A Study of Excited Nitrogen Assist Chemical Reaction at PTFE Surface Treated by the Discharge in Smaller pd Region

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Abstract - The magnitude of γ_s^p PTFE surface treated by the discharge in smaller pd region becomes large compared with other treatment methods. To make clear the mechanism, the magnitude of γ_s^p was measured with and without light (340 to 600 nm) irradiation into the discharge space. The XPS analysis with chemical labeling was carried out to show the relationship between the γ_s^p and the number of polar components introduced on the surface. From these results, it is deduced that $A^3\Sigma_u^+$ state of nitrogen plays an important role on introducing polar groups on the surface.

1. Introduction

The authors have measured the surface energy at the treated PTFE surface by the discharge in smaller pd region, p is a pressure and d is an electrode distance.

For example, the surface energy of PTFE treated by the discharge was compared with that of PTFE treated by RF discharge. The result showed that the γ_s^d was approximately equal or a little smaller than the value treated by RF discharge, on the other hand, the γ_s^p was 10 times larger than that of RF treatment [1]. Results of XPS analysis showed a decrease the peak of binding energy at 292 eV and an increase the peak at 288 and 284 eV which were depending on treatment time [2]. These peaks mean the introduction of polar groups at the treated surface. Therefore, it was assumed that the increasing of γ_s^p was due to the increase of polar compounds.

It is expected that contribution of ions on surface reactions may be effective. So the surface energy by ion irradiation was obtained. A kinetic energy of ions was about 100 eV, and this magnitude was a mean value of ions near cathode region calculated by Monte-Calro method [3]. The γ_s^p was compared with the value of non-treated surface. The increase of the γ_s^p was not observed. This result was different from the result treated by the discharge and was similar to the result by RF discharge. Therefore it is pointed out that the peculiarity of the method using the discharge brings

large γ_s^p more than other processes.

This paper describes the introduction process of polar components on the surface during the treatment.

2. Experiment

2.1 Surface treatment in excited nitrogen molecules rich condition.

In this study, the authors try to clear the contribution of N_2^* on introducing polar components on the surface using the discharge.

Now, discharge space generates following particles or ray.

(a) Nitrogen ions (N_2^+)

(b) Excited nitrogen molecules (N_2^*)

(c) Electron

(d) Ultra violet ray

These species or ray are irradiated onto sample surface during processing. However, different γ_s^p values are obtained between each treatment method. The authors took attention to the flux of excited nitrogen molecules coming onto sample. Because the authors assumed that intensity of u.v. and ion flux is not so different remarkably from each treatment method.

2.1.1 Experimental condition and result

The apparatus for ion irradiation is shown in Fig.1. Commercially pure nitrogen (99.99%) was used as a treatment gas and the injected power for ion source was 25 W and the pressure was 1.3×10^{-2} Pa.

The samples (PTFE film : 50μm thickness) were cleaned supersonically in an ethanol bath and were kept in dry air at atmospheric pressure.

Ion energy was controlled by varying the applied voltage. The measured sheath voltage of this test was about 100 V. So the applied potential was set at -100 V to cancel the sheath potential. Therefore, number of ions are suppressed to irradiate sample. The sample was exposed in this condition and after that the contact angles of deionized water and methylene iodide were measured. And the surface energy was calculated from the results. The results were shown in Table 1.

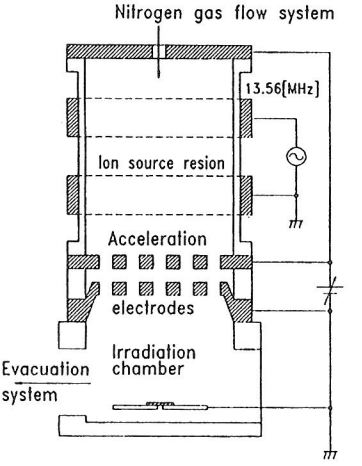

Fig.1 Apparatus for Ion Irradiation

2.1.2 Discussion

Sample treated in N_2^* rich condition shows increase of γ_s^p. The distance from discharge region of ion source to sample surface is 25 cm. So it takes about 400 μsec that N_2^* moved the distance. The radiation life time of $A^3\Sigma_u^+$ level is longer than 400 μsec. The potential energy of the level is about 6.1 eV [4]. The bonding energy of C-F bonds is about 5.0 eV[5]. Therefore it is assumed that nitrogen molecules

of $A^3\Sigma_u^+$ level may affect chemical reactions on surface.

Table 1. Surface Energy

Applied Potential	Arrival Particles	Exposure Time 10(min) γ_s^p	10(min) γ_s^d	60(min) γ_s^p	60(min) γ_s^d
-100 V	N_2^*, e	2.3	27.7	17.9	31.1
100 V	N_2^+, N_2^*, e	0.01	27.2	0.5	30.7

(unit : mJ/m^2)

2.2 PTFE surface treatment by the discharge in smaller pd region

Electron energy in this discharge distributes up to 100 eV and peak positions of nitrogen excitation cross sections exist around this energy range generally. Thus excitation yield is larger than other type of discharges. Therefore the authors took attention to chemical reactions which assisted by excited nitrogen molecules at the PTFE surface, especially molecules of $A^3\Sigma_u^+$ level.

Next experiment was done to show that the number of $A^3\Sigma_u^+$ accumulated in the discharge relates with the change of γ_s^p at the treated surface.

2.2.1 Experiment and result

The samples were prepared as the same way as mentioned in (2.1.1). Used gas was the same .

The treatment apparatus is shown in Fig.2. The pressure was 9.33 Pa and the electrode distance was 20 mm. A full wave rectified voltage of commercial frequency was applied to the electrodes. The discharge current was 10 mA and the sample was placed on the cathode during the process.

Light which wavelength is 340 to 600 nm was irradiated into the discharge space during the process to pump up the excited particles from A state to B or C states. The life times of B and C are shorter than that of A state. So the authors expect that number of molecules with a level of A state decrease.

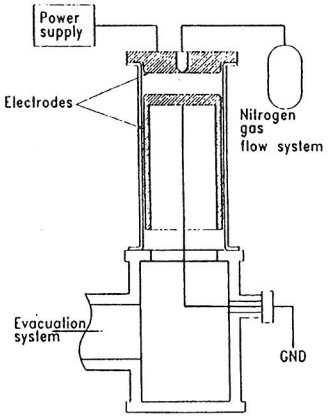

Fig.2 Treatment Apparatus

The surface energies of the treated surface by the discharge with and without irradiation are shown in Fig.3.

2.3 Chemical labeling on the PTFE treated surface

PTFE treated by the discharge without irradiation was treated by using Trimethylsilylating Reagents (TMS) for chemical labeling of the polar groups (ROH

and RCOOH) to show the change of γ_s^p relates with the change of polar group existing amount on the treated surface.

The used TMS is Hexamethyldisilazane (HMDS) - Trimethylchlorosilane (TMCS) - Pyridine solution. Reaction of HMDS with ROH and RCOOH are shown as following formulae.

$$2ROH + \underset{\text{HMDS}}{(CH_3)_3SiNHSi(CH_3)_3} \xrightarrow{\text{TMCS}} 2ROSi(CH_3)_3 + NH_3 \qquad (1)$$

$$2RCOOH + \underset{\text{HMDS}}{(CH_3)_3SiNHSi(CH_3)_3} \xrightarrow{\text{TMCS}} 2RCOOSi(CH_3)_3 + NH_3 \qquad (2)$$

2.3.1 Experiment and result

The discharge condition and sample preparation were same as (2.2). After that, the treated sample was put into the TMS reagent (1 μl) in dried reaction vial 5 min for the labeling. And the labeled sample was cleaned in the ethanol 5 min and kept in dry air at atmospheric pressure. The sample surface was analyzed by XPS. The XPS spectra of Si shows existence of ROH and RCOOH on the treated surface. The ratio which is the number of Si atoms to that of C atoms on the surface were calculated and the result is shown in Fig.4.

2.3.2 Discussion

The curve of Si/C ratio is similar to no irradiation γ_s^p curve. Therefore it is shown that change of γ_s^p relates with the number of polar groups on the surface which are ROH and RCOOH.

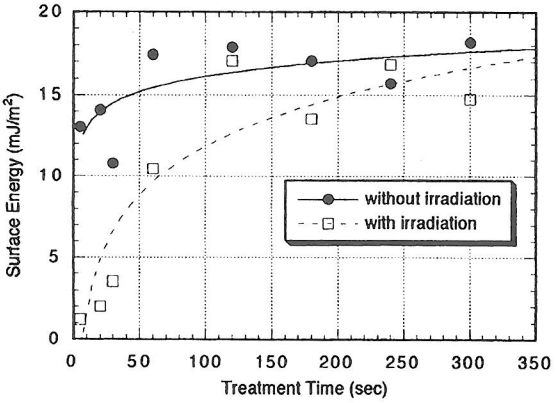

Fig.3 Surface Energy on the Treated Surface

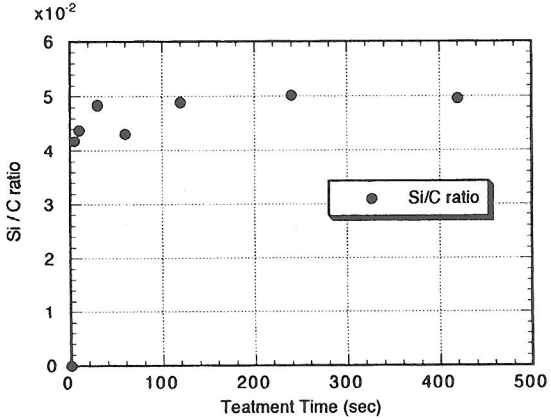

Fig.4 Ratio of Si and C on the Treated Surface
(Chemical Labeled)

3. Reaction formula

The reaction formula to describe the introduction process of polar groups at the treatment surface during the processing is shown as follows,

$$\frac{d\theta}{dt} = \alpha\{[N_2*][O_2]\}(1-\theta) - \{\beta[N_2*] + \gamma[Ion]\}\theta \qquad (3)$$

θ : the existing ratio of polar groups against unit area

$[N_2*]$: number of reached nitrogen excited particles at the surface

$[O_2]$: number of reached oxygen molecules at the surface

$[Ion]$: number of reached nitrogen ions at the surface

α / β / γ : coefficients

This formula stands on the conditions as follows,.

(a) New polar groups production do not occur at the area where polar groups are still existing .

(b) Polar groups production reaction occur on the surface only.

(c) Ion destroys the introduced polar groups on the surface.

The first term of the formula shows the production reaction process of polar groups on the surface, and the second term shows destroying process of the groups. Therefore it is assumed that excited nitrogen particles and oxygen molecules produce the polar groups and excited nitrogen particles and nitrogen ions destroy the groups.

$$\frac{d\theta}{dt} = \alpha\{[N_2*][O_2]\}(1-\theta) - \{\beta[N_2*] + \gamma[Ion]\}\theta$$

$$= -\{\alpha[N_2*][O_2] + \beta[N_2*] + \gamma[Ion]\}\theta + \alpha\{[N_2*][O_2]\}$$

where

$$A = \alpha[N_2{}^*][O_2] + \beta[N_2{}^*] + \gamma[Ion]$$

$$B = \alpha\{[N_2{}^*][O_2]\}$$

$$\frac{d\theta}{dt} = -A\theta + B \qquad (4)$$

Therefore,

$$\theta = \frac{B}{A}\left(1 - Ce^{-At}\right) \qquad (5)$$

The γ_s^p of untreated surface is approximately equal to zero, so the constant C=0 when the treatment time t=0. Therefore,

$$\theta = \frac{B}{A}\left(1 - e^{-At}\right) \qquad (6)$$

The difference between the curve of γ_s^p which are treated with and without the irradiation is the difference of the magnitude of "A" of the formula (6). The discharge current did not change during the irradiation, so it is assumed that the number of ions did not vary by the irradiation. If the number of nitrogen metastable molecules decreases by the irradiation, the magnitude of "A" may become a small value. It is observed that "A" of the treated surface with irradiation changes to a smaller value compared with the result without irradiation. And the formula (6) fits to the results as shown in Fig.3. Therefore the formula (3) showing the production process of polar groups on the surface is reasonable.

4. Conclusion

The magnitude of γ_s^p at the treated surface in nitrogen excited particles rich condition is larger than the magnitude of the treated surface by ion irradiation. And the increase of γ_s^p in the discharge of smaller pd region with irradiation is slow compared with that of the treated surface without irradiation.

It is shown that the change of γ_s^p relates with the number of polar groups on the surface.

A reasonable reaction formula for production of polar groups on the surface is shown.

5. References

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