

## Surface Modification of Fluorocarbon Polymer Film by High Density Microwave Plasma

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A surface-wave-excited plasma (SWP) source was applied to improvement of the surface hydrophilicity of polytetrafluoroethylene (PTFE). The contact angle of PTFE surface was observed to be drastically decreased by the SWP treatment within a very short time less than 5 s. The total ion dose in the PTFE sample is one of very important parameters to determine the change in the PTFE surface hydrophilicity by the plasma treatment. From X-ray photoelectron spectroscopy (XPS) measurement, drastic changes in the surface atomic composition, i.e., decrease in F atomic composition and increase in N and O atomic compositions were observed after the plasma treatment. Atomic force microscope (AFM) measurement indicated that the increase in the surface roughness after the plasma treatment. As origins of the hydrophilicity improvement, increases in both hydrophilic chemical bonds (C-O, C=O) and surface roughness were pointed out.

Key words: polytetrafluoroethylene, surface wave plasma, high-density plasma, hydrophilicity

### 1. INTRODUCTION

Fluorocarbon polymers such as polytetrafluoroethylene (PTFE) have good properties such as high electrical insulation and high resistance against chemical agents. However, addition of another property to the polymer by depositing thin films is difficult because the fluorocarbon polymers have strong chemical bonds between carbon and fluorine and have very high hydrophobicity. To improve surface adhesion property, PTFE surface was usually modified by DC/RF glow discharges at reduced pressures or dielectric barrier discharge at atmospheric pressure [1-3]. Plasma treatment with in reduced pressure is important technology in the case of surface treatment in conjunction with other plasma processes such as plasma CVD or sputtering. However, conventional DC/RF plasma sources have problems of narrow processing area and long treatment time (~2 min), that must be shortened less than a few seconds for the practical use. Surface wave-excited plasma (SWP) source is promising for such surface modification process because of its high plasma density and low electron temperature. In this paper, rapid modification of PTFE surfaces by the SWP is reported.

### 2. EXPERIMENTAL

Figure 1 shows schematic of experimental setup. An aluminum vacuum vessel (length: 32 cm, width: 10 cm, depth: 6 cm) was evacuated by a turbomolecular pump at a base pressure of  $\sim 10^{-2}$  Pa. Argon (Ar) gas was

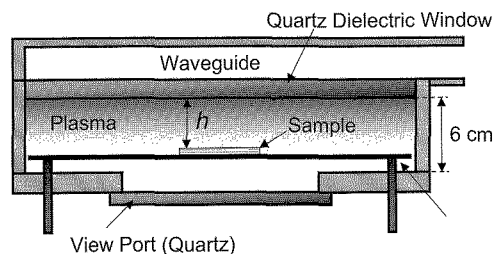


Fig.1 Schematic of experimental setup.

introduced into the vessel through a mass flow controller at a flow rate of 50 sccm, which corresponds to a pressure of 200 mTorr. Microwave power (frequency: 2.45 GHz, power: <500 W) was coupled to the plasma through a waveguide and a quartz dielectric window. Sample films of polytetrafluoroethylene (PTFE) were set on a sample holder (32 cm in length and 10 cm in width) that was positioned below the dielectric window without substrate cooling system. Estimated temperature increase was  $\sim 40$  K for 5 s plasma exposure.

Plasma treatment time ( $T_p$ ) was varied up to 25 s. Distance between the dielectric window and the sample holder ( $h$ ) was varied from 3 to 5 cm. To evaluate ion flux to the sample film, a small electrode was attached to the sample holder and ion current to the electrode was monitored.

After the surface modification of PTFE samples, their surface characteristics were investigated. Hydrophilicity was evaluated by a contact angle analyzer using pure water. Influence of plasma

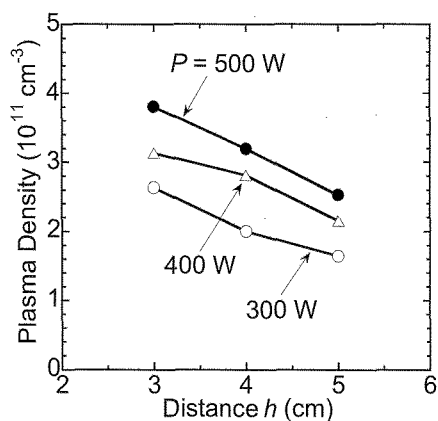


Fig.2 Spatial profile of the plasma density at microwave powers of 300, 400 and 500 W.

treatment on the surface atomic composition was measured by an X-ray photoelectron spectroscopy (XPS). Furthermore, PTFE surface roughness was measured by an atomic force microscope (AFM).

### 3. RESULTS AND DISCUSSION

Figure 2 shows plasma density as a function of the sample holder position at microwave powers of 300, 400 and 500 W. Plasma density as high as  $3.8 \times 10^{11} \text{ cm}^{-3}$  was observed at a distance of 3 cm and a microwave power of 500 W. Such high plasma density is almost one order of magnitude higher than those of conventional capacitively-coupled plasma sources. With increasing the distance from the dielectric window, however, the plasma density monotonically decreases. The spatial profile of the plasma density indicates that the plasma production is localized in the vicinity of the dielectric window. Measured electron temperature  $T_e$  was  $\sim 1.7$  eV irrespective of the sample position  $h$  from 3 to 5 cm. Based on the sheath theory, ion impingement energy is proportional to the electron temperature, and is almost constant at  $\sim 9$  eV for constant electron temperature of 1.7 eV. This implies that the plasma treatment is influenced not by the ion impingement energy but

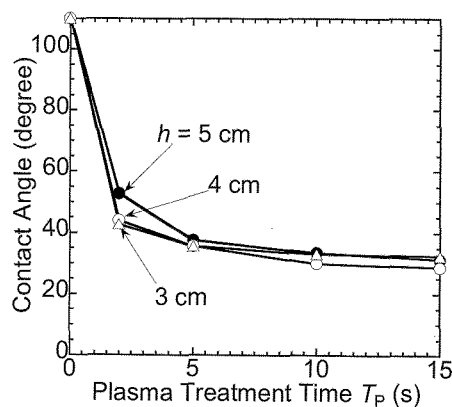


Fig.3 Contact angle of PTFE sample as a function of the plasma treatment time at a sample position of 3, 4 and 5 cm.

by the ion dose.

Figure 3 shows the contact angle of PTFE sample as a function of the plasma treatment time at sample positions of 3, 4 and 5 cm and a microwave power of 300 W. Before the plasma treatment, a contact angle of  $110^\circ$  was observed. After the plasma treatment for a very short period of 2 s, however, drastic decrease in the contact angle down to  $\sim 40^\circ$  was observed. With further increasing the plasma treatment time, the contact angle was  $\sim 30^\circ$ . This result clearly shows that the ion dose to the sample surface is one of important parameters that determine the contact angle of PTFE. It should be also noted that the plasma treatment time by the SWP is much shorter than conventional plasma sources such as an inductively-coupled plasma [1], and that the SWP is very effective to enhance the treatment efficiency.

In the plasma treatment of PTFE film by Ar plasma, the total number of ion impinging on the film surface is considered to be an important parameter to determine the surface hydrophilicity after the plasma treatment. To investigate this, contact angles of PTFE samples at various treatment conditions are re-plotted as a function of the total ion dose to the film. In this procedure, the ion flux to the sample surface is evaluated from the Langmuir probe measurement. The ion dose to the sample is evaluated from the following formula [4],

$$\Phi = 0.61 n_p u_B T_p \quad (1)$$

where,  $n_p$ ,  $u_B$  and  $T_p$  denote plasma density, ion Bohm velocity, and plasma treatment time, respectively. Bohm velocity is expressed by the following formula,

$$u_B = \sqrt{kT_e/M} \quad (2)$$

here,  $T_e$  and  $M$  denote electron temperature and Ar ion mass, respectively. Figure 4 shows contact angle of the PTFE film as a function of ion dose to the sample surface for sample positions of 3, 4 and 5 cm. The contact angle fits on a single curve irrespective of the sample position. This result clearly shows that the ion dose to the sample surface is one of important

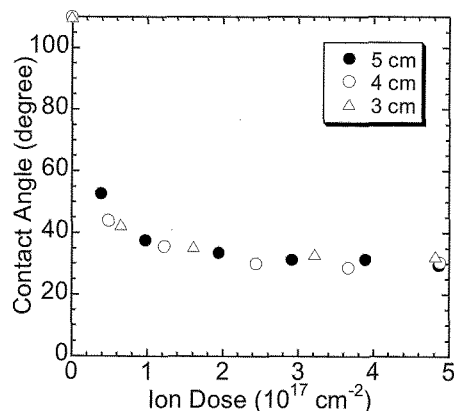


Fig.4 Contact angle of PTFE surface as a function of ion dose for different sample positions.

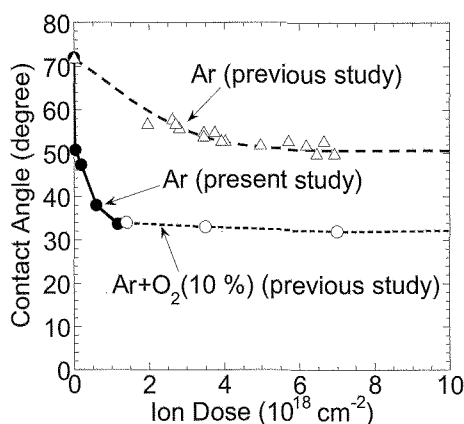


Fig. 5 Contact angle of PI film as a function of ion dose.

parameters that determine the contact angle of PTFE.

Previously, we reported treatment of polyimide (PI) surface by another surface-wave-excited plasma source [5], where drastic improvement of the surface hydrophilicity from  $72^\circ$  to  $33^\circ$  was reported by adding a small amount (10%) of  $O_2$  into Ar plasma. To investigate drastic improvement of the hydrophilicity in figs. 3 and 4, surface modification of PI film was carried out using the experimental setup of the present study. Figure 5 compares water the contact angle of PI films for the present study and for the previous study. As for the results of the previous study, results of both pure Ar plasma treatment and Ar with 10%  $O_2$  addition are indicated. The result obtained in the present experimental setup is in good agreement with the previous result of Ar/ $O_2$  plasma treatment rather than those of pure Ar treatment. This result suggests that the film treatment by the present experimental setup includes some chemical effect except for the Ar ion bombardment effect. In the present study, the base pressure of the vessel is  $\sim 10^{-4}$  Torr with a relatively low pumping speed of  $\sim$  a few l/s and without any load-lock system. In the previous study, however, the base pressure of the vessel was  $\sim 10^{-6}$  Torr and a load-lock system was used. Such difference in the base pressure and the equipment may be the origin of good hydrophilicity of PI film in the present study. This result also implies that the good hydrophilicity of PTFE film can be obtained by the SWP simply introducing a small amount of air into the vessel during the plasma treatment.

To investigate the change in the chemical state of the PTFE sample after the plasma treatment, sample surface was investigated by the XPS. In the experiment, samples are treated by Ar plasma at a sample position of 5 cm and a microwave power of 300 W. After the plasma treatment, samples were exposed to the atmosphere and were transferred to the XPS measurement system. Figure 6 shows C1s spectra of PTFE samples at plasma treatment time of 0, 2 and 25 s. In the case of  $T_p=0$ , i.e., as-received sample, the most dominant peak appears at a binding energy of  $\sim 292$  eV, which is originated from C-F<sub>2</sub> bonds on the surface. After the plasma treatment for 2 s, however, the C-F<sub>2</sub> peak drastically decreases and a peak appears at  $\sim 285$  eV, which is attributed to be C-C and C-H bonds. In

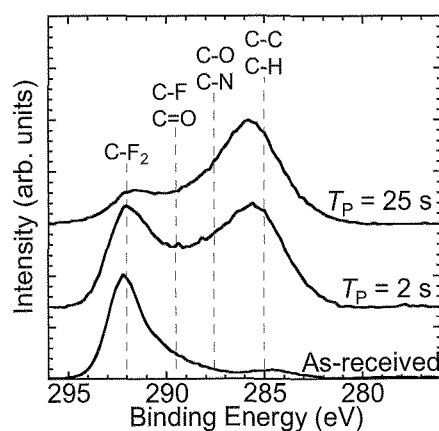


Fig. 6 C1s XPS spectra of PTFE samples for  $T_p$  of 0, 2 and 25 s.

addition, another slight signal is observed at binding energies around 287–290 eV, those are attributed to be C-O, C-N, C-F and C=O bonds. After the plasma treatment of 25 s, the C-F<sub>2</sub> peak further decreases and the peak of C-C, C-H bond becomes the most dominant one. This result shows that the surface chemical state drastically changes after the plasma treatment.

The XPS spectra suggest that the PTFE surface after the plasma treatment is composed not only of C and F atoms but also of N and O atoms. To investigate this, the surface atomic composition was evaluated. Figure 7 shows surface atomic composition of PTFE film as a function of the plasma treatment time. Without the plasma treatment, i.e., as-received sample, atomic composition of C and F are 36% and 64%, respectively, and is almost consistent of the bulk atomic composition of PTFE (C:33%, F:66%). With increasing the plasma treatment time, however, F atomic composition decreases rapidly and O and N peaks begin to appear. The origin of these atomic species is not clear, but may be due to the gas leakage during the plasma treatment and the chemical reaction of the plasma-activated surface with the air after the plasma treatment.

Figure 8 shows ratios of F, N and O atomic compositions with respect to the C atomic composition. Before the plasma treatment, F/C ratio is  $\sim 2$ . This

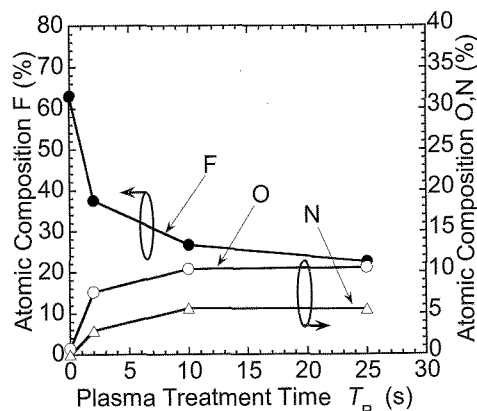


Fig. 7 Surface atomic composition of PTFE films as a function of the plasma treatment time.

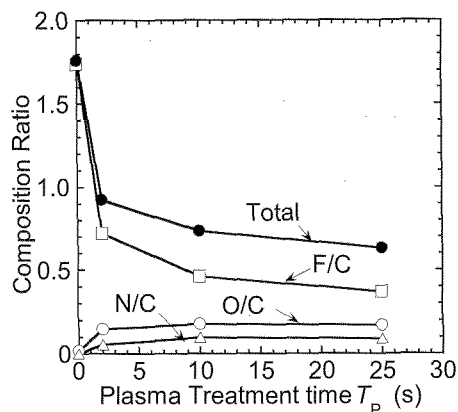


Fig.8 Ratio of atomic composition with respect to the C atomic composition as a function of the plasma treatment time.

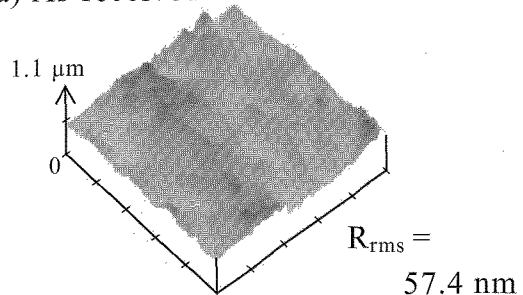
result indicates that the each C atom has two chemical bonds with F atoms and that the PTFE surface has polymer structure. With increasing the plasma treatment time, however, the summation of F/C, N/C and O/C decreases and is almost  $\sim 0.65$  at a plasma treatment time of 25 s. The results in Figs. 6 and 8 suggest the PTFE surface changes from the polymer structure to amorphous structure, where C atoms have three chemical bonds to form three dimensional networks.

Figure 9 shows AFM result of PTFE samples before and after the plasma treatment for  $10\mu\text{m} \times 10\mu\text{m}$  areas. As-received sample (fig. 9(a)) shows an RMS surface roughness, represented to  $R_{\text{rms}}$  in Fig.9, of 57.4 nm. After a plasma treatment for 2 s and 25 s, however, the RMS surface roughness drastically increases up to 146.6 nm and 174.0 nm, respectively. Furthermore, the plasma treated surface shows large grain-like structure compared with the as-received sample. Such drastic change in the surface morphology may be origin of the improvement of the surface hydrophilicity of the PTFE.

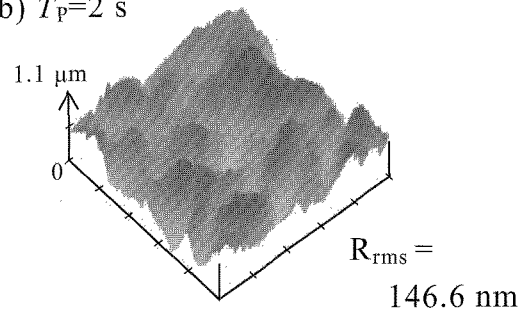
#### 4. Conclusion

In this study, a surface-wave-excited plasma (SWP) source was applied to the improvement of the surface hydrophilicity of polytetrafluoroethylene (PTFE). It was demonstrated that contact angle of the PTFE surface was drastically decreased by the SWP treatment with a very short time less than 5 s. The total ion dose in the PTFE sample was found to be one of very important parameters to determine the change in the PTFE surface hydrophilicity by the plasma treatment. From X-ray photoelectron spectroscopy (XPS) measurement, drastic changes in the surface atomic composition, i.e., F atom decrease and N and O atom increase were observed after the plasma treatment. It was also pointed out that the chemical structure of the PTFE surface changes from polymer structure to amorphous structure by the plasma treatment. An atomic force microscope (AFM) measurement indicated that the increase in the surface roughness after the plasma treatment. Increase in both hydrophilic chemical bonds (C-O, C=O) and surface roughness may be origins of the improvement of the hydrophilicity of the PTFE surface.

(a) As-received



(b)  $T_p=2$  s



(c)  $T_p=25$  s

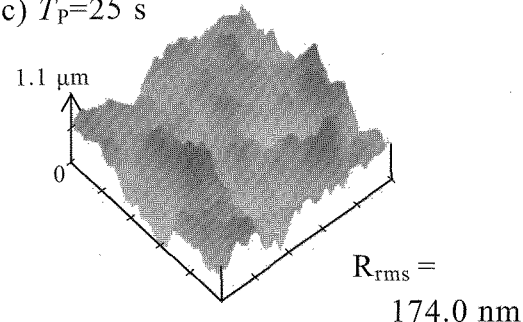


Fig.9 AFM measurements of PTFE samples before and after the plasma treatment for  $10\mu\text{m} \times 10\mu\text{m}$  areas. (a): As received sample. (b) and (c): plasma treated samples for 2 and 25 s, respectively.

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