Improvement of adhesive strength of PTFE using nitrogen ion irradiation

- Relation between the depth of cross-link formation and the adhesive strength -

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Abstract**:** Nitrogen ions with two different energy were irradiated to improve adhesive strength of PTFE(Poly-Tetra-Fluoro-Ethylene). The peel strength was measured by changing ion energy and its dose. Chemical changes at the PTFE surface were also analized by the XPS(X-ray-Photoelectron-Spectroscopy). As a result, it is concluded that the depth of cross-linking formation is important to improve the adhesive strength.

Keywords**:** PTFE, Nitrogen ion, Ion energy, Adhesive strength, Polar groups, Cross-linking structure

1. Introduction

PTFE (Poly-Tetra-Fluoro-Ethylene) has many excellent characteristics, such as low dielectric constant, low dielectric loss tangent, chemical stability and so on [1]. However, its adhesive strength is very weak. Therefore, improvement in adhesive strength is desired with keeping the excellent characteristic. The authors have studied on surface modification of PTFE by using nitrogen ion irradiation with low energy. Because under nitrogen ion irradiation, unevenness of the surface did not increase so much. In addition, the depth of modification layer can be controlled by changing the acceleration voltage of ions.

There are many reports related to the surface modification of PTFE [2]. But, there are few reports that the adhesive strength of PTFE improves remarkably even if the surface is activated by electrical discharges. It is well known that PTFE is one of the collapse type polymer since the binding energy of main chain (C-C) is smaller than that of side chain (C-F). Then, it is expected that adhesive strength may improve by suppressing the cutting of main chain. It is also expected that introduction of cross-linking structure may suppress the collapse of structure. Now, it has been confirmed that a lot of polar radicals are introduced at the surface of PTFE by irradiation of nitrogen ion with energy around 30 eV [3]. Accordingly, surface energy by polar component should increase by nitrogen ion irradiation with low energy. On the other hand, it is reported that cross-linking structures are introduced by the irradiation of electrons with a several 100 eV. On this occasion, penetration depth of electron is deeper than that of nitrogen ion. Therefore, it is expected that cross-linking structure may be introduced by ion irradiation with higher than that of electron. In this study, adhesive strength of samples were measured by irradiating of ions with low energy and high energy continuously. From these results, the depth of cross-linking formation contributing on the improvement of adhesive strength is discussed.

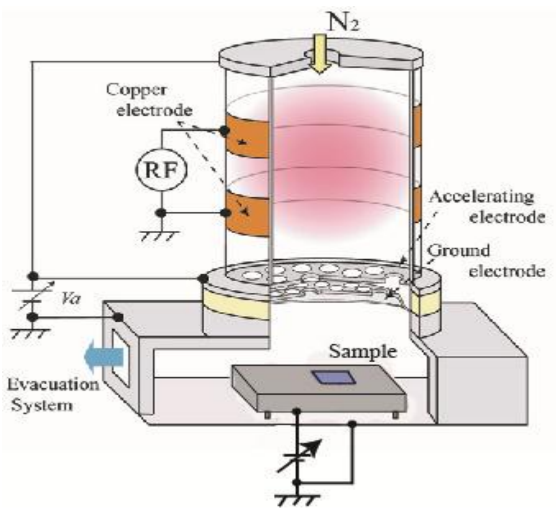

Fig.1 Ion irradiation apparatus.

2. Experiments

As shown in Fig.1, ions are irradiated onto sample by using capacitive coupled type RF electric discharge (13.56 MHz) in nitrogen. Injected power is 25 W. Plasma potential was around 60 V. The ions gain energy by acceleration voltage and plasma potential. Ion energy is controlled by changing the acceleration voltage and the retarding potential which

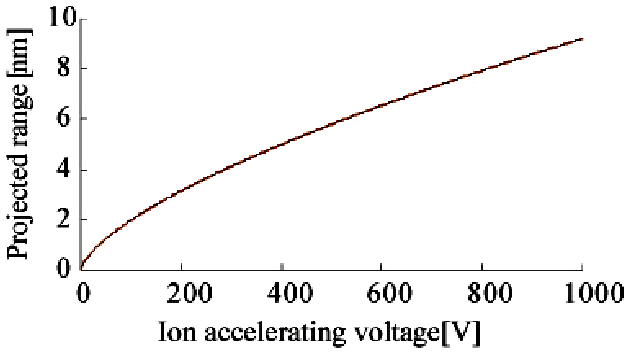

Fig.2 Projected range of N_2^+in PTFE.

is applied on the electrode placed the sample on it. The sample is PTFE film, its diameter is 30 mm and its thickness is 0.1 μm.

The sample was cleaned in ethanol bath by an ultrasonic washing machine for 10 minutes to remove surface impurities and dried it in desiccator more than 24 hours. In this study, ions with different energy were irradiated at two steps. At the first step, nitrogen ions with 30 eV were irradiated for 300 seconds to introduce polar components on the surface. At the next step, nitrogen ions with high energy were irradiated to form cross-linking structure. It is expected that cross-linking structure may be introduced around the projected range of ions. The calculated projected range of nitrogen ion in PTFE is shown in Fig.2 [4].

Surface energy can be divided into two components which are the surface energy of γ_s^p and γ_s^d, by using formula proposed by Owens et al [5]. Magnitude of γ_s^p depends on the amount of the polar groups mainly introduced on the surface. Magnitude of γ_s^d depends on the surface unevenness. Adhesive strength was measures by the 180 degrees peel test. The sample after processing (10 mm × 50 mm) is pasted up with a tape (Sumitomo 3M Ltd) using epoxy adhesive (Nichiban Co., Ltd.) . After adhesion, the force was measured at the rate of 100 mm/min.

XPS (X-ray photoelectron spectroscopy) was used to examine the density distribution of elements in depth direction and the amount of C-N bonds caused by cross-linking structure [6].

3. Result and discussion

3.1. Surface energy and peel strength

The results of surface energy and peel strength are shown in Fig.3 to Fig.6. Fig.3 and Fig.5 show the results of surface energy. Fig.3 was obtained by changing irradiation time of 1000 eV after irradiation

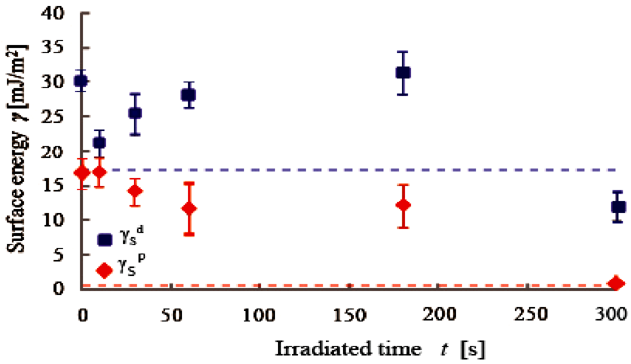

Fig.3 Surface energy of PTFE irradiated by 1000 eV after irradiation of 30 eV for 300 s.

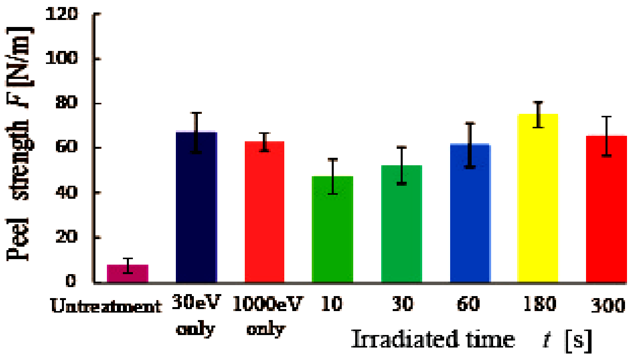

Fig.4 Peel strength of PTFE irradiated by 1000 eV after irradiation of 30 eV for 300 s.

of 30 eV for 300 seconds. Dotted lines mean the magnitude of γ_s^p and γ_s^d of untreated sample. From the results, the magnitude of γ_s^p shows the maximum at 10 seconds and decreases gradually with irradiation time of 1000 eV. On the other hand, that of γ_s^d showed the bottom at 10 seconds and the maximum at 180 seconds. It is thought that polar components introduced by irradiation of ions with 30 eV may be cut off. Fig.4 shows the results of peel test. In the Fig.4, the magnitude of untreated sample, that of irradiated sample by 30 eV only for 300 seconds and that by 1000 eV only for 300 seconds are shown. The strength shows the maximum at 180 seconds in irradiation time. The tendency of increase and decrease shows the similar to that of γ_s^d shown in Fig.3. It is clear that the change of γ_s^p does not correspond to that of the peel strength. It is deduced that peel strength may be brought about the anchor effect.

Fig.5 was obtained by changing irradiation time of 300 eV after irradiation of 30 eV for 300 seconds.

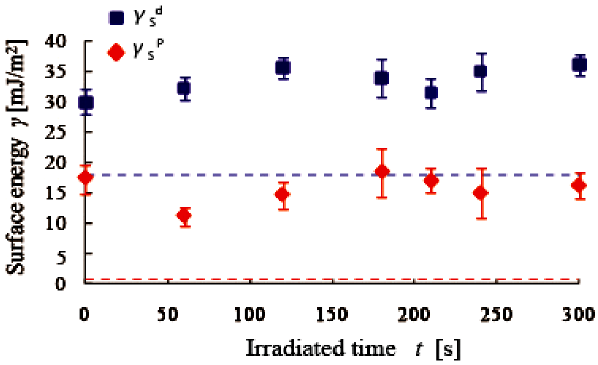

Fig.5 Surface energy of PTFE irradiated by 300 eV after irradiation of 30 eV for 300 s.

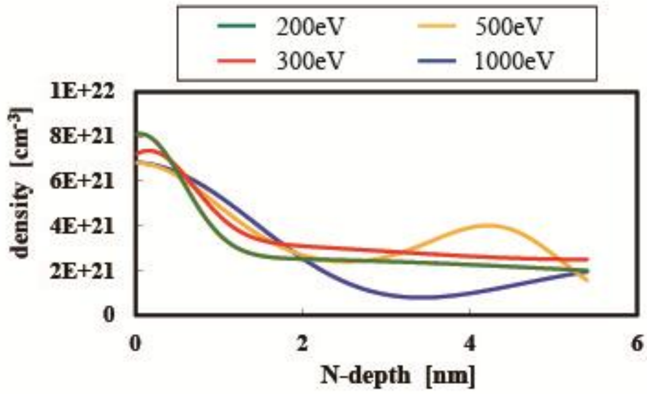

Fig.7 Density distribution of Nitrogen.

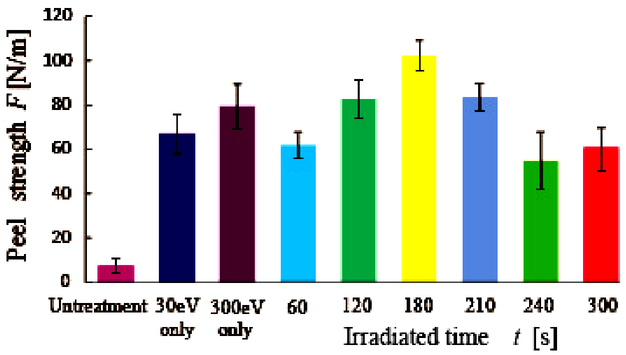

Fig.6 Peel strength of PTFE irradiated by 300 eV after irradiation of 30 eV for 300 s.

Dotted lines are the same as Fig.3. In this case, the magnitude of γ_s^p shows minimum at 60 seconds and maximum at 180 seconds. That of γ_s^p does not decrease remarkably under the test condition. The results mean that polar components introduced remain after irradiation of ions with 300 eV. Fig.6 shows the results of peel strength. The magnitude of peel strength shows the maximum at 180 seconds in irradiation time of 300 eV. The tendency of increase and decrease of peel strength shows the good agreement with the magnitude of γ_s^p shown in Fig.5.

Now, the magnitude of γ_s^p shows the same value compared with the sample irradiated by ions with 30 eV only and that irradiated by ions with 300 eV for 180 seconds after 30 eV irradiation. However, the peel strength of sample irradiated by 300 eV is higher than that of 30 eV irradiation. The magnitude of γ_s^d at 180 seconds also shows the similar value compared with that of 300 eV and that of 1000 eV. However, the peel strength of the sample irradiated by 300 eV is higher. From these results, it is thought that polar components introduced at the surface contribute on the improvement of peel strength. It is also expected that the collapse may be suppressed.

3.2.Density distribution of element to depth direction

Density distributions of nitrogen for each acceleration energy are shown in Fig.7. Irradiated dose of ion is the same at 1.0 $\times 10^{20}$ ions/m^2. In Fig.7, increase of nitrogen density is seen near the projected range. For example, in care of 500 eV, the maximum of nitrogen density is observed around the projected range. In case of 1000 eV, the maximum may be observed around 8.0 nm which is the depth in the projected range of 1000 eV. In constant, in case of 200 eV and 300 eV increase in the density of nitrogen is seen near the surface.

In general, it is known that loss of ion energy increases around the projected range [7]. That is, it is expected that cross-linking reaction may occur around the projected range. Now, nitrogen is not so reactive element. So, there is anxious about that detected nitrogen dose not react with other elements composing PTFE. Then, chemical bondings was analyzed by using XPS.

3.3.The rate of chemical bondings to the depth direction

Fig.8 shows the results of deconvolution of N1s spectrum obtained by irradiation of ions with 300 eV only. The spectrum could be devided with two peaks. Each peaks corresponds to the chemical bonds of N≡C, C-N=C and C-N-C. Chemical sift of N≡C and C-N=C are the similar value. So, it is difficult to divide into 2 peaks. From these results, it is confirmed that nitrogen reacts with C as chemical bonds. The bonds of C-N-C is expected to cause cross-linking structure. That is, it is thought that many cross-linking structure may be introduced. The rate of bondings is shown in Table1. In the table, the depth means the escape depth evaluated by changing the take off angle. For each ion energy, it is obtained that the rate of bonding of C-N-C which is originated with cross-linking structure increases around the projected range. For example, in case of 300 eV, many bonding of C-N-C was detected at a shallow layer than 1000 eV. In contrast, in case of 1000 eV, C-N-C was detected at a deep layer than 300 eV.

From these results, it is confirmed that the depth of cross-linking formation changes depending on the ion energy, and changes the peel strength.

4. Summary

Ions with different energy were irradiated to improve the adhesive strength of PTFE. Surface energy was evaluated by measuring the contact angle of liquids. As a result, the magnitude of γ_s^p increased by irradiation of ions with 30 eV. However, the magnitude of γ_s^p decreased by irradiation of ions with 1000 eV after irradiation of 30 eV. On the other hand, its value did not decrease by irradiated of 300 eV. The adhesive strength increased corresponding to the magnitude of γ_S^P in case of 300 eV.

As a result of XPS analysis, increase of nitrogen density was observed around the projected range. It can be expected that chemical reaction may occur near the projected range for each acceleration voltage. From the results of deconvolution of N1s spectrum, it is confirmed that many bonding of C-N-C which is originated with cross-linking structure is introduced around the projected range of ions. From these results, it is concluded that formation of cross-linking structure at a shallow layer and introduction of polar groups are important to improve the adhesive strength.

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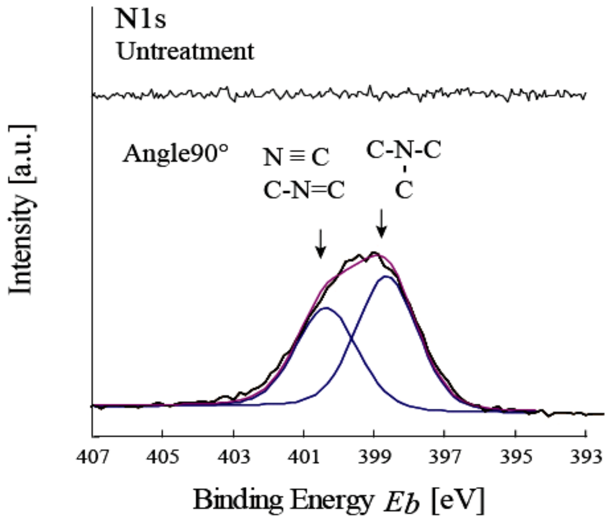

Fig.8 N1s spectrum by irradiation of ions with 300 eV only (analysis angle 90 degrees).

Table1 The rate of bondings to the depth direction.

Percentage [%]

Binding energy [eV]	Chemical bond	[V]	200			300		
		Depth[nm]	0.31	4.07	5.40	0.31	4.07	5.40
398.8	C-N-C		6.16	3.72	3.64	5.21	3.95	3.93
400.2	N≡C C-N=C		5.26	3.92	3.90	4.98	3.36	3.87

Binding energy [eV]	Chemical bond	[V]	500			1000		
		Depth[nm]	0.31	4.07	5.40	0.31	4.07	5.40
398.8	C-N-C		4.65	4.58	3.80	4.52	2.94	4.41
400.2	N≡C C-N=C		3.61	3.70	3.45	3.77	2.72	2.52

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