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Optimization of Amino Group Introduction onto Polyurethane Surface Using Ammonia and Argon Surface-Wave Plasma

Akihisa Ogino*, Suguru Noguchi¹, and Masaaki Nagatsu

Graduate School of Science and Technology, Shizuoka University, Hamamatsu 432-8011, Japan

¹*Graduate School of Science and Engineering, Shizuoka University, Hamamatsu 432-8561, Japan*

Effects of hydrogen and NH_x species produced by a surface-wave excited Ar/NH_3 plasma on amino group introduction onto a polyurethane surface were studied by comparing the results of optical emission spectroscopy (OES) and primary amino group concentration. For increasing the introduced primary amino group concentration on the surface, the monitoring and control of the concentration of NH_x species as a precursor and that of atomic hydrogen as an etchant are important. From the results of X-ray photoelectron spectroscopy (XPS) and OES analysis, the primary amino group concentration and the emission intensity of H_β reached a minimum and a maximum, respectively, at around 25% NH_3 gas mixture ratio. An excess of atomic hydrogen over nitrogen grafting species might reduce the amino group selectivity and N/C surface density. To increase the concentration of NH_x species produced in a plasma, the enhancement of NH_x generation by the Penning effect was examined by adding Ar gas. As a result, the primary amino group concentration increased with the increase in the emission intensity of NH . However, the amino group selectivity became lower than that in the case of pure NH_3 plasma treatment since not only the primary amino group concentration but also the secondary and tertiary amino group concentrations increased with the enhanced decomposition of NH_3 by Ar metastables.

* E- mail address: taogino@ipc.shizuoka.ac.jp

1. Introduction

For forming micro- or nanosized biochips, immobilization techniques for specific biomolecules on substrate surfaces are important. With dry plasma processing, one can modify small areas on substrate surfaces at low temperatures without using chemical solvents. The most important feature of plasma processing is that the surface properties can be modified without any changes in bulk properties. This is a great advantage of nonequilibrium plasma processing in treating polymers and biomaterials, which are easily affected by heat. In medical treatments, the surface properties of medical equipment, such as biocompatibility, are especially important. When catheters made of polyurethane (PU) are exposed to blood, plasma proteins within blood are adsorbed onto the material surfaces, followed by the activation of clotting factors or the adhesion and activation of platelets, and finally the formation of a fibrin network. PU has excellent mechanical properties and good blood tolerance, and has been used in many types of blood-contacting equipment. However, the antithrombogenicity of PU should be improved for use in blood vessels. To satisfy this requirement, heparin, which is the most suitable biomolecule for the inhibition of thrombus formation, has been used as an immobilizing biomolecule. To immobilize heparin, the UV irradiation emitted from the plasma is often used to treat the surface as a unique and versatile method and a fast functionalization process.^{1, 2)} For amino group addition onto the polymer surface, ammonia, nitrogen/hydrogen gas mixture, and/or other gas admixtures are used to obtain a sufficient concentration of NH_2 .³⁻⁵⁾ The primary amino group exhibits a high reactivity for binding oxygen-containing functional groups (e.g., $-\text{COOH}$, $-\text{OH}$, and $-\text{CHO}$). To further increase the introduced primary amino group concentration, an

efficient method of generating NH_x radicals should be considered in plasma processing. A reduction of hydrogen radicals is also one of the important issues because hydrogen radicals also act as an etchant that reduces amino groups. Umemoto *et al.* reported a NH_2 radical density of 10^{12} cm^{-3} obtained by a laser-induced fluorescence technique in a low-pressure plasma.⁶⁾ Kurosawa *et al.* also studied the properties of an Ar and NH_3 mixture gas plasma by RF discharge and reported that the dominant radical was NH_2 in the plasma; however, the dominant ion and concentration ratio of each species largely depended on discharge conditions, such as electron temperature, gas mixture ratio, and pressure.⁷⁾ Furthermore, a higher NH_2 density of 6-8 vol% NH_3 concentration in high-pressure dielectric barrier discharge was reported by Leipold *et al.*⁸⁾ However, the effect of the concentration ratio between NH_x and hydrogen radicals on amino group introduction has not yet been clarified.

For increasing the introduced primary amino group concentration on the surface, the monitoring and control of the concentration of NH_x species as a precursor and atomic hydrogen as an etchant are important. Therefore, the effect of these species excited by a surface-wave plasma on amino group introduction was investigated by comparing the results of optical emission spectroscopy (OES) and primary amino group concentration. This method offers the possibilities of scaling up to produce large quantities necessary for commercial use and realizing a multifunctional biochip with biomolecules arranged in micro- and nanosized patterns.

2. Experimental Procedure

The plasma reactor used consisted of a cylindrical vacuum chamber with a microwave launcher and a 2.45 GHz microwave generator.^{9,10} The vacuum chamber was 400 mm in diameter and 400 mm in height. Microwaves generated by magnetrons are coupled to the discharge chamber through slot antennas cut in a rectangular waveguide placed on a quartz plate located on top of the chamber. The treated PU sheets with a thickness of 0.5 mm were used for this study. The sheets of 4 cm² in size were cut and placed on a glass stage in a discharge chamber after ultrasonic cleaning with ethanol. The distance from the quartz plate to the sample surfaces was 100 mm. To introduce amino groups onto PU surfaces, an NH₃ and Ar mixture gas was introduced after evacuation to $\sim 10^{-3}$ Pa using a turbomolecular pump. The total gas flow rate was kept constant at 100 sccm and the total gas pressure was kept at 13 Pa during all the experiments. The ammonia gas mixture ratio NH₃/(Ar+NH₃) was varied from 0 to 100%. The plasma treatment time was 1 min. The net microwave power was typically 700 W and the reflected microwave power was maintained at roughly 20-30 W by adjusting the E-H tuner.

To obtain information on the plasma, the OES measurement was performed with SpectraPro 2300 (Acton), equipped with 1200 grooves/mm grating and photons were detected with a R928 photomultiplier (Hamamatsu) whose spectral response ranges from 185 to 950 nm. Moreover, the axial distribution of ion saturation current was measured by using a Langmuir probe at the voltage of -40 V. The probe tip made of platinum wire with a diameter of 0.7 mm and a length of 3 mm was fixed at the center in the radial direction.

The effect of plasma treatment on the sample surface was examined by X-ray photoelectron spectroscopy (XPS). The XPS apparatus employed in this experiment was Shimadzu ESCA-3400 with a Mg K α X-ray source. The X-ray was generated at 10 kV and 20 mA. The XPS spectra were scanned at a photoelectron takeoff angle of 90°. The analyzed depth of XPS analysis is expected to be roughly a few nanometers from the surface. Data acquisition and manipulation were deconvoluted using a Kratos Vision data system. The spectra were referenced to the 285.0 eV C 1s level to eliminate the charge effect. To estimate the concentration of primary amino groups introduced by the plasma treatment, the treated surface was examined by a chemical derivation technique. The samples were immersed in trifluoromethyl-benzaldehyde (TFB, C₈H₅F₃O) in methanol solution (0.1 M) and kept at room temperature for 12 h. Subsequently, the samples were ultrasonically rinsed in methanol solution and then dried in vacuum. The derivatization reaction was allowed to occur after these processes. Using this technique, fluorine atoms of TFB were utilized to label primary amino groups among other functional groups.^{3,11)} Primary amino group concentration (NH₂/C) was calculated from the peak area of F 1s and C 1s of XPS results, and primary amino group selectivity (NH₂/N) was also calculated as the ratio of primary amino group concentration to nitrogen concentration.

In the process of heparin immobilization on the plasma-treated PU surfaces, the PU sheets were put in a 1% heparin/water solution containing 10% ethanol for a few seconds. To avoid or minimize the effect of the reaction with the atmospheric constituents, the heparin immobilization process was immediately carried out after the plasma treatment. The immersed polymer samples were dried in a desiccator, and then the formed heparin composites on polymer sheets were carefully washed by

ultrasonic cleaning in ethanol for 3 min in order to rinse the unimmobilized heparin. The immobilized heparin was also identified from S 2p spectra by XPS.

3. Results and Discussion

Typical XPS spectra in C 1s of surface modification by plasma treatment are shown in Fig. 1. The C 1s region yields several different peaks, whose positions can be associated with the functional groups of chemical bonds, such as C-C, C-H, C-N, C-O, C=O, and O-C=O. The relative ratios of such bonds estimated from C 1s deconvolution are also listed in the figure. The component of nitrogen in the untreated sample is due to the PU component ($-\text{NHCOO}-$) in the principal chain by nature. The peak intensities assigned to the C-O and O-C=O bonds decreased compared with those in the case of an untreated surface. The quantitative XPS result shows that the relative ratio of oxygen to carbon (O/C) decreased from 0.32 to 0.23 after NH_3 plasma treatment. The change in O/C ratio by Ar plasma treatment was only less than 0.03. This result indicates that the oxygen contents were reduced by atomic hydrogen via the chemical reaction at the interface between the plasma and the polymer surface. On the other hand, the intensity assigned to the C=O bond slightly increased after plasma treatment. It is speculated that the C-O bond in O-C=O, which was the main component of the principal chain of PU, was broken and changed to the C=O bond. The other possibility seems to be the removal of the oxygen-containing functional group, such as the hydroxy group ($-\text{OH}$), from the surface. There were no significant changes in the C 1s spectra observed by varying the NH_3 and Ar

gas mixture ratio.

Figure 2 shows the NH_3 and Ar gas mixture ratio dependence of introduced NH_2/C and NH_2/N . In general, the surface is affected by the reaction with the atmospheric constituents, such as oxygen, water vapor, and CO_2 . To prevent the effect of atmosphere as long as possible, the derivatization using TFB solution was carried out within 120 s after taking out the plasma-treated samples from the plasma chamber. The derivatized amino group is more stable in the atmosphere and optimized for primary amine measurement by XPS. The highest NH_2/C and NH_2/N values were about 2.1 and 34% at 75% NH_3 gas mixture ratio, respectively. NH_2/C and NH_2/N reached a minimum at around 25% NH_3 gas mixture ratio. Regardless of the decrease in NH_3 concentration, NH_2/C and NH_2/N increased with decreasing NH_3 gas mixture ratio from 25 to 10%. To discuss the experimental results shown in Fig. 2, the effects of NH_x species and atomic hydrogen produced in the plasma on the primary amino group concentration were investigated.

In the plasma processing of polymer surfaces, the effect of charged particles is also an important factor. Figure 3 shows the axial distributions of ion saturation current measured in Ar and NH_3 plasmas. The surface-wave plasma is localized in the vicinity of the quartz plate and subsequently diffuses into the volume of the chamber. Hence, the plasma density decreases exponentially along the z -axis with increasing distance from the quartz plate surface. The effect of plasma density in the pure NH_3 plasma on amino group introduction was investigated and reported in our previous paper.¹²⁾ In the previous paper, it was reported that the highest NH_2/N and NH_2/C values were 52.6 and 3.0% at z

= 60 mm, respectively. The NH_2 ratio of the samples treated with a higher plasma density in the vicinity of the quartz plate ($z < 50$ mm) decreased compared with that at $z = 60$ mm. This is due to the possibility that ion bombardment, surface charge, and etching by an excess of atomic hydrogen over nitrogen grafting species reduce the amino group selectivity and N/C surface density. Ion bombardment can modify the polymer surface and create dangling bonds that can then more easily react and produce an aminated surface. Some researchers have reported that Ar treatment induces the formation of highly grafted and crosslinked structures on the polymer surface.¹³⁻¹⁵⁾ In this paper, the effect of Ar and NH_3 gas mixture ratio is an interesting feature to analyze. Therefore, the polymer substrates were placed in the downstream region ($z = 100$ mm), where the ion saturation current in the NH_3 plasma was smaller than maximum by 2 orders of magnitude, to alleviate the effect of charged particles. Figure 4 shows ion saturation current as a function of NH_3 gas mixture ratio at $z = 100$ mm. Although the ion saturation current decreased markedly with the addition of a small amount of NH_3 (< 3%) to Ar, a further increase in NH_3 gas mixture ratio resulted in the gradual decrease in ion saturation current. From the results shown in Figs. 3 and 4, it is speculated that the effects of ions are small at $z = 100$ mm except for the conditions of an NH_3 gas mixture ratio lower than about 3%.

To obtain information on the species in the plasma, OES measurement was carried out. The main advantage of OES is that it is a noninvasive technique for obtaining the relative concentrations of species. Figure 5 shows the typical emission spectra in the visible range of the Ar and NH_3 gas mixture plasma. No optical emission from NH_2 species was detected in the visible range, which can be attributed to an efficient quenching process. The detection limit of NH_2 species is about 200 times

smaller than that of NH species.¹⁶⁾ The NH species is also an important gaseous precursor of the amino groups attached on the surface. The peak intensity corresponding to the NH species could be observed at 336.0 nm;¹⁶⁾ such species are not the primary products but are produced in secondary reactions, such as $\text{NH}_2 + \text{H} \rightarrow \text{NH} + \text{H}_2$ and $\text{NH}_2 + \text{NH}_2 \rightarrow \text{NH} + \text{NH}_3$. H_β (486.1 nm) and H_γ (434.1 nm) lines resulted mainly from the fragmentation of the NH_3 molecules along with the chain scission of the polymer. There are channels for NH_2 species creation that are related to NH and atomic hydrogen in the following ways: $\text{NH}_3 + \text{NH} \rightarrow \text{NH}_2 + \text{NH}_2$ and/or $\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2$. The NH species plays an important role in the introduction of nitrogen onto the surface as well as the NH_2 species. The second positive system of N_2 as well as the first negative system of the N_2^+ line at 391.4 nm was also observed. N_2 and H_2 molecules were produced as stable-state fragmentation products. To understand the effect of species on the optimum condition of amino group introduction, the emission intensities of NH, N_2 , and H_β are plotted as a function of NH_3 gas mixture ratio in Fig. 6(a). Figure 6(b) shows their relative emission intensities. The emission intensity depends on not only the species concentration but also the electron temperature. The comparison of relative intensities is the simplest way to reduce the dependence of electron temperature and to obtain information on relative concentration. As shown in Fig. 6(a), the emission intensities at 336.0 and 486.1 nm that are attributed to NH and H_β , respectively, are largely varied compared with that attributed to N_2 . From the results of OES, three distinctive gas mixture ratios, namely, 1) NH_3 rich: 75-100%, 2) lower NH_2/C : 20-40%, and 3) Ar rich: 1-10%, were discussed. At the gas mixture ratio of 1) 75-100%, the total concentration of NH_2 , which is the primary decomposition product of NH_3 in the gas phase, increases

with an increase in NH_3 partial pressure, and then the higher NH_2/C and NH_2/N values shown in Fig. 2 are obtained by plasma treatment. At the gas mixture ratio of 2) 20-40%, the emission intensity of H_β is high. The atomic hydrogen formed as an intermediate product is highly reactive and plays an important role in forming dangling bonds on a polymer surface in the following way: $\text{C-H}(\text{surface}) + \cdot\text{H} \rightarrow \cdot\text{C}(\text{surface}) + \text{H}_2$. The hydrogen abstraction of the polymer surface may have a positive effect that creates the required dangling bonds. However, some of the introduced amino groups will also be reduced in the following way: $\text{C-NH}_2(\text{surface}) + \cdot\text{H} \rightarrow \cdot\text{C}(\text{surface}) + \text{NH}_3$. Therefore, an excess of atomic hydrogen over nitrogen grafting species might decrease the amino group selectivity and N/C surface density shown in Fig. 2. From the results of NH_2/C and OES, the concentration ratio of NH to H species is determined to be one of the important factors that increase NH_2/C . The relative intensity of NH/H_β reached a maximum at around 3% NH_3 gas mixture ratio; therefore, the phenomena at the gas mixture ratio of 3) 1-10% were investigated with the above-mentioned expectations and discussed. Under Ar-rich conditions, Ar metastables with long lifetimes aid in the dissociation of NH_3 by energy exchange, such as $\text{NH}_3 + \text{Ar}(^3\text{P}_2, ^3\text{P}_0) \rightarrow \text{NH}_2 + \text{H} + \text{Ar}$ and $\text{NH}_2 + \text{Ar}(^3\text{P}_2, ^3\text{P}_0) \rightarrow \text{NH} + \text{H}_2 + \text{Ar}$. The ionization energy threshold of NH_3 (10.6 eV) is lower than the excitation potential of Ar metastables. The potential energy of Ar metastables is consumed to dissociate and ionize NH_3 molecules at a low gas mixture ratio of NH_3 . As shown in Fig. 6, the NH species is produced mostly in reactions with Ar metastables; thus, its concentration depends on the Ar atom concentration. Under these conditions, the nitrogen, NH , and NH_2 species are effectively produced by Ar metastables and result in the increase in immobilized primary amino group

concentration on the surface shown in Fig. 2. The 25% NH_2/N measured at 2% NH_3 gas mixture ratio was slightly lower than the 33% NH_2/N obtained with the pure NH_3 plasma shown in Fig. 2, although the NH_2/C was higher. This seems to be due to the increases in primary, secondary (NHR), and tertiary (NRR') amino group concentrations induced by the enhanced decomposition of NH_3 by Ar metastables. As a result, the NH_2/N decreased compared with that in the case of pure NH_3 plasma treatment. Other reasons for the lower NH_2/N are ion bombardment and surface charge effects. As shown in Fig. 4, the ion saturation current under Ar-rich plasma conditions is slightly higher than that under NH_3 rich conditions.

The plasma-treated samples were also analyzed after the immobilization of heparin with sugar chains. To clarify the effects of the plasma treatment and primary amino group on the surface concentration of heparin, the components of sulfur contained in heparin ($-\text{OSO}_3^-$ and $-\text{NHSO}_3^-$) immobilized on the PU surface were analyzed using the S 2p signal of XPS. According to the results of XPS analysis, the immobilized S/C ratio ranged between 6 and 9% for plasma-treated PU surfaces with about 2% NH_2/C . On the other hand, the S/C ratio of the natural PU surface without plasma treatment was less than 0.5%. This result indicates that the primary amino group is an important factor for heparin immobilization. The primary amino group exhibits a high reactivity for binding oxygen-containing functional groups, such as hydroxy ($-\text{OH}$), carboxy ($-\text{COOH}$), and aldehyde ($-\text{CHO}$) groups. Such functional groups at the side chain of heparin react with the primary amino group on the plasma-treated surface and bind each other effectively. Figure 7 shows the aging effect of S/C ratio on the treated polymer surface stored in the atmosphere. Although the sample surface

was ultrasonically rinsed in ethanol before XPS analysis, the quantitative results obtained by XPS were stable for at least 30 days.

4. Conclusions

In this work, the optimization of amino group introduction onto a polyurethane surface using ammonia and argon surface-wave plasmas was studied by comparing the results of optical emission spectroscopy (OES) and primary amino group concentration. For increasing the introduced primary amino group concentration on the surface, the concentration ratio of NH_x species as a precursor to atomic hydrogen as an etchant is important. The results of XPS analysis indicate that primary amino group concentration and amino selectivity reached a minimum at around 25% NH_3 gas mixture ratio. The result of OES suggests that the NH_2/C decrease is caused by the increase in the reduction rate of the amino group due to an excess of atomic hydrogen against amino group introduction. With a low NH_3 gas mixture ratio, NH_2/C is apt to increase and correlate with the relative emission intensities of NH/N_2 and NH/H . At the low NH_3 gas mixture ratio in Ar gas, not only the primary amino group concentration but also the secondary (NHR) and tertiary (NRR') amino group concentrations increased with the enhanced decomposition of NH_3 with Ar metastables. The highest concentration and selectivity of the primary amino group were obtained at 75% NH_3 gas mixture ratio. The plasma-treated samples were also analyzed after the immobilization of heparin with sugar chains. The immobilized S/C ratio ranged between 6 and 9% for plasma-treated PU surfaces with

about 2% NH_2/C . On the other hand, the S/C ratio of the natural PU surface without plasma treatment was less than 0.5%. This result indicates that the primary amino group is an important factor for heparin immobilization.

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Figure captions

Fig. 1. XPS spectra in C 1s regions of untreated and plasma-treated polyurethane surfaces.

Fig. 2. Dependence of primary amino group concentration (NH_2/C) and amino selectivity (NH_2/N) on NH_3 gas mixture ratio.

Fig. 3. Axial distributions of ion saturation current in Ar and NH_3 plasmas measured by Langmuir probe at a gas pressure of 13 Pa and a microwave power of 700 W.

Fig. 4. Dependence of ion saturation current on NH_3 gas mixture ratio measured by Langmuir probe at a distance $z=100$ mm from quartz plate and a gas pressure of 13 Pa.

Fig. 5. Optical emission spectra of NH and H species in NH_3 and Ar mixture gas plasma at a gas pressure of 13 Pa and net microwave power of 700 W. The emission intensity for the 100% NH_3 plasma is 10 times as large as the real intensity.

Fig. 6. Dependence of (a) emission intensity and (b) relative emission intensity on NH_3 gas mixture ratio.

Fig. 7. Ratio of immobilized sulfur (S/C) contained in heparin as a function of primary amino group concentration (NH_2/C) introduced by plasma treatment.

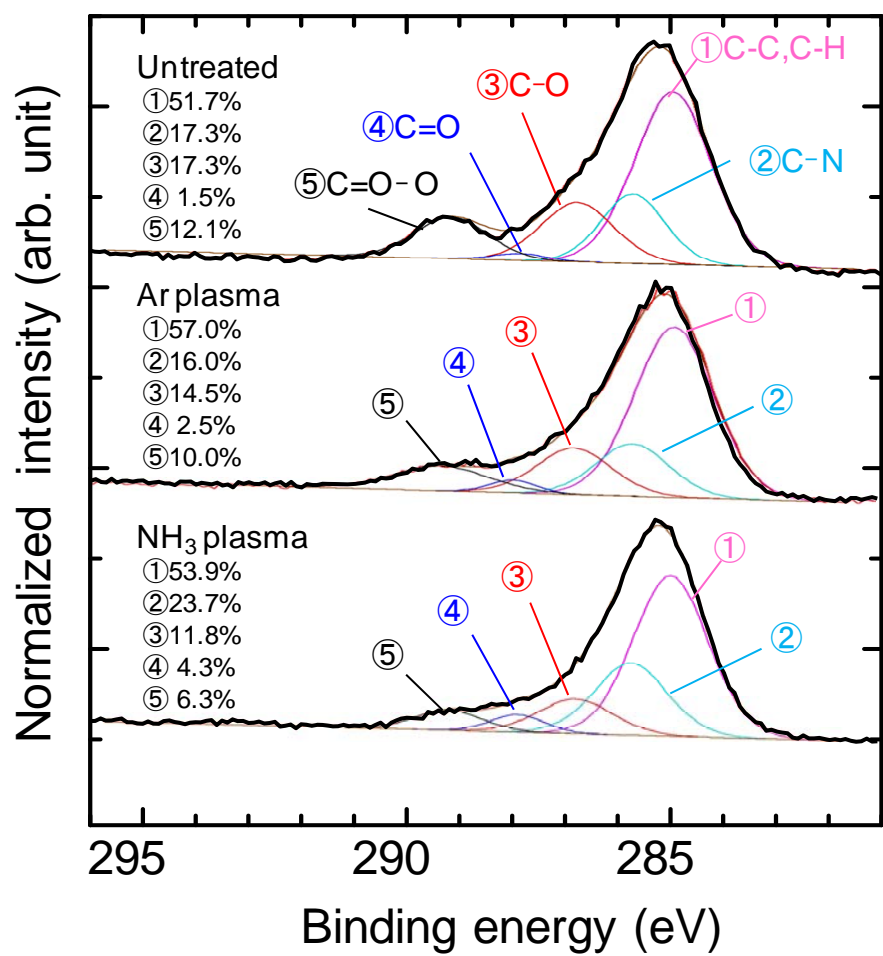


Fig. 1

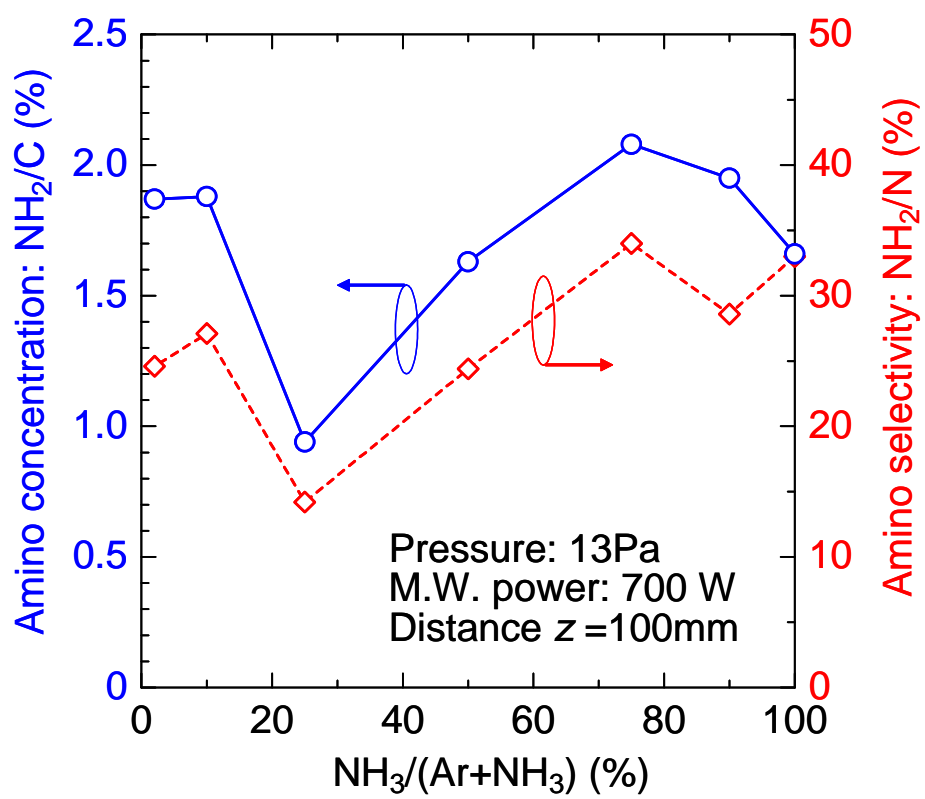


Fig. 2

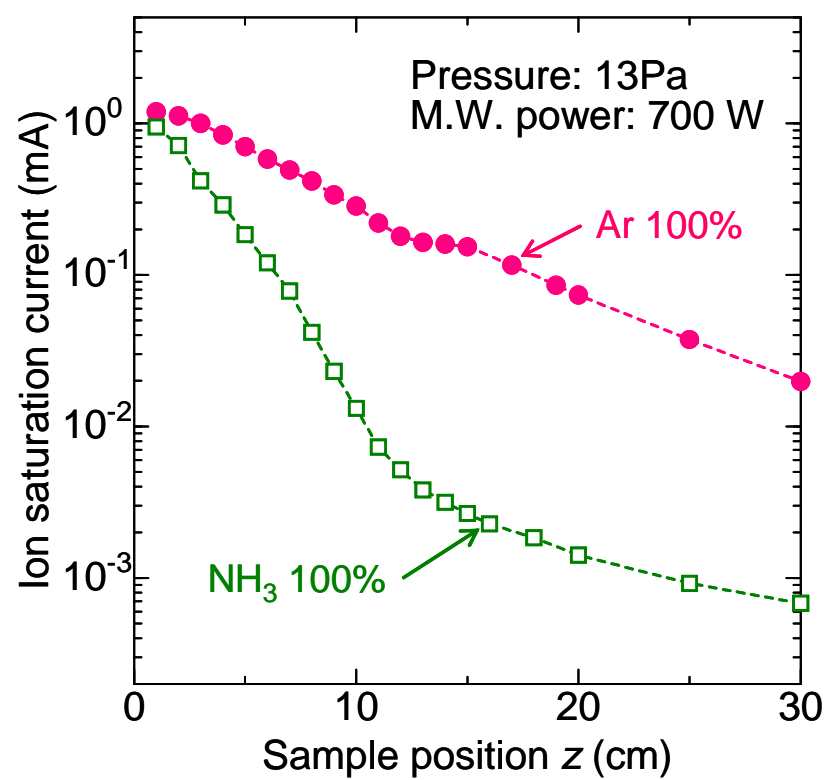


Fig. 3

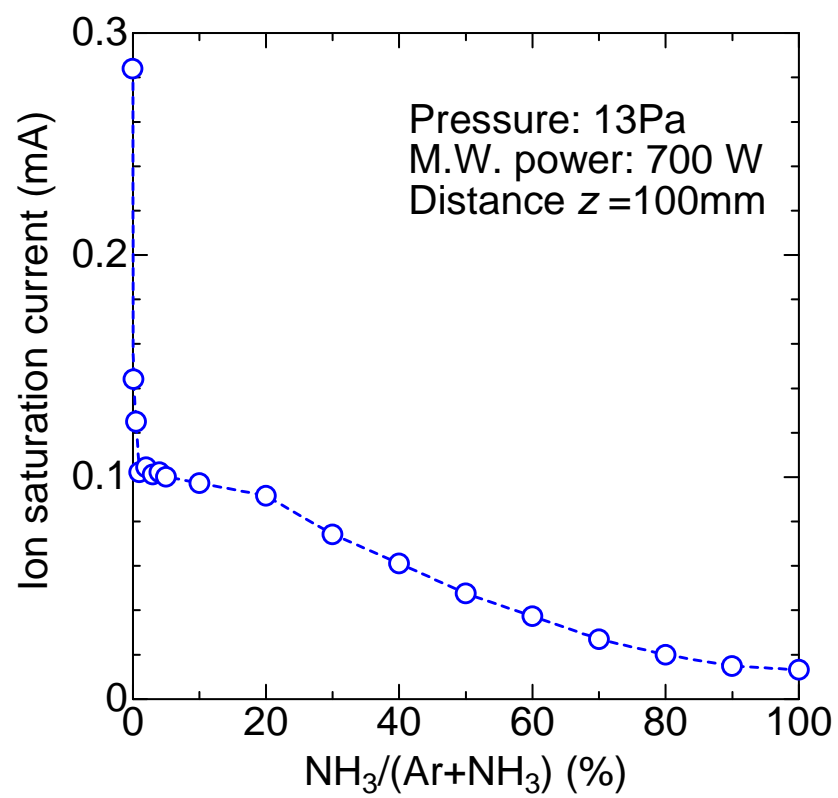


Fig. 4

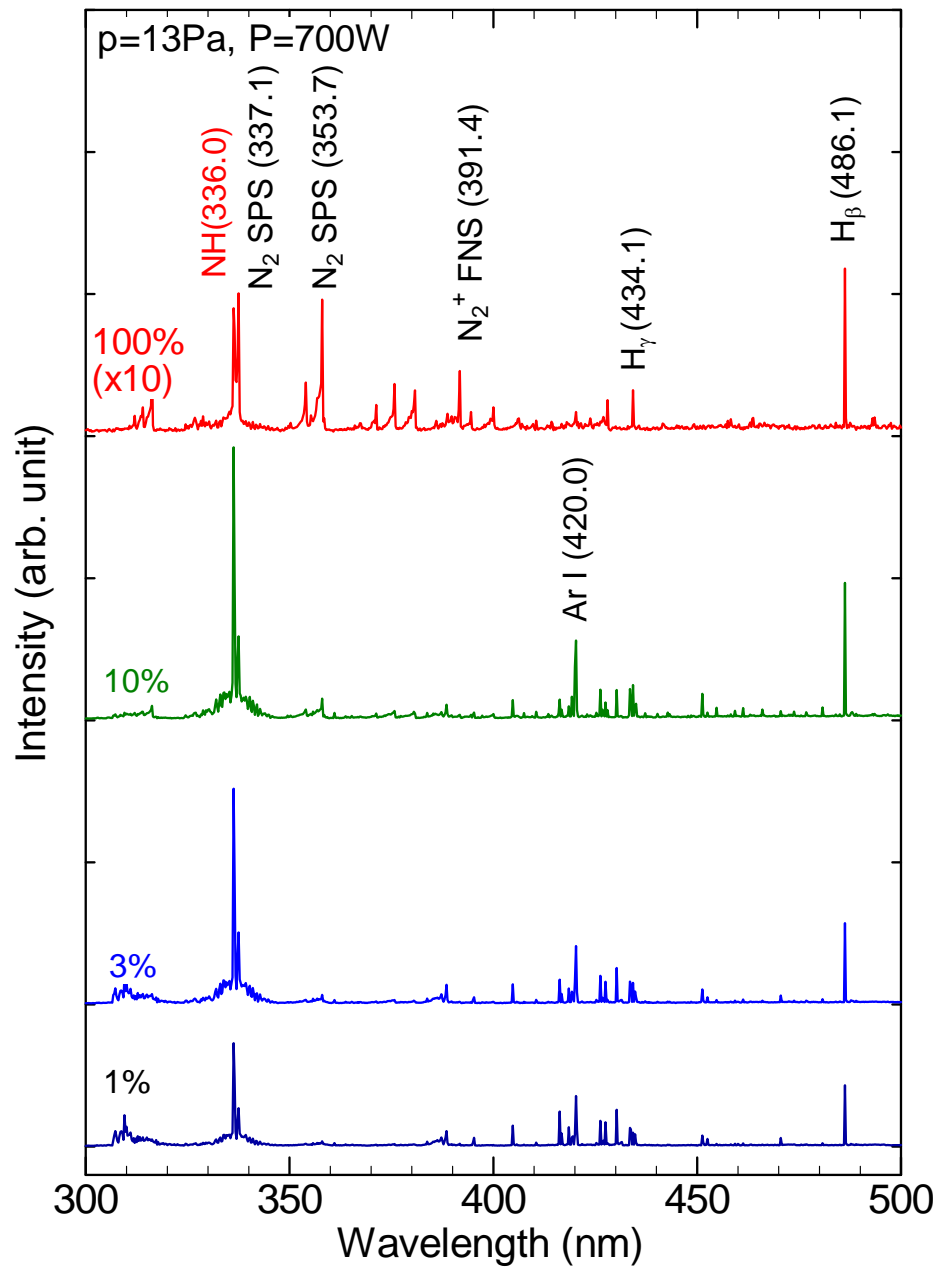


Fig. 5

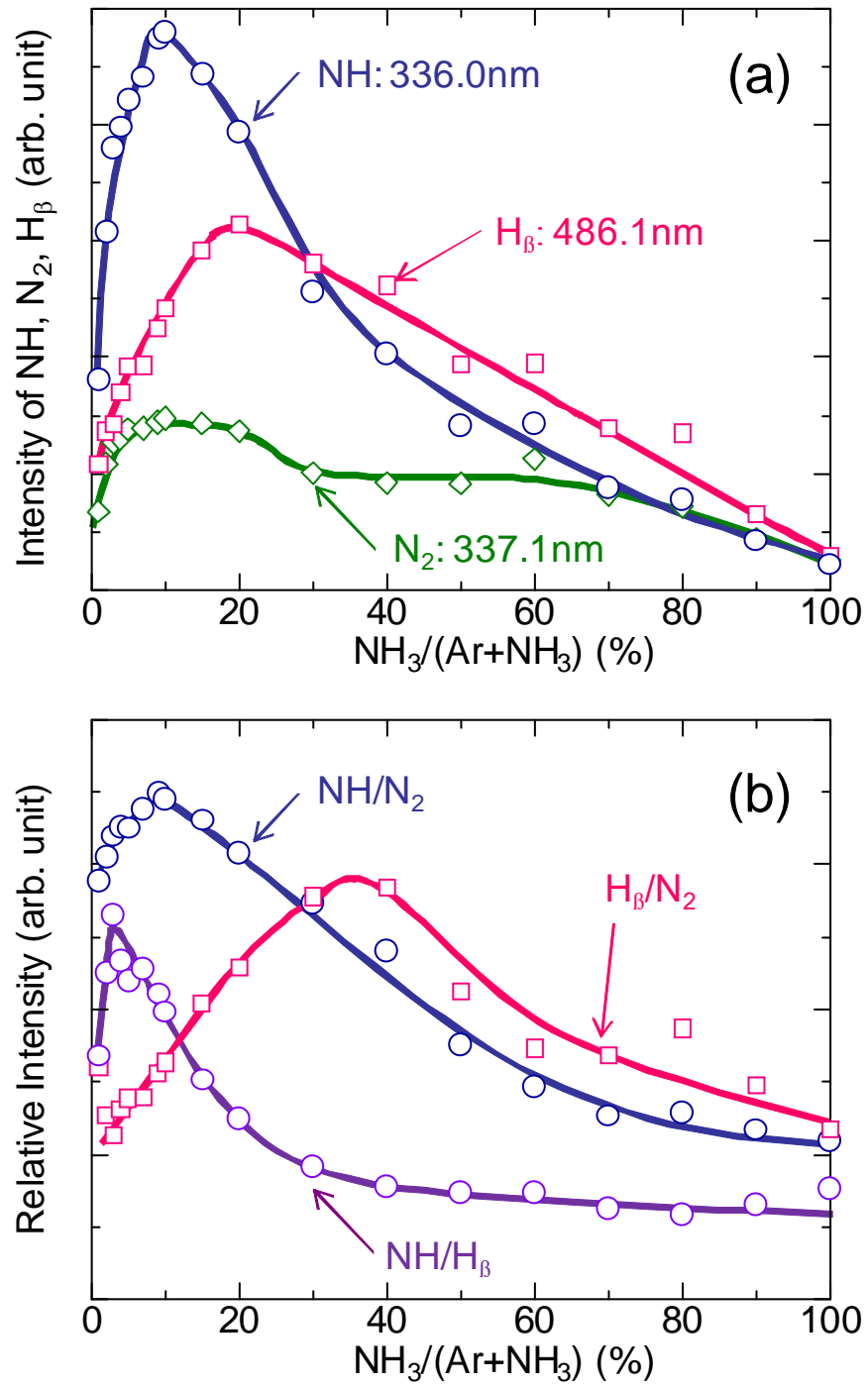


Fig. 6

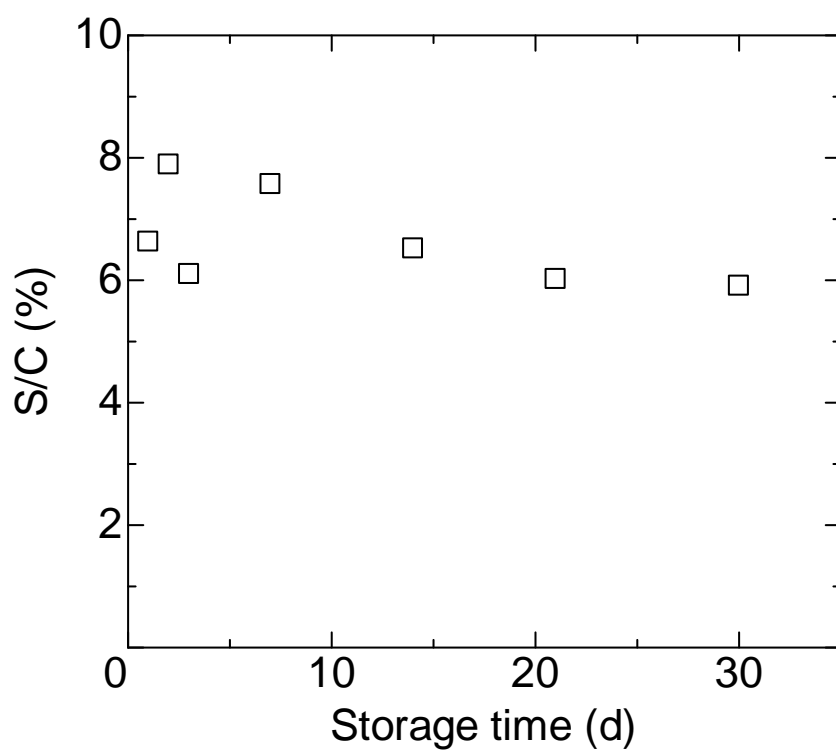


Fig. 7