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Synthesis of Ammonia in High-frequency Discharges[1]

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The synthesis of ammonia from nitrogen–hydrogen plasma prepared using radiofrequency discharge and microwave discharge was studied under the same experimental conditions except the driving frequency. Twice larger amounts of ammonia were adsorbed on zeolite used as adsorbent in the microwave discharge than in the radiofrequency discharge. Relative intensities of NH band head ($A^3\Pi - X^3\Sigma^-$, 0–0) as well as hydrogen atomic line (Hβ) observed in the plasma prepared using microwave discharge were one order of magnitude larger than those in the plasma prepared using radiofrequency discharge. Since NH_x radicals and H atoms are considered ammonia precursors, the advantage of microwave discharge over radiofrequency discharge on ammonia synthesis is discussed from the results obtained above and from the plasma parameters, kT_e and n_e, obtained by the electric double probe technique.

KEY WORDS: ammonia synthesis; radiofrequency discharge; microwave discharge; NH_x radicals.

1. INTRODUCTION

A number of papers on plasma synthesis of ammonia from a nitrogen–hydrogen mixture at low pressure have been published and it is considered that ammonia molecules are formed by the reaction between NH_x radicals and hydrogen atoms in the discharge on the surface of the cold trap.[1-7] In some cases, catalysts were placed in the discharge region, in the afterglow region, or on the cold trap wall in order to enhance the ammonia yield. In our previous paper[8] for the formation of ammonia in the nitrogen–hydrogen plasma prepared using radiofrequency discharge, we reported that the amounts of ammonia trapped on zeolite set downstream of the gas flow were several times larger than that obtained when a cold trap was simply used at 200 K.[3] In the case of using zeolite, the surface reaction of

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NH_x radicals adsorbed on the zeolites with hydrogen atoms facilitates ammonia synthesis.

The plasma prepared using a microwave (2450 MHz) discharge differs essentially in some respects from that prepared using a radiofrequency (13.56 MHz) discharge and promotes the chemical reactions furthermore.[9] For example, the reaction rate for the nitriding of titanium in nitrogen plasma prepared using microwave discharge was larger than the case using radiofrequency discharge.[10] The fact that excited atomic nitrogen N $(2p^2(^3P)3p)$ was identified only in the nitrogen plasma prepared using microwave discharge[11] indicated that nitrogen atoms play an important role in the nitriding of titanium.

In general, the average power transferred to a unit volume of gas in the high-frequency discharge is given by

$$\bar{P} = \frac{e^2 E^2 n}{2m} \cdot \frac{\nu_c}{\nu_c^2 + \omega^2} \tag{1}$$

where E is the maximum field strength, n the electron concentration, m the electron mass, ν_c the electron collision frequency, and ω the frequency of the applied field.[12] The value of ν_c usually lies between 10^9 and $10^{11}\ s^{-1}$. Thus, for a radiofrequency of 13.56 MHz, $\omega \approx 10^7\ s^{-1}$ and $\nu_c \gg \omega$, so there is no effect of the driving frequency. However, for a microwave frequency of 2450 MHz, $\omega \approx 10^{10}\ s^{-1}$ and $\nu_c \approx \omega$. Thus, the effect of the driving frequency appears in the microwave discharge because it can produce higher field strength than the radiofrequency discharge.

The formation of larger amounts of NH_x radicals and hydrogen atoms, which are considered ammonia precursors,[3] is expected in the microwave discharge because of its higher field strength. Therefore, we have applied the microwave discharge to the synthesis of ammonia in addition to the radiofrequency discharge.

In the present work, the synthesis of ammonia in both microwave and radiofrequency discharges is studied under the same experimental conditions except the driving frequency, with identification of the products in the gas phase as well as on the zeolite. The results obtained in the plasma prepared using both discharges are mutually compared and the advantage of the microwave discharge on the synthesis of ammonia is discussed.

2. EXPERIMENTAL

2.1. Materials

Zeolite used for adsorption of the discharge products was molecular sieve 13X, in the form of 1/16 inch pellet (binder content was 20 wt.%). Purified nitrogen and hydrogen (both 99.999%) were used as the plasma gas.

2.2. Apparatus and Experimental Procedures

Experimental apparatus and procedures for the radiofrequency discharge were described previously.[8] The apparatus for the microwave discharge is shown in Fig. 1. Microwave power at 2450 MHz from a 1.2-kW magnetron was transferred to the quartz discharge tube (0.8 m long and 18 mm in diameter) placed transversely through the cavity set at the same position in place of the coil of the radiofrequency discharge,[8] via a rectangular wave guide. A continuous discharge was maintained. The power delivered by the generator was measured by a wattmeter set in the wave guide. A shortening plunger and three stabs tuner were used for matching.

Dehydrated zeolite prepared by heating at 620 K for 1 h under vacuum was placed in the U-tube which was attached downstream of the gas flow. Before applying the discharge, the discharge tube was evacuated to a pressure of 0.3 Pa, and then nitrogen–hydrogen (4:1) mixed gas or only nitrogen gas was introduced into the discharge tube. Discharge conditions were as follows: gas flow rate, 1.2 $dm^3 \cdot h^{-1}$; pressure, 650 Pa; power supplied, 200 W. These values were the same in both discharges. The discharge was carried out for 3 h in every case. The zeolite temperature was maintained at 300 K, 273 K, or 200 K during the adsorption. After the discharge, the identification of the adsorbed species on the zeolite was carried out by IR spectroscopy and by the temperature-programmed desorption method using

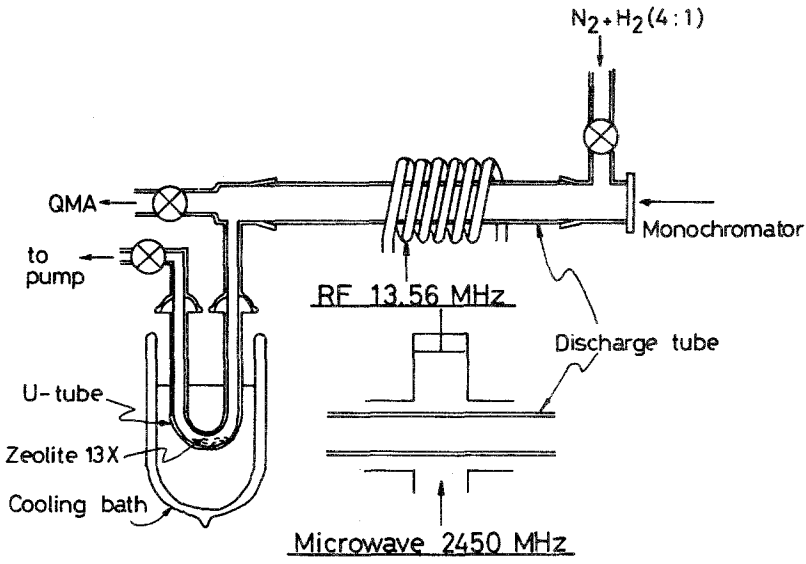

Fig. 1. Experimental apparatus.

a mass spectrometer (TPD). The adsorbed amount of ammonia on zeolite was determined by the Kjeldahl method.

The plasma diagnostics were carried out using emission spectroscopy, mass spectroscopy, and an electric double probe technique. The emission spectra were obtained in a direction parallel to the gas flow from the upper stream of the gas flow using a monochromator. Mass spectra were taken downstream of the gas flow by extracting the species in the plasmas through an orifice of 30 μm diameter to the quadrupole mass analyzer by differential pumping. A small double probe, consisting of the plane ends of a tungsten wire 0.35 mm in diameter, was enclosed in a quartz tube and situated at various points in the discharge tube.

3. RESULTS AND DISCUSSION

3.1. Identification and Chemical Analysis of Adsorbed Species on Zeolite

The IR spectra of the zeolite adsorbed discharge products at 300 K are shown in Fig. 2. For comparison, the spectrum of the zeolite itself is also shown. The absorption band at 1400 cm^{-1} attributed to ammonium ion was

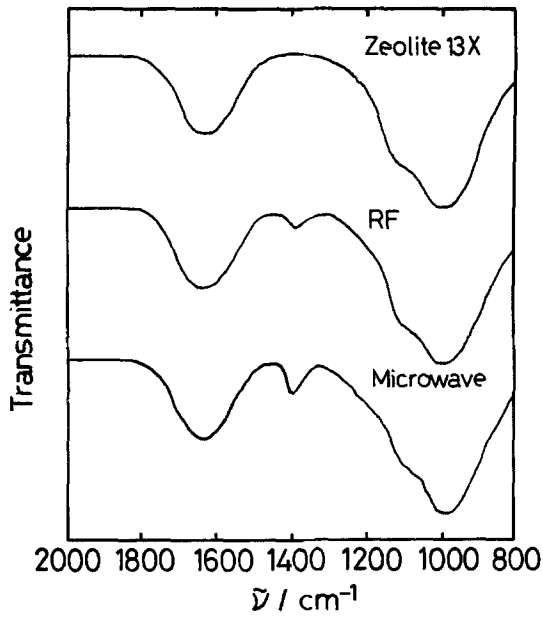

Fig. 2. IR spectra of zeolites which adsorbed discharge products at 300 K.

observed in the spectra of the zeolite after discharge in both cases together with the absorption bands of the zeolite itself. It was found that ammonia was adsorbed on the zeolite as ammonium ion, and its relative intensity in the microwave discharge was twice that in the radiofrequency discharge.

Typical TPD curves of desorbed gases from the zeolite adsorbed discharge products at 300 K are shown in Fig. 3. The desorption was carried out between room temperature and 620 K. The desorption of the species of $m/e = 16$, 17, and 18 were detected above room temperature from the adsorbed discharge products in both radiofrequency and microwave discharges. The species of $m/e = 16$, 17, and 18 were assigned to NH_2^+, NH_3^+, and H_2O^+, respectively. NH_4^+ dissociates to NH_3^+ and H. The intensities of the peaks due to H_2O^+ originating from residual water in the zeolite were approximately the same in both discharges. In the case of the microwave discharge, the intensities of the peaks due to NH_2^+ and NH_3^+ were twice those in the radiofrequency discharge.

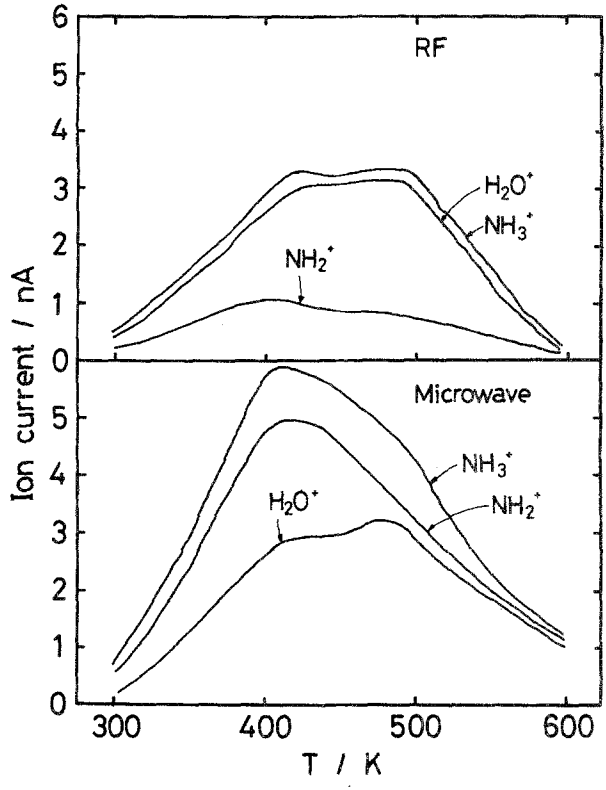

Fig. 3. TPD curves of zeolites.

As both the IR spectra and TPD curves showed that twice larger amounts of ammonia are adsorbed on the zeolite in the microwave discharge, the adsorbed amounts of ammonia were determined by chemical analysis. The amount of ammonia per unit time vs. the adsorption temperature is shown in Fig. 4. The amount of ammonia increased linearly with decreasing adsorption temperature in both discharges. The amount of ammonia in the microwave discharge was approximately twice that in the radiofrequency discharge at every adsorption temperature.

The adsorbed amount obtained in the nitrogen plasma prepared using both discharges and for a flow of nitrogen-hydrogen mixture without discharge were also determined as reference. These amounts were 10–20 μmol · g^{-1} · h^{-1} in the nitrogen plasmas and less than 10 μmol · g^{-1} · h^{-1} for the flow of nitrogen-hydrogen mixture without discharge, respectively. These values were less than 10% of the amounts obtained with discharge. Thus the preparation of nitrogen-hydrogen plasma is necessary to form ammonia.

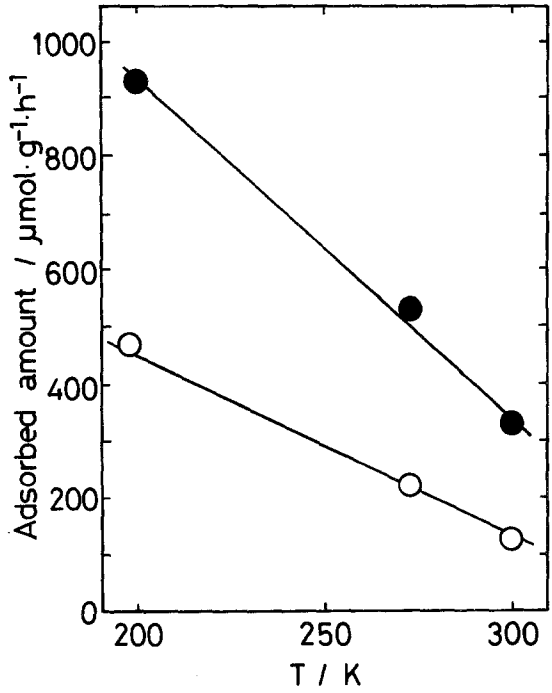

Fig. 4. Adsorbed amount of ammonia on zeolite in both discharges of nitrogen-hydrogen mixture vs. zeolite temperature: ○, radiofrequency discharge; ●, microwave discharge.

3.2. Plasma Diagnostics

Since a larger amount of ammonia was trapped on zeolite in the microwave discharge as described in the previous section, it is considered that larger amounts of ammonia precursors,[3] such as NH_x radicals and hydrogen atoms, form in the plasma prepared using microwave discharge. Thus the species in the plasma was identified by emission spectroscopy as well as mass spectroscopy, and electron energy and electron density in the plasmas were measured by a double probe technique.

The emission spectra from the nitrogen-hydrogen plasma prepared using both discharges were obtained with a monochromator in the wavelength region between 700 and 200 nm. The species and the electronic transitions observed in both plasmas are given in Table I. The 1st, 2nd, and 4th positive systems of N_2, the 1st negative system of N_2^+, the 3360 Å system ($A^3\Pi - X^3\Sigma^-$) of NH, and hydrogen atomic lines of the Balmer series were observed in the nitrogen-hydrogen plasmas prepared using both discharges. Although the observed species and electronic transitions were the same, the intensities of the band head of NH and the line of hydrogen atom in the emission spectra in the plasma prepared using microwave discharge were one order of magnitude stronger than in the plasma prepared using radiofrequency discharge, as shown in Table II.

The mass spectra measured downstream of the nitrogen-hydrogen plasma prepared using both discharges are shown in Fig. 5. During discharge, the peaks due to NH^+, NH_2^+, and NH_3^+ were observed in addition to those of residual gases in both discharges, and the peaks due to H^+ were increased. The intensities of the peaks of NH_x radicals obtained in the plasma prepared using microwave discharge were larger than in the plasma prepared using radiofrequency discharge. Small amounts of ammonia are formed also in the afterglow of the microwave discharge.

Table I. Electronic Transitions Observed in Emission Spectra of Nitrogen-Hydrogen Plasma Prepared Using Radiofrequency Discharge and Microwave Discharge

Species observed at 700-200 nm	RF discharge	Microwave discharge
N_2, $B^3\Pi_g - A^3\Sigma_u^+$	$\Delta v = 3 \sim 5$ ($v' \leq 8$)	$\Delta v = 3 \sim 5$ ($v' \leq 8$)
$C^3\Pi_u - B^3\Pi_g$	$\Delta v = -6 \sim 3$ ($v' \leq 8$)	$\Delta v = -5 \sim 3$ ($v' \leq 7$)
$D^3\Sigma_u^+ - B^3\Pi_g$	$\Delta v = -5 \sim 0$ ($v' \leq 0$)	$\Delta v = -4 \sim 0$ ($v' \leq 0$)
N_2^+, $B^2\Sigma_u^+ - X^2\Sigma_g^+$	$\Delta v = 0$(0-0, 1-1)	$\Delta v = 0$ (0-0, 1-1)
NH, $A^3\Pi - X^3\Sigma^-$	$\Delta v = 0$ (0-0)	$\Delta v = 0$ (0-0, 1-1)
H, Balmer series	$H\alpha$, $H\beta$	$H\alpha$, $H\beta$, $H\gamma$

Table II. Relative Intensities of Emission Spectrum Band Heads and Line Obtained in Nitrogen-Hydrogen Plasma Prepared Using Radiofrequency Discharge and Microwave Discharge

Transition	RF discharge	Microwave discharge
N_2, $C^3\Pi_u - B^3\Pi_g$, 0-0	300	4200
N_2^+, $B^2\Sigma_u^+ - X^2\Sigma_g^+$, 0-0	20	25
NH, $A^3\Pi - X^3\Sigma^-$, 0-0	50	2000
H, Hβ	1	20

The relations between the electron energy and electron density of plasma calculated from the i-V characteristic curve obtained by the double probe technique and the distance from the center of the cavity in the microwave discharge and of the coil in the radiofrequency discharge toward the downstream direction are shown in Fig. 6[13]. The electron energy drastically decreased upon leaving the center of the cavity in the microwave

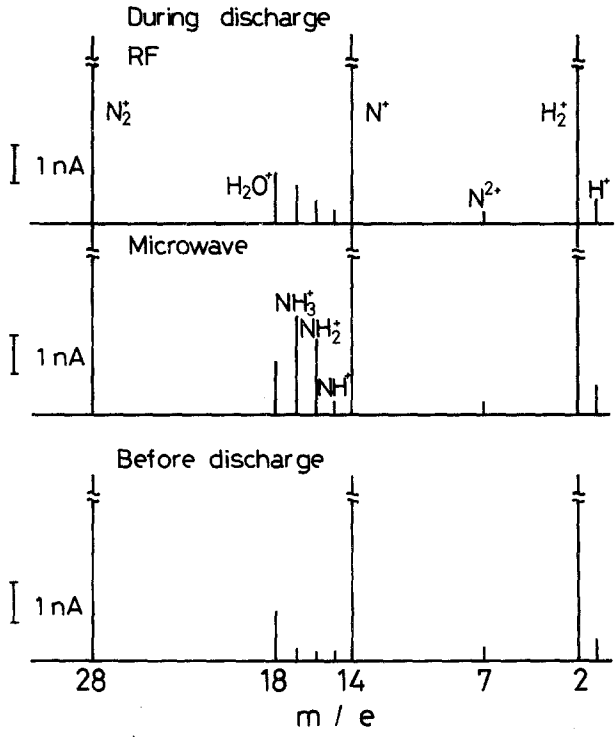

Fig. 5. Mass spectra of nitrogen-hydrogen plasmas prepared using both discharges.

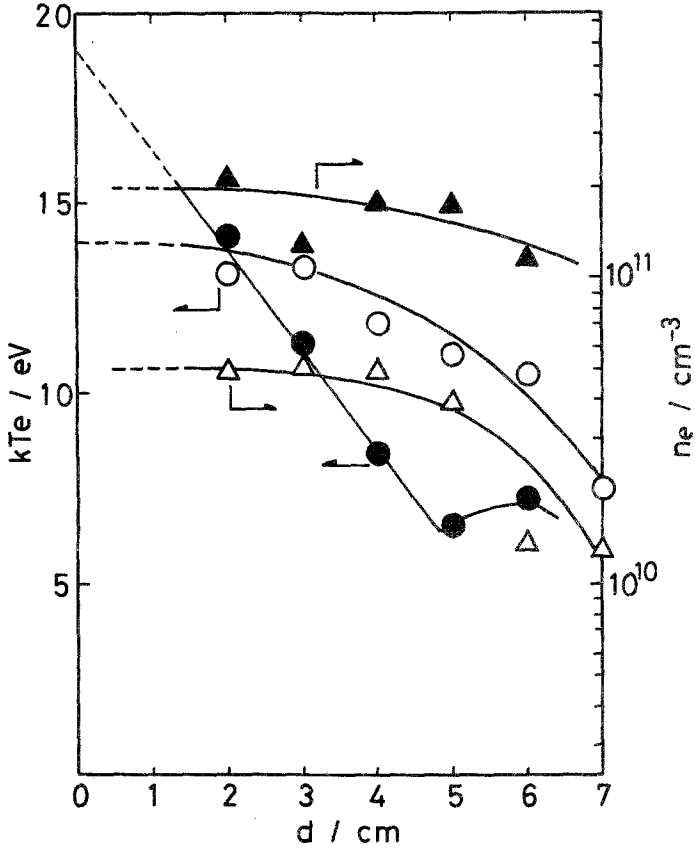

Fig. 6. Electron temperature kT_e (○, ●) and electron density n_e (△, ▲) vs. distance from the center of the coil or the cavity in both discharges: ○ and △, radiofrequency discharge; ● and ▲, microwave discharge.

discharge but did not change in the radiofrequency discharge in spite of leaving from the coil. In both the cavity and the coil, the curves fluctuated by high-frequency noise radiation into the measurement circuit.[14] So the values obtained in the outer regions of the cavity and the coil are extrapolated to the center of the cavity and the coil assuming that the electron energy change follows the same trend in the cavity and the coil as that in the outer region. The extrapolated values of the electron energies were about 19 eV for the microwave discharge and about 14 eV for the radiofrequency discharge, respectively. The electron density gradually decreased with increasing distance from the center of the cavity and the coil. The extrapolated

values were about 2×10^{11} cm^{-3} for the microwave discharge and about 5×10^{10} cm^{-3} for the radiofrequency discharge, respectively. The floating potentials calculated from the electron energies were -70 V for the radiofrequency discharge and -100 V for the microwave discharge, respectively.[14] As these values reflect the field strength given by Eq. (1), the field strength in the plasma prepared using microwave discharge is 1.5 times larger than that in the plasma prepared using radiofrequency discharge.

3.3. Advantage of Microwave Discharge over Radiofrequency Discharge in the Synthesis of Ammonia

In a previous paper[8] it was considered that the ammonia synthesis is facilitated by the surface reaction of the NH_x radicals adsorbed on zeolite with hydrogen atoms. The amounts of NH_x radicals and hydrogen atoms identified in nitrogen–hydrogen plasma prepared using microwave discharge were one order of magnitude larger than in the plasma prepared using radiofrequency discharge. As a result, twice larger amounts of ammonia are trapped on the zeolite in the microwave discharge than in the radiofrequency discharge.

NH radicals, which are considered ammonia precursors, would be produced through the reactions with the participation of N_2^+ ions, N atoms, and hydrogen molecules and atoms as given in Eqs. (2)–(7)[15–19]:

$$N_2 + e^- \rightarrow N_2^+ + 2e^- \tag{2}$$

$$H_2 + e^- \rightarrow 2H + e^- \tag{3}$$

$$N_2^+ + H_2 \rightarrow N_2H^+ + H \tag{4}$$

$$N_2^+ + H \rightarrow N_2H^+ \tag{5}$$

$$N_2H^+ + e^- \rightarrow NH + N \tag{6}$$

$$N + H \rightarrow NH \tag{7}$$

Because the formation of N_2^+ ions and N atoms as well as H atoms is necessary to form NH radicals in the nitrogen–hydrogen plasma, the electron energy has to be larger than the ionization potential and dissociation energy of the nitrogen molecule (15.6 and 9.8 eV) and the dissociation energy of the hydrogen molecule (4.5 eV), respectively, in order to produce a larger amount of NH radicals and hydrogen atoms.

Because double probes are always negative with respect to the plasma, only the high-energy tail of the electron energy distribution function is sampled.[20] So the measured values of the electron energy are not considered the mean values. The electron energy is considerably larger than the ionization potential and dissociation energy of the nitrogen molecule in the plasma

Table III. Relative Intensities of Emission Spectrum Band Heads Obtained in Nitrogen Plasma Prepared Using Radiofrequency Discharge and Microwave Discharge

Transition	RF discharge	Microwave discharge
N_2, $C^3\Pi_u - B^3\Pi_g$, 0-0	280	4000
N_2^+, $B^2\Sigma_u^+ - X^2\Sigma_g^+$, 0-0	30	130

prepared using microwave discharge. But it is lower than the ionization potential in the plasma prepared using radiofrequency discharge. The relative peak head intensity of N_2^+ ions in the nitrogen plasma prepared using microwave discharge was one order of magnitude larger than that in the plasma prepared using radiofrequency discharge, as shown in Table III. The band head intensity of N_2^+ ions was approximately the same in the nitrogen-hydrogen plasmas prepared using both discharges, as shown in Table II. This suggests that N_2^+ ions react with hydrogen molecules or atoms forming NH radicals through reactions (4)-(6). Weak nitrogen atomic lines were observed in the nitrogen plasma prepared using microwave discharge. These lines were not identified in the nitrogen plasma prepared using radiofrequency discharge. When hydrogen was added to the nitrogen plasma, the lines disappeared. So NH radicals would also be formed through reaction (7). Thus larger amounts of NH radicals were formed from the larger amounts of N_2^+ ions, N atoms, and hydrogen atoms in the plasma prepared using microwave discharge than radiofrequency discharge.

In conclusion, the effect of the driving frequency is manifested in the synthesis of ammonia in the plasma, that is, large amounts of NH_x radicals and hydrogen atoms, which are considered ammonia precursors, are formed in the plasma prepared using microwave discharge by its higher field strength.

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REFERENCES

1. E. N. Eremin, A. N. Mal'tsev, and V. M. Belova, *Dokl. Akad. Nauk SSSR* **190,** 629 (1970).
2. E. N. Eremin, A. N. Mal'tsev, and V. M. Belova, *Russ. J. Phys. Chem.* **45,** 635 (1971).
3. G. Y. Botchway and M. Venugopalan, *Z. Phys. Chem. Neue Folge* **120,** 103 (1980).
4. O. Nomura, H. Oyama, and Y. Sakamoto, *Sci. Paper IPCR* **75,** 124 (1981).
5. K. S. Yin and M. Venugopalan, *Plasma Chem. Plasma Process.* **3,** 343 (1983).

6. K. Miyahara, *Chem. Lett.*, 1871 (1983).
7. M. Touvelle, J. L. Munoz Licea, and M. Venugopalan, *Plasma Chem. Plasma Process.* **7**, 101 (1987).
8. H. Uyama, T. Uchikura, H. Niijima, and O. Matsumoto, *Chem. Lett.*, 555 (1987).
9. R. L. McCarthy, *J. Chem. Phys.* **22**, 1360 (1954).
10. T. Shibutami and O. Matsumoto, *J. Less-Common Met.* **120**, 93 (1986).
11. T. Shibutami, Y. Kanzaki, and O. Matsumoto, *J. Less-Common Met.* **113**, 177 (1985).
12. R. F. Baddour and R. H. Dundas, *The Application of Plasma to Chemical Processing*, R. F. Baddour and S. Timmins, eds., The MIT Press, Cambridge, Massachusetts (1967), p. 87.
13. K. Yamamoto and T. Okuda, *J. Phys. Soc. Jpn.* **11**, 57 (1956).
14. J. L. Vossen, *J. Electrochem. Soc.* **126**, 319 (1978).
15. E. J. Hellund, *The Plasma State*, Reinhold, New York (1961), p. 91.
16. R. J. Donovan and D. Husain, *Chem. Rev.* **70**, 489 (1970).
17. D. Smith, N. G. Adams, and T. M. Miller, *J. Chem. Phys.* **69**, 308 (1978).
18. B. D. Green and G. E. Caledonia, *J. Chem. Phys.* **77**, 3821 (1982).
19. M. Venugopalan, *Nucl. Instrum. Methods B* **23**, 405 (1987).
20. R. M. Clements, *J. Vac. Sci. Technol.* **15**, 193 (1978).