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Reaction Scheme of Ammonia Synthesis in the ECR Plasmas

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The reaction scheme of ammonia synthesis in the ECR plasma apparatus was investigated from both identifications of the species in the plasmas and the adsorbed species on the surface of a steel substrate placed in the plasmas. The adsorbed species were considerably different when different kinds of plasmas are used. NH_x species were adsorbed on the steel substrate surface in the nitrogen–hydrogen plasma, and N_2 molecules were adsorbed in the nitrogen plasma. By the application of a negative bias potential on the substrate, the adsorption of N atom or Fe–N bond formation was identified on the steel substrate surface. When the stainless steel wall of the chamber was covered with aluminum foil, the yield of NH_x radicals, which were on both the substrate and in the plasma, decreased. By exposure of the substrate, on which N_2 molecules or N atoms adsorbed, to the hydrogen plasma, N_2 and N disappeared from the steel substrate surface, forming ammonia. Moreover, the adsorption of NH_x radicals disappeared when the stainless steel wall surface was covered with aluminum foil. Thus, the surface of the stainless steel wall acts as a catalyst in ammonia formation. The formation of ammonia in the nitrogen–hydrogen ECR plasma, in which the steel substrate served as the catalyst, is not only through the dissociative adsorption of excited nitrogen molecules but also through the dissociative adsorption of nitrogen molecular ions.

KEY WORDS: Iron catalyst; ECR plasmas; XPS; ammonia.

1. INTRODUCTION

When an iron catalyst is used as electrode material and placed in the plasma region or in the afterglow region of a nitrogen–hydrogen plasma prepared by dc or low-frequency ac discharge, the ammonia yield is enhanced.(1,2) We have carried out ammonia synthesis with iron catalyst in radio-frequency and microwave plasmas and observed an enhancement in ammonia yield with iron catalyst and the adsorption of NH_x radicals on the iron catalyst in nitrogen–hydrogen plasmas. Otherwise, the formation of the

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Fe-N bond or adsorption of nitrogen atom was identified on the catalyst which was placed in the nitrogen plasma.(3,4)

Nomura *et al.* reported the mechanism of ammonia synthesis by the reaction between nitrogen and hydrogen molecules in the ECR plasma apparatus at a pressure of 3×10^{-2} Pa. They found H, N, NH_2, and NH_3 with N_2 and H_2 in the nitrogen-hydrogen plasma by quadrupole mass analysis (QMA). They considered that the species in the plasma did not collide and reaction proceeded only on the surface of the stainless steel wall of the chamber. Thus, the NH_x identified in the plasma is evidence of the surface reaction. Moreover, they varied the nitrogen pressure and found that a higher ammonia yield was obtained at higher nitrogen pressure. From these results they postulate a mechanism of low-pressure ammonia synthesis in which an excited nitrogen molecule in the plasma arrives at the wall of the chamber, serving as the catalyst, to be dissociatively adsorbed and reacts with the preadsorbed hydrogen to yield ammonia(5,6):

$N_2 \rightarrow N_2^*$ excitation

$N_2^* \rightarrow 2N(a)$ dissociative adsorption

$N(a) + 3H(a) \rightarrow NH_3$ surface reaction

However, this proposal is only speculative. It is based only on the identification of the species in the plasma, and the surface of the catalyst is not characterized. So we feel that ammonia may be formed in the plasma without catalyst.(7,8)

Recently, XPS analysis has been applied to characterize the adsorption species on the catalyst surface, and the adsorption of NH_x on the iron surface and on the industrial iron ammonia catalyst in the synthesis of ammonia under Haber-Bosch conditions was identified.(9-11) Therefore, it is necessary to identify the adsorption species on the steel wall serving as catalyst in addition to the identification of the species in the plasma in the synthesis of ammonia in the ECR apparatus at lower pressures when discussing the ammonia formation mechanism. On the other hand, Eremin proposed that the positive nitrogen ions, which bombard the cathode in the dc glow discharge, are neutralized on the surface and may dissociate into atoms that remain in the adsorbed state. In ammonia synthesis, this is followed by the reactions of the atoms with hydrogen arriving from the plasma.(12,13) We have investigated the nitriding of aluminum in the nitrogen-hydrogen ECR plasma and observed the formation of aluminum nitride by the application of a negative bias potential supplying rf power on the substrate even at ordinary temperatures.(14) Adsorption of NH_x species as well as nitrogen molecules on the aluminum surface was not identified since aluminum has no catalytic activity,(14) although NH radicals and N_2 molecules were identified in the plasma by optical emission spectroscopy and NH_x species were identified in the afterglow of the discharge by QMA. Therefore, the yield of ammonia would be decreased by covering the stainless steel wall of the chamber with aluminum foil during the discharge and following inhibition of the catalytic effect of the steel surface.

In the present paper, we have investigated the synthesis of ammonia in the nitrogen-hydrogen ECR plasma with or without covering the stainless steel wall of the apparatus, in which the steel sheet was placed, with aluminum foil. The synthesis procedure is discussed from both the identification of the species in the plasma and the adsorbed species on the steel substrate.

2. EXPERIMENTAL

2.1. Materials

Specimens of size $10 \times 10\ \text{mm}^2$, cut from a steel sheet (carbon content less than 0.2%, 0.8 mm thickness) polished and degreased in acetone, were used as the substrate for the adsorption of species. Commercially used aluminum foil was used as received to cover the stainless steel wall. Pure nitrogen and hydrogen were used as plasma gases.

2.2. Apparatus and Procedures

The apparatus used for the synthesis of ammonia was the ECR apparatus as schematically shown in Fig. 1.(14,15) Details on the apparatus and

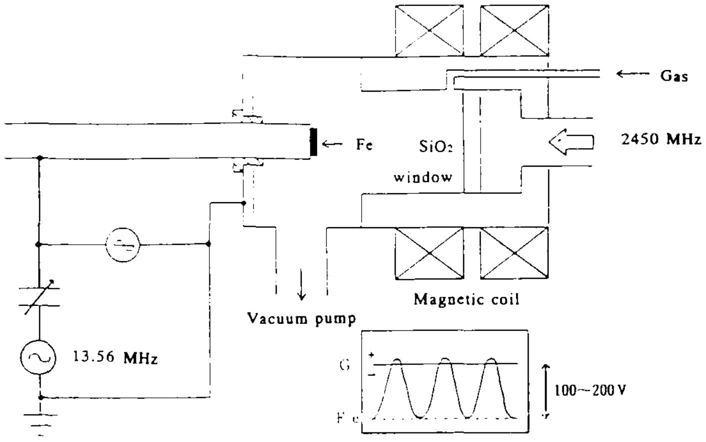

Fig. 1. Experimental apparatus.

Table I. Experimental Conditions

Plasma gas	N_2, N_2 (75% vol.%)-H_2 (25% vol.%)
Pressure Base	Below 6×10^{-4} Pa
Operation	6×10^{2} Pa
ECR resonant point	80 mm from the fused SiO_2 window
Substrate position	350 mm from the fused SiO_2 window
Microwave power	200 W
Bias potential	0 to −200 V
Substrate temperature	Room temperature
Exposure time	2 h

plasma generating process were described in the previous papers. The steel substrate was mounted on the holder placed downstream the gas flow. The substrate holder was coupled to an rf generator through an impedance matching network as shown in Fig. 1. The rf power was supplied between the grounded stainless steel chamber and the substrate holder, and a negative bias potential was applied to the substrate. The temperature of the substrate was controlled by a thermocouple placed behind the substrate.

The ammonia synthesis conditions are summarized in Table I. Nitrogen and nitrogen-hydrogen (25 vol.%) plasmas were prepared. During ammonia synthesis, the plasmas were diagnosed by optical emission spectroscopy, quadrupole mass spectroscopy, and electrical probe techniques. After exposure to the plasma for the desired period of time, the surface of the steel specimen was characterized by XPS.

3. RESULTS AND DISCUSSION

3.1. Without Aluminum Foil on the Wall of the Chamber

3.1.1. Diagnostics of Plasmas

Optical emission spectra of the plasma were recorded using a monochromator parallel to the gas flow through a fused silica window installed in the porch instead of the substrate holder. Identified species and electronic transitions are given in Table II. NH radicals and H atoms were identified

Table II. Identified Species and Electronic Transitions in Emission Spectra from Plasmas

Plasma	Species	Transition
N_2	N_2 N_2^+	$C^3\Pi_u$-$B^3\Pi_g$ $B^3\Sigma_u$-$X^2\Sigma_g^+$
N_2 (75 vol.%)-H_2 (25 vol.%)	N_2 NH H	$C^3\Pi_u$-$B^3\Pi_g$ $A^3\Pi$-$X^3\Sigma^-$ Hα, Hβ

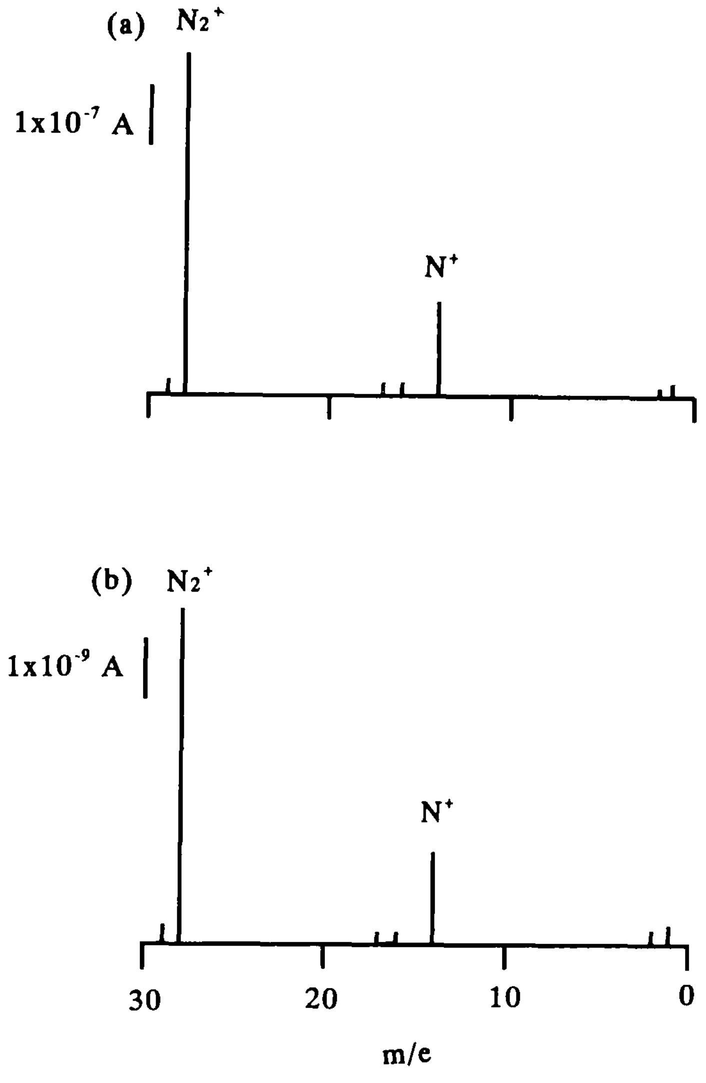

Fig. 2. Mass spectra of nitrogen plasma (A) and nitrogen (75 vol.%)-hydrogen (25 vol.%) plasma (B). (a) Ionization filament is in on state; (b) ionization filament is in off state.

in the nitrogen-hydrogen plasma in addition to N_2 molecules and N_2^+ ions which were identified in the nitrogen plasma.

Mass spectra obtained by extraction of both plasmas during ammonia synthesis into the quadrupole mass spectrometer downstream the gas flow are shown in Fig. 2. The spectra were taken with the ionization filament in

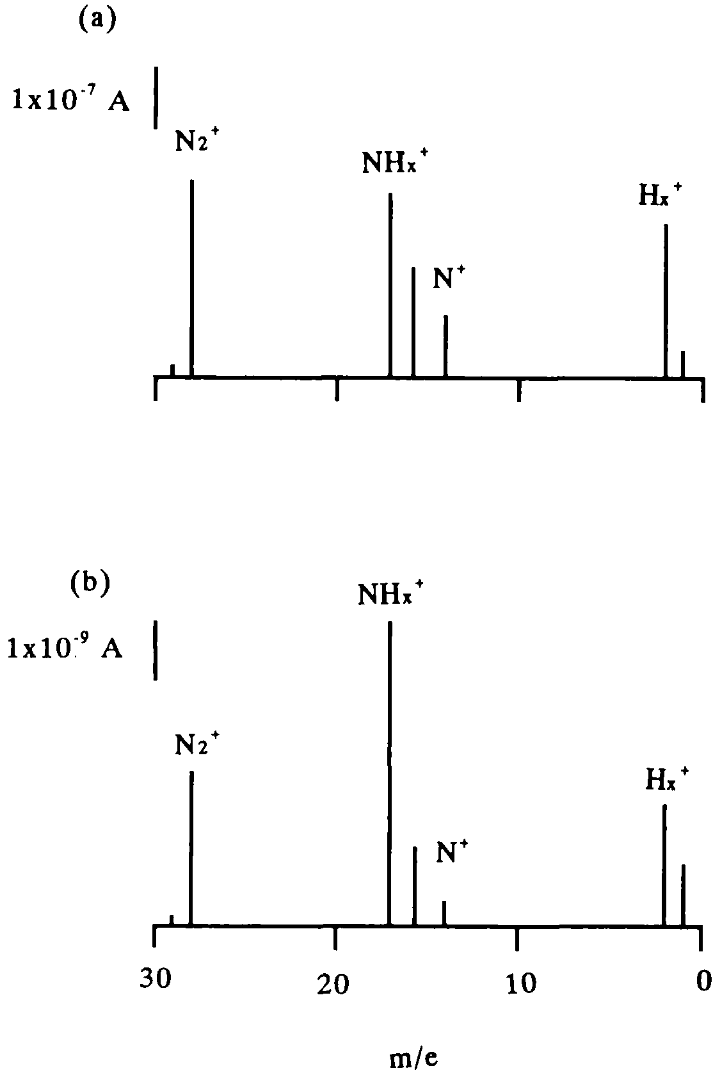

Fig. 2. Continued.

both the on and the off states. Approximately the same species were identified in both states in the same plasma, but the intensity was substantially different. Nomura *et al.* identified the formation of NH_3 in the plasma with NH_2, which was not identified before the plasma formation.$^{(5,6)}$ When the ionization filament was on, the species identified represents the sum of neutral and positive ions. On the other hand, species identified by the ionization filament in the off state were positive ions. The density of positive ions in the plasmas was two orders of magnitude smaller than that of neutrals. NH radicals that were identified in the nitrogen–hydrogen plasma by optical emission spectroscopy were not identified in the mass spectra. NH radicals would be stabilized by the formation of NH_3 or NH_2 by the reaction with H_2 molecules or H atoms.

The distribution curves of the electron energy (kT_e) and the ion density (n_i) in the nitrogen and nitrogen–hydrogen (25 vol.%) plasma in the center of the chamber were measured by the electrical double probe method. kT_e and n_i of both plasmas changed with changing probe position and had maximum values at the ECR resonant point. The maximum values of kT_e were 20 eV in the nitrogen plasma and 14 eV in the nitrogen–hydrogen plasma, respectively. The value of n_i had the maximum value of 2×10^{11} cm^{-3} in both plasmas. These values decreased near the substrate: kT_e was 5–10 eV and n_i was about 1×10^{11} cm^{-3}, which corresponded with literature values.(16) The ionization rate was estimated to be about 1% in both plasmas, and it was comparable with that estimated by the QMA as mentioned above.

Summing up the results obtained in the emission spectroscopy, mass spectroscopy, and electrical double probe technique, we conclude that the following phenomena occur in the plasmas. Several excited molecules, molecular ions, atoms, and atomic ions were formed in the plasmas. The ionization rate in the plasma was about 1%.

As we reported previously, several atomic and molecular ions, including nitrogen, N^+, NH_2^+, NH_3^+, and N_2^+, were formed in the nitrogen–hydrogen radio-frequency plasma, and the ions reacted with the negatively biased metals, the floating potential of which was about −40 V.(3) Therefore, the plasma potential distributions in the plasmas were measured by the Langmuir probe method using a stainless steel chamber as the reference electrode. The potential distribution curves are shown in Fig. 3. Approximately the same curve was observed in both plasmas. The substrate was about 10 V negatively biased versus the plasma. In this case, the surface temperature of the steel substrate was about 320 K in both plasmas.

3.1.2. Analysis of Adsorption Species on the Steel Substrate Surface

3.1.2.1. Identification of Species on the Surface after Exposure to the Plasma. After the discharges of nitrogen and nitrogen–hydrogen (25 vol.%) mixtures were continued for a period of 2 h, the adsorbed species on the steel substrate surface mounted on the sample holder were identified by X-ray photoelectron spectroscopy (XPS). The XPS spectra of N1*s* electrons are shown in Fig. 4 with those of the raw materials.

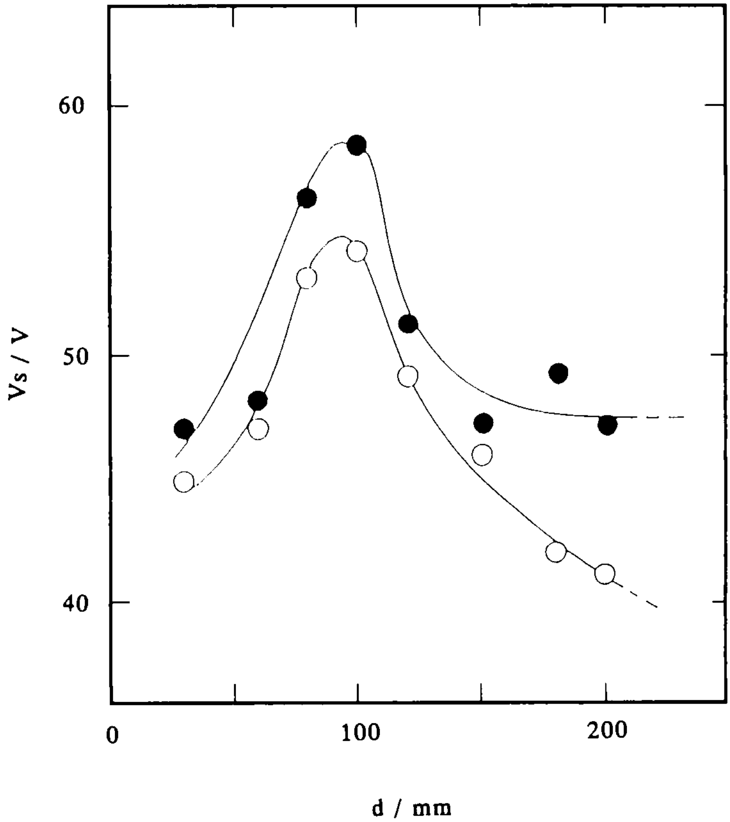

Fig. 3. Distribution of plasma potential in nitrogen plasma (●) and nitrogen (75 vol.%)-hydrogen (25 vol.%) plasma (○) as a function of the distance from the fused silica window.

After exposure of the steel substrate to the nitrogen-hydrogen plasma, the adsorption of NH_x on the steel surface was identified by XPS. The adsorption of NH_3 at about 401 eV as well as NH_2 and/or NH at about 398.5 eV was identified. Moreover, a weak peak at about 396.5 eV was identified as the peak due to the adsorbed nitrogen atom and/or the Fe-N bond formed.(9-11) These peaks are approximately the same as those observed in the formation of ammonia from nitrogen-hydrogen radio-frequency plasmas.(3)

On the other hand, the adsorbed species on the surface of the steel substrate exposed to the nitrogen plasma was almost single phase and is identified as due to adsorbed N_2 molecules. This peak may be not only adsorbed nitrogen molecules but also NH_x species identified on the steel surface after exposure to the nitrogen-hydrogen plasma. However, it is

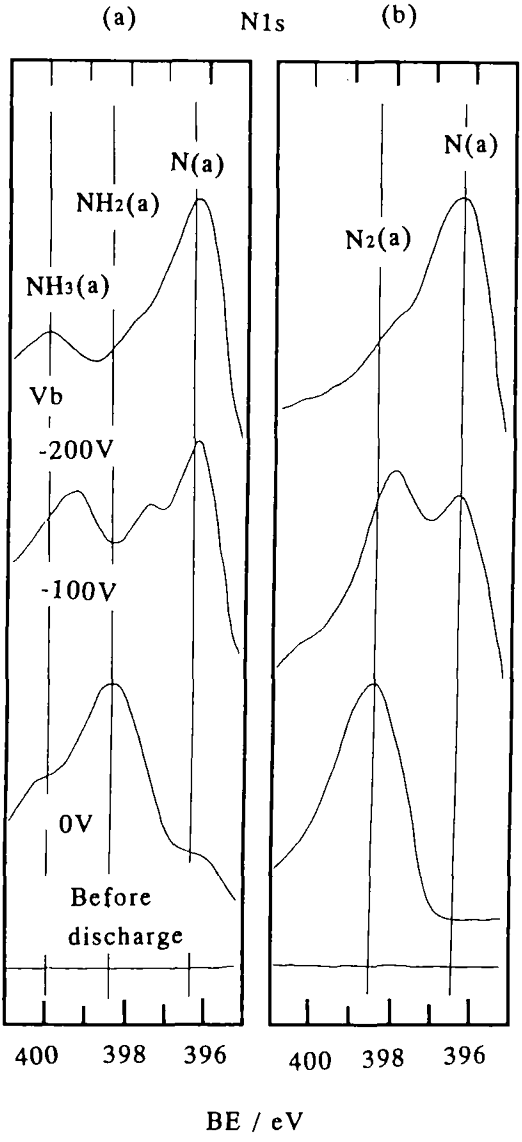

Fig. 4. XPS spectra of N1*s* electrons on steel substrates exposed to nitrogen (75 vol.%)-hydrogen (25 vol.%) plasma (a) and nitrogen plasma (b).

considered that the peak is due to the adsorbed nitrogen molecule because the peak corresponds to the single phase and the nitrogen molecule was only identified in the nitrogen plasma without NH_x species as shown in Fig. 2.

The species formed in the plasma would be only adsorbed on the steel substrate surface without chemical reaction because the surface was at room temperature and the self-bias potential of the substrate was low. Thus, the effect of negative bias potential on the substrate upon application of rf power was investigated. To join the ions prepared in the plasmas more positively to the ammonia synthesis through their adsorption on the steel substrate surface, −100 V and −200 V negative bias potential was applied on the substrate.

The XPS spectra of N1*s* electrons observed on the steel substrate exposed to both plasmas are also shown in Fig. 4. In the XPS spectra of the substrate surface after exposure to both plasmas and with application of negative bias potential, the areas of the peaks at about 401 and 398.5 eV were decreased and that at about 396.5 eV was increased in both plasmas. When the negative bias potential was applied on the steel substrate, the peaks due to the adsorbed species N_2, NH, NH_2, and NH_3 decreased with increasing negative bias potential. When the negative bias potential reached −200 V, the adsorbed molecular species almost disappeared and only the peak at about 396.5 eV, which was identified as the peak due to the adsorbed N atom or Fe–N bond, was identified. It is reported that the peaks at about 397 eV disappeared only above 670 K, although the peaks at about 400 and 399 eV disappeared by heating at 370 K and the nitrogen atoms were only attached to the metallic iron and formed a strong Fe–N bond.(10) In the application of negative bias potential, similar phenomenon occurred. Namely, the areas of the peaks at about 401 and 398.5 eV decreased with increasing negative bias potential and almost disappeared upon application of −200 V of bias potential. Only the peak at about 396.5 eV was observed. By the application of negative bias potential on the substrate, the dissociative adsorption of nitrogen positive molecular ions on the substrate was observed. Since the stainless steel wall of the ECR reaction chamber is negatively biased versus plasma,(17) nitrogen molecular ions also dissociatively adsorb on the wall.

3.1.2.2. Reaction of Adsorbed Species with Hydrogen Plasma. As described in the previous paragraph, the adsorption of N_2 molecules and of N atoms on the steel substrate or the formation of Fe–N bonds was identified by exposure of the steel substrate to the ECR plasma. In the formation of ammonia in a low-pressure plasma, the reaction scheme is as follows: Excited N_2 molecules and/or N_2^+ molecular ions dissociatively adsorb on the catalyst surface and react with the hydrogen atoms.(1,2,12) Thus, the reaction between

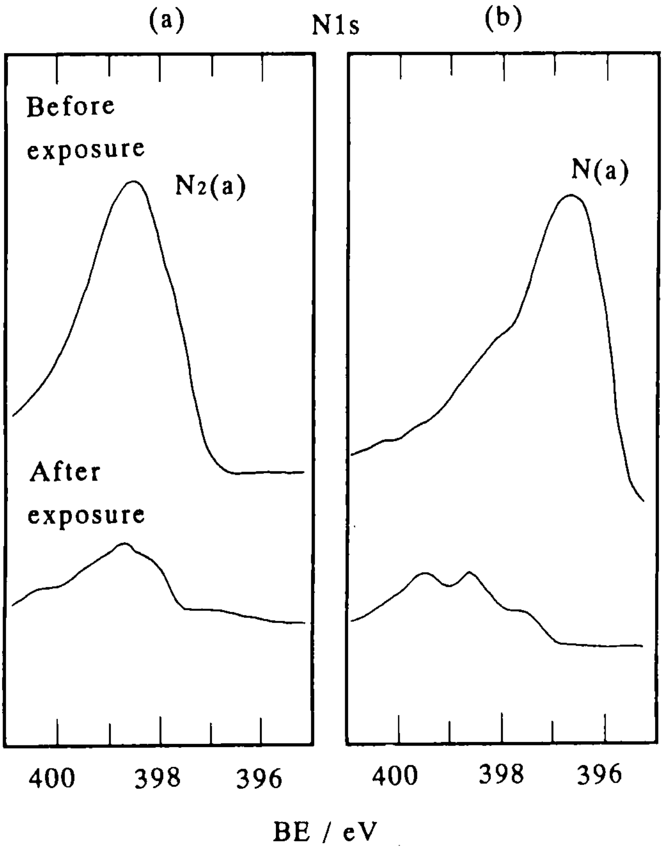

Fig. 5. XPS spectra of N1*s* electrons on the steel substrate before and after exposure to the hydrogen plasma. (a) Steel substrate nitrided without application of the bias potential; (b) steel substrate nitrided with application of the bias potential.

adsorbed N_2 molecules and N atoms on the steel substrate, which were prepared by the exposure of the steel substrate to the nitrogen ECR plasma with and without negative bias potential and hydrogen ECR plasma, is examined. The conditions of preparation of the hydrogen plasma are the same as those in Table I except for the kind of gas used. The reaction was carried out for 15 min.

The XPS spectra of the N1*s* electrons of the steel substrate before and after exposure to the hydrogen plasma is shown in Fig. 5. Upon exposure of the steel substrate that adsorbed N_2 molecules, the peak area at about 398.5 eV decreased and the binding energy of the peak head shifted slightly to higher value. The adsorbed N_2 molecules reacted with hydrogen atoms

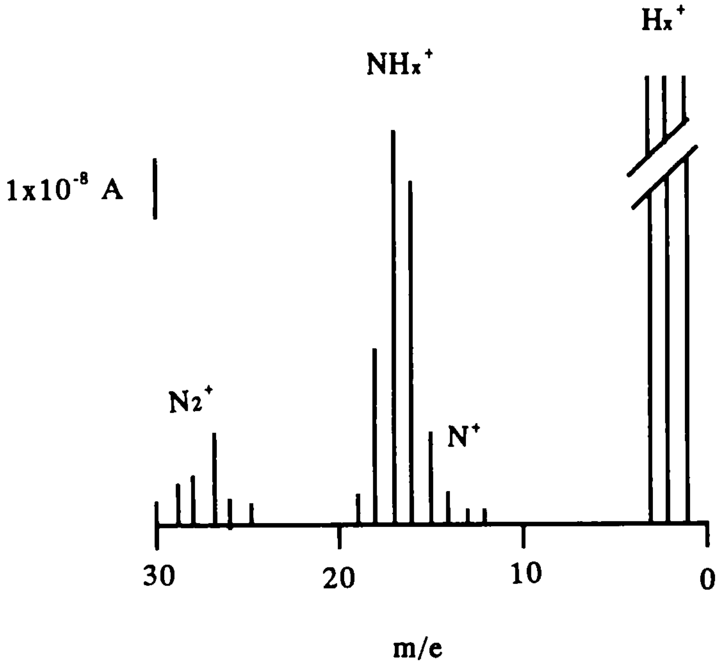

Fig. 6. Mass spectra of hydrogen plasma in which the nitrided steel substrate was placed.

in the plasma and NH and/or NH_2 may be formed. Otherwise, the peak at about 396.5 eV, identified as being due to N atoms, disappeared and weak peaks at about 400 eV and 398.5 eV appeared upon exposure of the steel substrate to the hydrogen plasma. The adsorbed N atoms also reacted with hydrogen atoms in the plasma, and NH and/or NH_2 were formed. The QMA method was used to identify the species formed by the reaction between adsorbed species on the steel substrate and hydrogen atoms which were observed in the plasma. Mass spectra obtained during the reaction are shown in Fig. 6. NH_x ($x = 0$–4) were identified with H_2^+ and H^+. The adsorbed nitrogen species, N_2 molecules and N atoms, reacted with hydrogen atom in the plasma to form ammonia. In this case, the peak head intensity of the NH_x species was very strong. Thus, it is considered that the large amounts of nitrogen and/or nitrogen-hydrogen species would also adsorb on the stainless steel wall of the reaction chamber of the ECR apparatus.

3.2. With Covering by Aluminum Foil on the Wall of the Chamber

By optical emission spectroscopy, almost the same species were observed in the nitrogen-hydrogen plasma whether the wall was covered

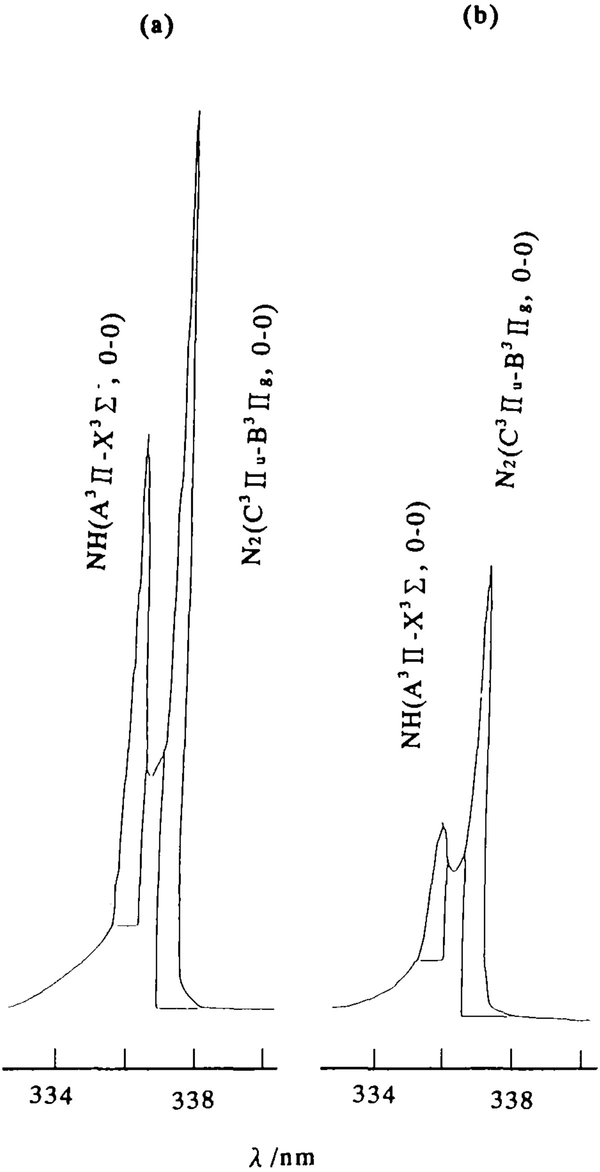

Fig. 7. Comparison of emission spectra from nitrogen-hydrogen plasma prepared in the ECR with (b) or without (a) covering the stainless steel wall with Al foil.

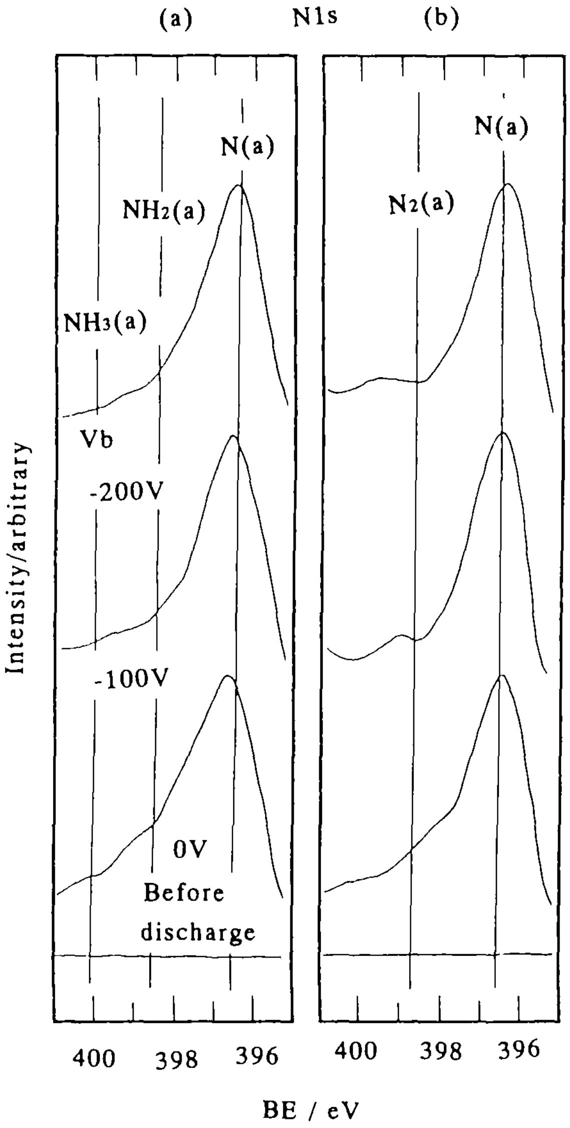

Fig. 8. XPS spectra of N1*s* electrons on the steel substrate exposed to nitrogen (75 vol.%)-hydrogen (25 vol.%) plasma (a) and nitrogen plasma (b) prepared in the ECR chamber, the stainless steel wall of which was covered with Al foil.

with aluminum foil or not. However, the peak head intensity of NH radical was substantially decreased by covering the wall of the chamber with aluminum foil, as shown in Fig. 7. Moreover, the ion current in the mass spectra of the nitrogen-hydrogen plasma also decreased by covering.

After the discharges of the nitrogen and nitrogen-hydrogen mixtures in the chamber, with the wall covered by aluminum foil, were continued for a period of 2 h, the adsorbed species on the surface of the steel substrate mounted on the sample holder were identified by XPS. XPS spectra of N1*s* electrons are shown in Fig. 8. The adsorption of NH_x radicals on the surface of the steel substrate could not be observed although the substrate was placed in the nitrogen-hydrogen plasma.

Plasma diagnostics and XPS analysis of the adsorbed species on the surface showed that large amounts of NH_x radicals are formed using the surface of the stainless steel wall of the ECR chamber as catalyst.

4. CONCLUSION

In the synthesis of ammonia in a nitrogen-hydrogen ECR plasma, the following reaction schemes are clarified using both surface analysis of the catalyst surface and plasma diagnostics:

1. Dissociative adsorption of nitrogen molecules and/or molecular ions as well as adsorption of NH_x on the stainless steel wall of the reaction chamber:

$$N_2 \rightarrow 2N(a)$$

$$N_2^+ + e \rightarrow 2N(a)$$

$$NH_x \rightarrow NH_x(a)$$

2. Reaction between adsorbed species on the surface and hydrogen in the plasma, forming adsorbed NH_x:

$$N(a) + xH \rightarrow NH_x(a)$$

3. Desorption of the products:

$$NH_x(a) \rightarrow NH_3$$

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