 1.6 ml/min when distilled water is injected

Table 2 Assignment of emission lines employed

Wavelength/ nm	Assignment		
	Upper/eV	—	Lower/eV
Zn I 213.86	5.796, 4s4p $^1P_1$	—	0.000, $(4s)^2$ $^1S_0$
Zn II 202.55	6.119, 4p $^2P_{3/2}$	—	0.000, 4s $^2S_{1/2}$
Zn II 206.19	6.011, 4p $^2P_{1/2}$	—	0.000, 4s $^2S_{1/2}$
Ar I 419.83	14.58, 5p $[1/2]_2$	—	11.62, 4s $[3/2]_1$
Ar I 425.93	14.74, 5p $[1/2]_2$	—	11.83, 4s $[1/2]_1$
Ar I 427.22	14.52, 5p $[3/2]_1$	—	11.62, 4s $[3/2]_1$
Ar I 433.36	14.69, 5p $[3/2]_2$	—	11.83, 4s $[1/2]_1$
Ar I 549.53	15.35, 6d $[3/2]_0$	—	13.09, 4p $[5/2]_2$
Ar I 555.87	15.14, 5d $[3/2]_0$	—	12.91, 4p $[1/2]_1$
H I 486.13 (H_β)	12.75, 4p $^2P_{1/2,3/2}$	—	10.20, 2s $^2S_{1/2}$

were added to the argon flow. The nitrogen flow rate was varied from 0 to 0.6 l/min. Because the matching network in our instrumentation was designed for pure argon gas, it is difficult to control the reflected power appropriately at higher nitrogen flow rates. The discharges became unstable and extinguished when the reflected power exceeded more than about 40 W. Therefore, the upper limit of the nitrogen content was restricted by the instrumental ability to adjust the reflected power. The allowed content of nitrogen was lowered with a decrease in the r.f. incident power.

The plasma was initiated with pure argon gas. Once a stable discharge was obtained, an appropriate amount of nitrogen was gradually added while any variation in the reflected power was checked.

The FWHMs of the argon lines and the H_β line were determined from duplicate individual measurements. The emission intensities of the argon lines were calculated from the average peak heights for six to eight replicates. The intensities of the zinc lines were evaluated from four or five determinations. The results exhibited good precision and the relative standard deviations were within a few percents.

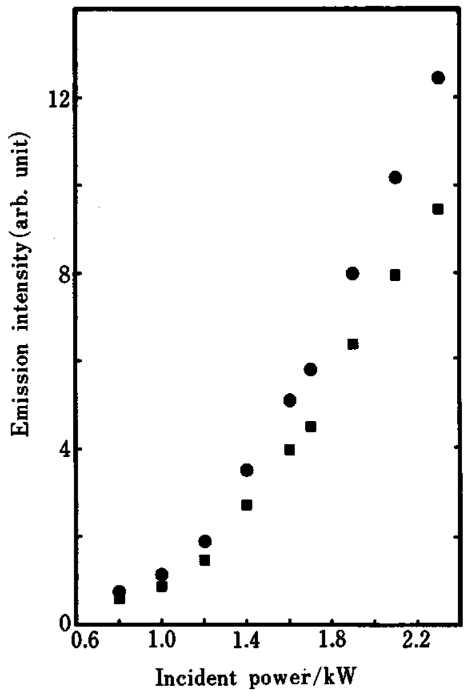

Fig. 1 Incident power dependence of emission intensities of the Ar I 419.8 nm (●) and Ar I 433.4 nm (■) lines. Observation height: 14 mm ALC.

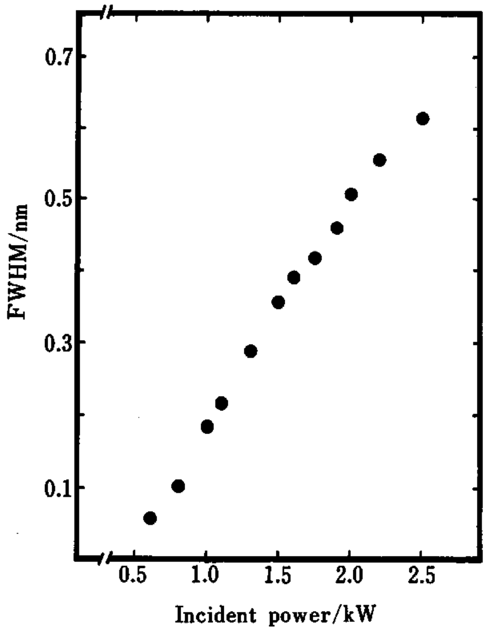

Fig. 2 Incident power dependence of the FWHM of the H I 486.1 nm line. Observation height: 14 mm ALC.

Results and Discussion

Argon emission intensities versus incident r.f. power

Both the plasma temperature and the electron density increase with the supplied r.f. power. Figure 1 shows the relation between the emission intensities of the Ar I lines and the incident r.f. power when pure argon is used as the outer gas flow. The intensities increase by a factor of *ca.* 16 as the power is varied from 0.8 to 2.3 kW, whereas the intensity ratio of the Ar I lines whose excitation energies are almost the same remained constant (1.29±0.02), independent of the r.f. power. These observations imply that the emission intensities of the argon lines are free from any self-absorption effects and result from the excitation processes in the plasma.

Figure 2 indicates the dependence of the FWHM value of the H_β line on the incident r.f. power. A linear increase in the FWHMs is observed when the power is varied from 0.6 to 2.5 kW. A theoretical calculation by Griem[17] predicts that the electron densities in our ICP are of the order of 10^{15} cm^{-3} when the power is more than *ca.* 1.0 kW. Such densities are similar to the results reported in the previous works.[18-20] Therefore, we can consider that the resultant FWHMs are governed mainly by the electron density of the plasma.

The Stark broadening of the argon lines is not large enough to overcome other contributions such as the Doppler broadening.[15] It may be necessary to correct other broadening effects when the electron density is computed from the FWHMs. However, it is considered that the relative variation can be derived from the uncorrected spectral widths. In fact, a straightforward relation between the FWHMs and the r.f. powers as in Fig. 2 was found also in the argon emission lines.[21]

The intensities and the line widths of the argon emission lines can be employed as a sensitive indicator representing the state of the ICP.

Argon emission lines in Ar–N_2 mixed gas plasmas

Figure 3 indicates variations in the FWHMs of the argon lines as well as the H_β line as a function of the nitrogen flow rate in the outer gas flow. It is found that the FWHM values increase with the flow rates and then reach steady states at *ca.* 0.3 l/min N_2. Compared with values in the pure argon plasma, the electron densities are raised in the argon-matrix ICP containing nitrogen in the range of up to 2%. This result suggests that, in the argon–nitrogen mixed gas ICP, very small amounts of nitrogen cause a noticeable change of the plasma. Because the hotter zone surrounding the aerosol channel[16] is a major source of the argon emission lines, the measurements described above also show that the nitrogen addition especially affects the characteristics of the plasma core.

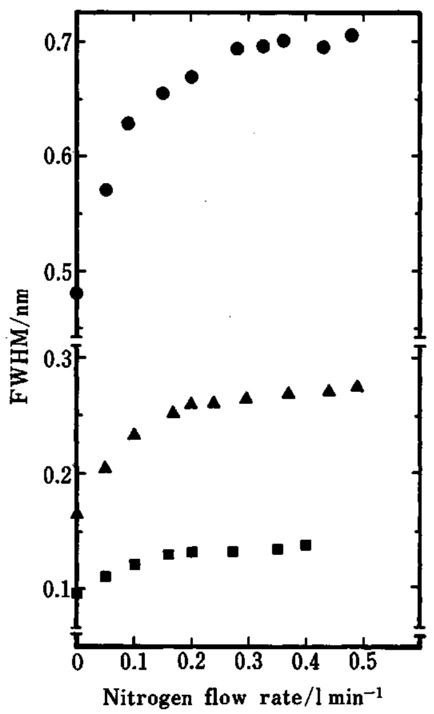

Fig. 3 Effect of the nitrogen flow rate added on the FWHM of the Ar I 549.5 nm (▲) and Ar I 555.9 nm (■) lines and of the H I 486.1 nm line (●). Observation height: 14 mm ALC; incident r.f. power: 1.9 kW.

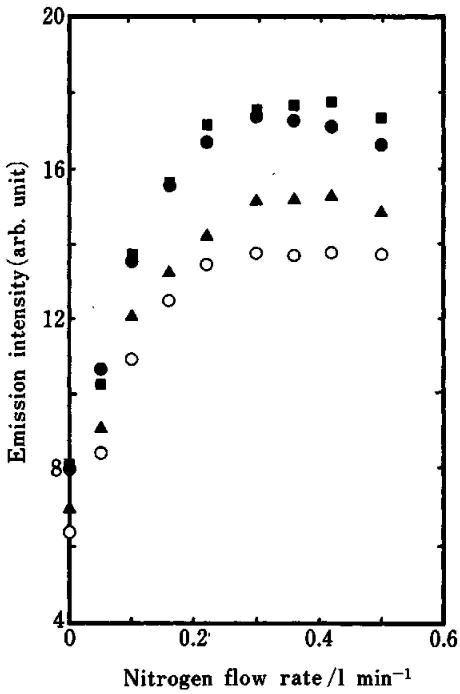

Fig. 4 Plots of the emission intensities of the Ar I 419.8 nm (●), Ar I 425.9 nm (■), Ar I 427.2 nm (▲), and Ar I 433.4 nm (○) lines against the nitrogen flow rate. Observation height: 14 mm ALC; incident r.f. power: 1.9 kW.

Plots of the argon emission intensity when the nitrogen flow rate is varied from 0 to 0.5 l/min are shown in Fig. 4. The argon intensities are elevated with increasing the nitrogen flow rate. The emission intensities follow a similar variation against the nitrogen flow rate, regardless of the kind of the argon lines selected. In fact, the intensity ratios of these lines are little dependent on the nitrogen flow rate. Further, it should be noted that the changes in the intensities are very similar to those in the FWHMs shown in Fig. 3. The emission intensities as well as the spectral widths of the argon lines can suggest an increment in the plasma temperatures when nitrogen gas is introduced in the plasma.

Zinc emission intensity in Ar–N_2 mixed gas plasmas

Figure 5(a) shows a variation in the emission intensities of the zinc emission lines as a function of the nitrogen flow rate in the outer gas flow. Furthermore, the intensity ratios between these lines are plotted in Fig. 5(b). The intensities are raised with increasing the flow rate and then reach steady states. It is found that, in the case of the ionic lines, the emission intensities increase by a factor of *ca.* 4 when only 2% nitrogen gas is added. The intensity changes of the ionic lines are greater than the change in the atomic line, which results in an increase in the intensity ratio of the ionic line to the atomic line as illustrated in Fig. 5(b). The results concerning the zinc intensities correspond well with those for the argon emission lines. Figure 5(b) also indicates that the intensity ratio between the two ionic lines whose excitation energies are almost the same stays constant, independent of the amount of nitrogen added.

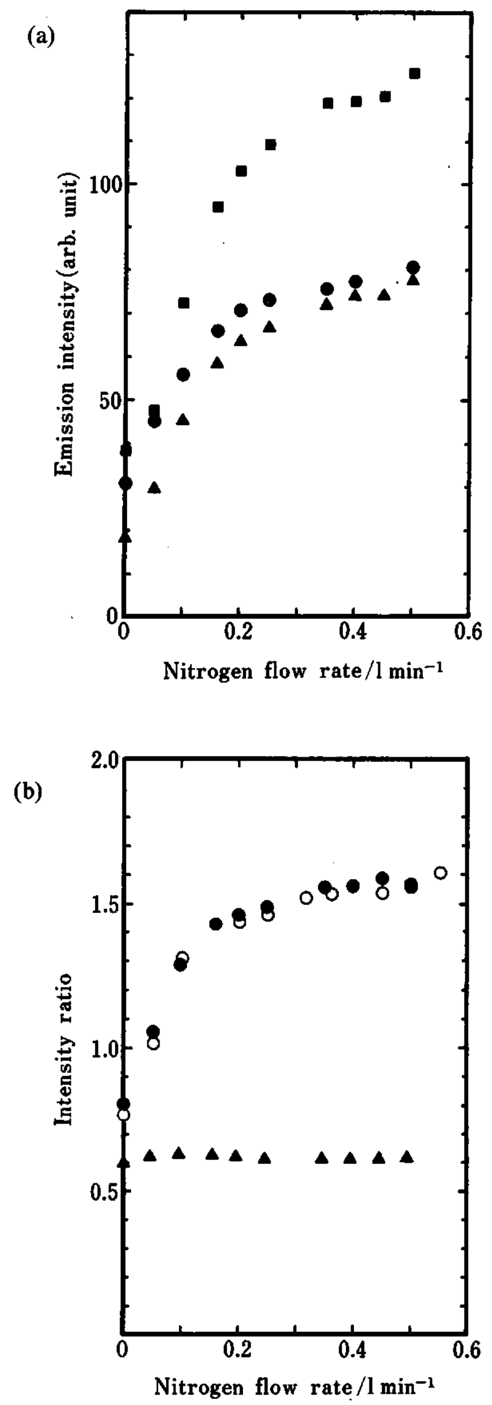

Fig. 5 (a) Variation in the emission intensities of the Zn I 213.9 nm (●), Zn II 202.6 nm (■), and Zn II 206.2 nm (▲) lines as a function of the nitrogen flow rate, (b) variation in the intensity ratios, Zn II 202.6/Zn I 213.9 (●) and Zn II 206.2/Zn II 202.6 (▲). Open circles in Fig. 5(b) represent the intensity ratio (Zn II 202.6/Zn I 213.9) when nitrogen-20% oxygen gas is added to the argon ICP instead of pure nitrogen. The observation height and the r.f. power are the same as in Fig. 4.

We also investigated the influence of the addition of a nitrogen-20% oxygen gas (air gas) instead of pure nitrogen. The open circles in Fig. 5(b) represent the ion-to-atom intensity ratio of the zinc lines when the air gas is added. The result using pure nitrogen gas (closed circle in Fig. 5(b)) is about the same.

An improvement of the excitation efficiency for the zinc atomic and ionic species takes place when nitrogen gas is mixed in the argon ICP. The variation in the ion-to-atom intensity ratio is derived from more active ionization in the argon-nitrogen ICP. It is feasible to suggest that the nitrogen addition contributes to an increment in the plasma temperature at a central portion of the plasma where the zinc species are principally excited and ionized.

Effect of incident r.f. power

Figure 6 shows a relation between the emission intensities of the Ar I 419.8 nm line and the nitrogen flow rate for several incident r.f. power values. In all the cases measured, the nitrogen addition induces the enhancement of the argon intensities. Further, when the supplied r.f. power is reduced from 2.1 to 1.2 kW, the intensities are saturated at smaller flow rates of nitrogen gas added to the plasma. Similarly, the spectral width of the Ar I 549.5 nm line is recorded as a function of the nitrogen flow rate when the r.f. power is varied as the experimental parameter, as illustrated in Fig. 7. We can recognize a good correspondence between these two observations concerning the argon emission lines.

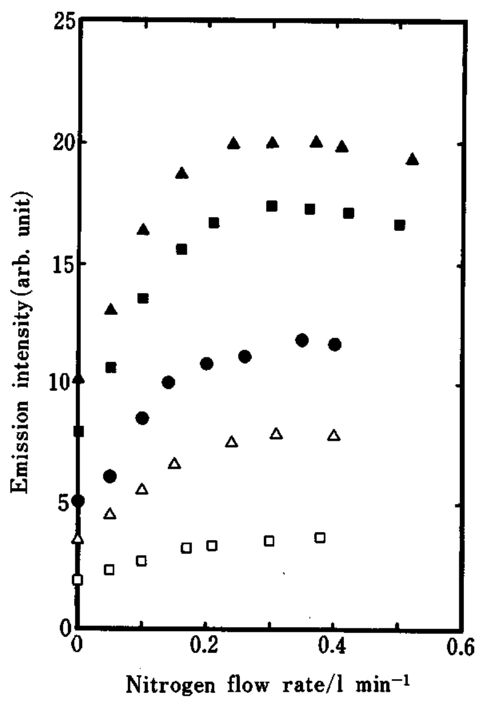

Fig. 6 Change in the emission intensities of the Ar I 419.8 nm line for various r.f. power values: 1.2 kW (□), 1.4 kW (△), 1.6 kW (●), 1.9 kW (■), and 2.1 kW (▲). Observation height: 14 mm ALC.

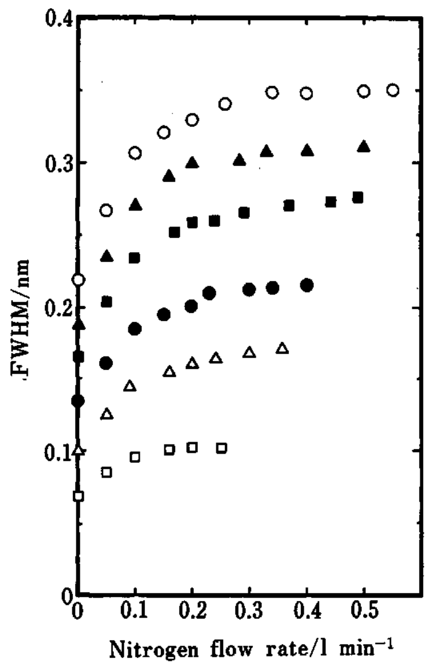

Fig. 7 Plots of the FWHM of the Ar I 549.5 nm line against the nitrogen flow rate for various r.f. power values: 1.2 kW (□), 1.4 kW (△), 1.6 kW (●), 1.9 kW (■), 2.1 kW (▲), and 2.3 kW (○). Observation height: 14 mm ALC.

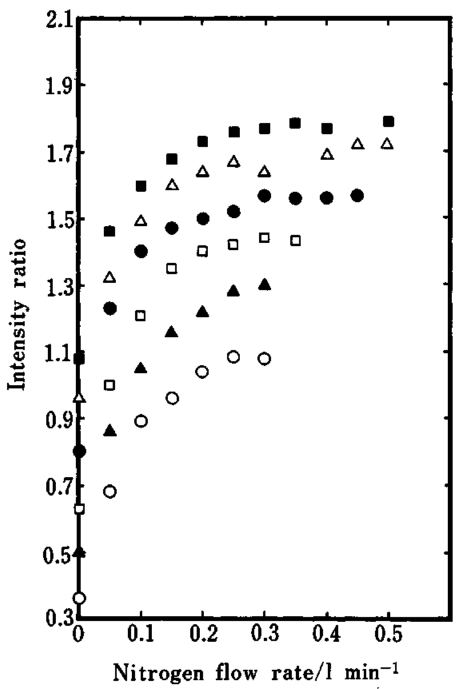

Fig. 8 Variation in the intensity ratio of the Zn II 202.6 nm to the Zn I 213.9 nm as a function of the nitrogen flow rate added for various r.f. power values: 1.2 kW (○), 1.4 kW (▲), 1.6 kW (□), 1.8 kW (●), 2.1 kW (△), and 2.3 kW (■). Observation height: 14 mm ALC.

Regardless of the supplied r.f. powers, the nitrogen addition exerts a positive effect on the excitation in the mixed gas plasma.

Figure 8 indicates a variation in the ion-to-atom ratio of the zinc lines against the nitrogen flow rate for different incident r.f. powers. In agreement with the measurements of the argon emission lines described in Figs. 6 and 7, the nitrogen addition results in an increase in the intensity ratios. In lower r.f. power values, larger changes in the ratio are observed.

Correlation between argon and zinc emission intensities

As described above, our observations suggest that the elevation in the plasma temperatures is caused by the nitrogen addition to the argon-matrix ICP. Because the results obtained using the argon lines are similar to those with the zinc lines, this effect extends in the whole portions of the plasma; the induction zone and the central channel of the ICP.

The heat content of nitrogen is rather greater than that of argon.[22] Therefore, nitrogen molecules can act as energy reservoirs in the plasma, thus leading to an increment in the temperatures. The literature[22] also indicates that the heat content of oxygen is almost the same as that of nitrogen. As described in Fig. 5(b), the zinc intensity ratios are almost the same for pure nitrogen gas and for air gas. This result may be due to the similarity in the heat content between nitrogen and oxygen gas, and therefore may imply that the excitation phenomena in the ICP are governed principally by the heat properties of the plasma gas.

In addition to the heat content, the thermal conductivity of nitrogen is larger compared to that of argon.[23] The zinc species introduced into the plasma indirectly receive energies from the load coil through the induction zone surrounding the central channel. Nitrogen molecules can be effective energy carriers from the hotter region to the colder zone of the plasma where the zinc species are excited. The nitrogen addition also may contribute to an increase in the plasma temperature at the central portion of the plasma.

Effect of observation height

Our investigations already described were carried out at an observation height of 14 mm above the load coil (ALC), and thus were obtained for a so-called normal analytical zone[16] which is best suited for the ICP emission analyses. We studied the effect of the observation height in the argon–nitrogen mixed gas ICP to investigate the different regions of the ICP. The results are illustrated in Fig. 9 for the ion-to-atom ratio of the zinc lines and in Fig. 10 for the FWHM value of the argon lines.

Figure 9 shows a variation in the intensity ratio of the zinc lines as a function of the nitrogen flow rate at three different positions of observation. Whereas the ratio obtained at 14 mm ALC reaches a plateau at the nitrogen rate of about 0.3 l/min, that at 4 mm ALC increases up to 0.5 l/min. In the pure Ar ICP, the measurement at the position of 4 mm ALC, which is called the initial radiation zone[16], yields the lowest intensity ratio. This result is mainly due to relatively lower temperatures in this region. However, the intensity ratio rapidly increases when nitrogen gas is added to the argon ICP and exceeds the ratio obtained at 14 mm ALC, which implies that the nitrogen addition causes larger changes in the plasma temperature at the initial radiation zone. This zone is surrounded with hotter and massive regions of the plasma core. Therefore, it is possible to consider that the initial radiation zone is declined by the nitrogen addition. The observation at 24 mm ALC is carried out for a portion of the tail flame above the normal analytical zone. The induction zone, which forms the core of the plasma as a hotter region, surrounds the normal analytical zone and the initial radiation zone. However, the tail frame region is not affected directly from the plasma core. Though an increase in the ratio is also caused by the nitrogen addition, the intensity ratios which are observed at 24 mm ALC are always the lowest.

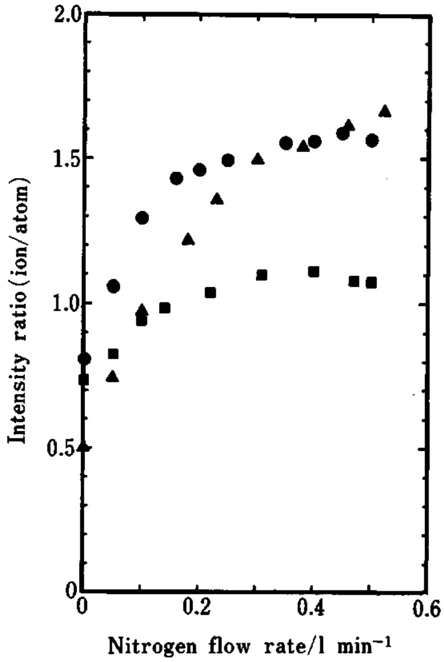

Fig. 9 Relation between the intensity ratio of the Zn II 202.6 nm to the Zn I 213.9 nm and the nitrogen flow rate for several observation heights: 4 mm (▲), 14 mm (●), and 24 mm (■). Incident r.f. power: 1.9 kW.

Figure 10 indicates a change in the FWHM of the argon line obtained for various observation heights. In contrast to the intensity ratios of the zinc lines (Fig. 9), the FWHM values measured at 4 mm ALC are always the highest, independent of the nitrogen flow rates, which means that the portions having the higher electron densities are observed. This feature could correspond to the position of the induction zone just above the load coil.[18] These variations in the FWHM can be interpreted from the difference in the plasma position from which the argon and the zinc lines are emitted. At higher observation heights, the changes in the FWHM are not prominent, and especially at 33 mm ALC, the FWHMs are obviously reduced.

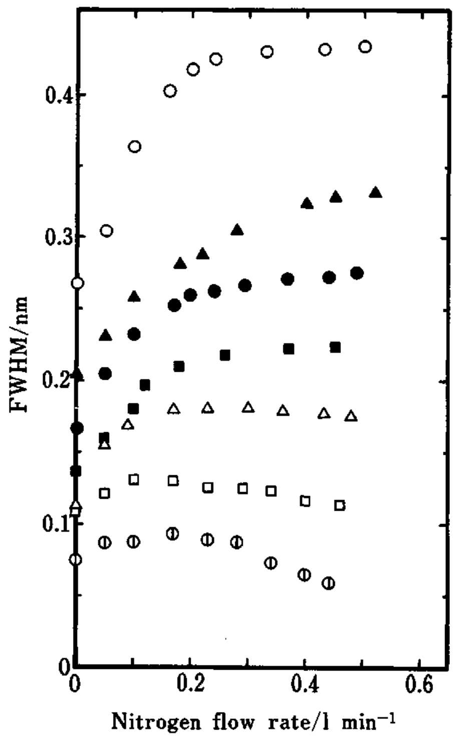

Fig. 10 Change in the FWHM of the Ar I 549.5 nm line caused by the nitrogen addition to the Ar-matrix ICP for several observation heights: 4 mm (○), 9 mm (▲), 14 mm (●), 19 mm (■), 23 mm (△), 28 mm (□), and 33 mm (⦶). Incident r.f. power: 1.9 kW.

Behavior of background levels

Figure 11 indicates a change in the background level

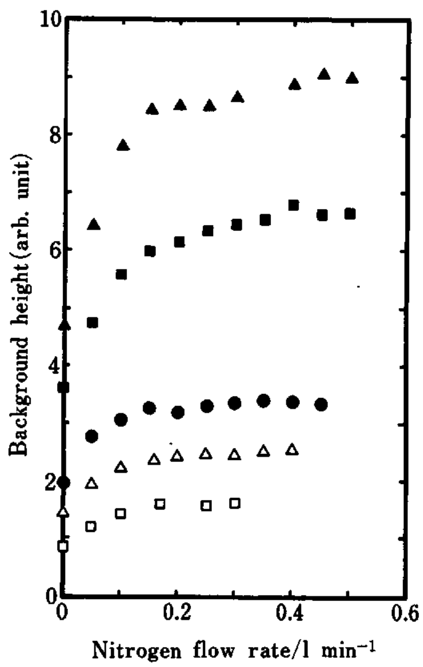

Fig. 11 Variation in the background height measured at 220.0 nm as a function of the nitrogen flow rate. The r.f. power is varied under the same conditions as in Fig. 6.

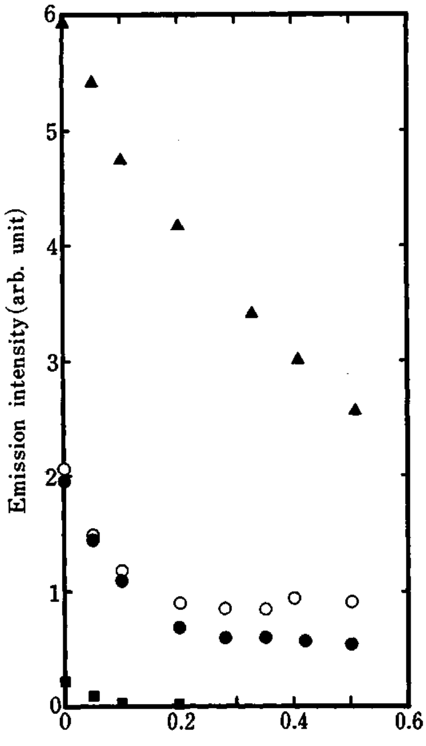

Fig. 12 Behavior of the NO band head (214.8 nm) when nitrogen gas is added to the argon ICP. Observation height: 9 mm (■), 14 mm (●), and 24 mm (▲) ALC; incident r.f. power: 1.9 kW. Open circles show the result obtained using nitrogen-20% oxygen gas at 14 mm ALC.

measured at 220.0 nm as a function of the nitrogen flow rate. It is found that the background level is elevated with increasing the amount of nitrogen. This result agrees with the previous reports.[9,12]

The continuum background of ICP results primarily from radiative recombination between argon ions and fast electrons.[14] In this reaction, kinetic energies of the fast electrons are released as photons having a certain range of energies.

As elucidated in Figs. 3 and 7, the electron density increases when nitrogen gas is added to the argon-matrix ICP. The recombination reaction probably occurs more actively in the argon–nitrogen ICP compared to in the pure argon plasma because the collision probability between the argon ion and the electron is closely dependent on the electron density in the plasma.

We also investigated variations in emission intensities of NO band spectrum in the argon–nitrogen ICP. Figure 12 illustrates the dependence of the NO band head intensities on the nitrogen flow rate for different observation heights. The intensities of the NO band head (measured at 214.8 nm) are drastically reduced with an increase in the nitrogen flow rate. Further, when the air gas (nitrogen gas containing oxygen of 20%) is employed instead of pure nitrogen gas, a decrease in the intensities is also observed as indicated in Fig. 12 (open circles). The NO radicals generally result from the entrainment of air in pure argon ICPs; the bands extend from about 195 to 300 nm.[24] Because spectral interferences from the NO bands create problems, in some cases, come into problems, it is an advantage in the argon–nitrogen mixed gas ICP that the contribution can be reduced.

Such behavior of the NO bands can be explained from a more complete decomposition of the radicals due to the increase in the plasma temperature. It is interesting that the NO bands are eliminated even though nitrogen or oxygen species are supplied to the plasma.

References

1. S. Greenfield, J. L. Jones and G. T. Berry, *Analyst* [London], **89**, 713 (1964).
2. S. Greenfield, H. McD. McGreachin and P. B. Smith, *Talanta*, **22**, 1 (1975).
3. D. Truitt and J. W. Robinson, *Anal. Chim. Acta*, **50**, 61 (1970).
4. D. Truitt and J. W. Robinson, *Anal. Chim. Acta*, **49**, 401 (1970).
5. K. Ohls and D. Sommer, *Fresenius' Z. Anal. Chem.*, **295**, 337 (1979).
6. L. Ebdon, M. R. Cave and D. J. Mowthrope, *Anal. Chim. Acta*, **115**, 171 (1980).
7. L. Ebdon, D. J. Mowthrope and M. R. Cave, *Anal. Chim. Acta*, **115**, 179 (1980).
8. S. Greenfield and D. T. Burns, *Anal. Chim. Acta*, **113**, 205 (1980).
9. A. Montaser and J. Mortazavi, *Anal. Chem.*, **52**, 225 (1980).
10. A. Montaser, V. A. Fassel and J. Zalewski, *Appl. Spectrosc.*, **35**, 292 (1981).
11. E. H. Choot and G. Horlick, *Spectrochim. Acta*, **41B**, 889 (1986).
12. E. H. Choot and G. Horlick, *Spectrochim. Acta*, **41B**, 925 (1986).
13. E. H. Choot and G. Horlick, *Spectrochim. Acta*, **41B**, 907 (1986).
14. J. M. Mermet, "*Inductively Coupled Plasma Emission Spectroscopy*", ed. P. W. J. M. Boumans, Part II, Chap. 10, John Wiley & Sons, New York, 1987.
15. H. R. Griem, "*Plasma Spectroscopy*", McGraw-Hill, New York, 1964.
16. S. R. Koirtyohann, J. S. Jones, C. P. Jester and D. A. Yates, *Spectrochim. Acta*, **36B**, 53 (1981).
17. P. Kepple and H. R. Griem, *Phys. Rev.*, **173**, 317 (1968).
18. B. L. Caughlin and M. W. Blades, *Spectrochim. Acta*, **40B**, 98 (1985).
19. T. Hasegawa and H. Haraguchi, *Spectrochim. Acta*, **40B**, 1510 (1985).
20. N. Furuta, Y. Nojiri, K. Fuwa, *Spectrochim. Acta*, **40B**, 429 (1985).
21. K. Wagatsuma and K. Hirokawa, *Anal. Sci.*, **9**, 83 (1993).
22. J. Hilsenrath, "*Tables of Thermal Properties of Gases*", NBS Circular, 1955, 564.
23. Y. S. Touloukian, "*Thermophysical Properties of Matter*", Vol. I, Plenum Press, New York, 1970.
24. R. W. B. Pearse, A. G. Gaydon, "*Identification of Molecular Spectra*", Chapman and Hall, London, 1965.

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