Surface Modification of Tetrafluoroethylene–Perfluoroalkyl Vinylether Copolymer (PFA) by Plasmas for Copper Metallization

N. INAGAKI, K. NARUSHIMA, T. YAMAMOTO

Laboratory of Polymer Chemistry, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432-8561, Japan

ABSTRACT: Tetrafluoroethylene–perfluoroalkyl vinylether copolymer (PFA) sheet surfaces were modified with argon, helium, oxygen, and hydrogen plasmas. How the four plasmas modified the PFA sheet surfaces was investigated. All plasmas modified the PFA surfaces and at the same time initiated degradation of the PFA polymer chains. The balance between modification and degradation was strongly influenced by the magnitude of the discharge current in the plasmas. Efficiency of the plasmas in modification was hydrogen plasma > oxygen plasma > argon plasma > helium plasma. The modification involved defluorination of CF_2 carbons into CHF and CH_2 carbons and oxidation into $O-CH_2$, $O-CHF$, and $O-CF_2$ groups. The surface-modification technique (a combination of hydrogen plasma treatment and silane coupling treatment) proposed in this study was applied for copper metallization of the PFA surface. The utility of the technique was confirmed. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1087–1097, 2002

Key words: tetrafluoroethylene–perfluoroalkyl vinylether copolymer; PFA; surface modification; water contact angle; defluorination; silane coupling; peel strength

INTRODUCTION

Plasma treatment is a good way for surface modification of polymeric materials. When a polymer surface is exposed to plasma, two main reactions occur simultaneously on the polymer surface: One is the introduction of functional groups such as carbonyl and hydroxyl. Radicals in plasma contribute mainly to the formation of functional groups. The other is the degradation of polymer chains to products with low molecular weight. Ions and electrons in plasma mainly initiate the degradation reactions.[1,2] The former reaction contributes to surface modification, but the latter reaction never contributes to surface modification. Therefore, to perform effective modification, a key is how to accelerate the introduction reaction without the degradation reaction. What plasma and plasma conditions accelerate the introduction of functional groups is an important subject in order to seek good techniques for surface modification.
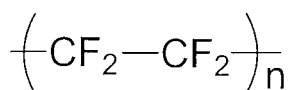
Many investigators use argon, helium, oxygen, and hydrogen plasmas for surface modification. In surface modification using the argon and helium plasmas, argon and helium ions in the plasmas bombard the polymer surface. As a result, hydrogen atoms are removed from the polymer surface to form carbon radicals on the surfaces. Most of the carbon radicals will be oxidized into oxygen functional groups, when the polymer spec-

imens are taken out from the plasma reactor after finishing the modification procedure. This may be the main reaction of surface modification by argon and helium plasma. In the modification by oxygen plasma, oxygen atoms in the oxygen plasma will lead directly to oxidation reactions of the polymer surfaces. When fluoropolymers are used as specimens, hydrogen plasma also may be effective in surface modification. Hydrogen atoms in hydrogen plasma will initiate defluorination on the fluoropolymer surfaces.
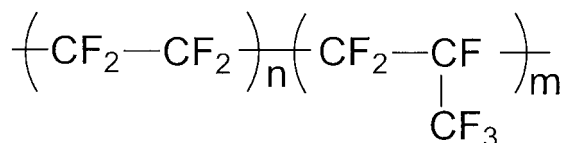
Polytetrafluoroethylene (PTFE), the tetrafluoroethylene–perfluoroalkyl vinyl ether copolymer (PFA), and the tetrafluoroethylene–hexafluoropropylene copolymer (FEP), whose chemical structures are illustrated in Figure 1, are typical fluoropolymers. They possess outstanding chemical and physical properties that involve high-temperature resistance, chemical resistance, hydrophobic and electrical properties, etc. Electrical properties such as high resistivity, low dielectric constant, and low dissipation factor are distinguished from those of other polymers.[3,4] From these viewpoints, we believe that fluoropolymers may be good raw materials for electrical insula-
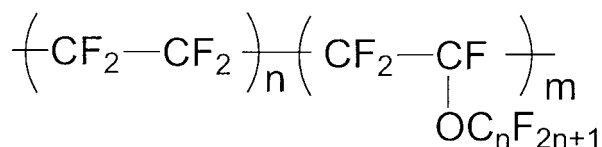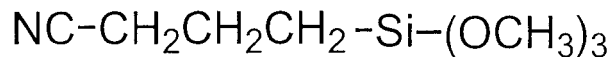
$$-\!\!\left(\!CF_2\!-\!CF_2\!\right)_{\!n}$$

Poly(tetrafluoroethylene), PTFE

$$-\!\!\left(\!CF_2\!-\!CF_2\!\right)_{\!n}\!\!\left(\!CF_2\!-\!CF\!\right)_{\!m}$$
$$OC_nF_{2n+1}$$

Tetrafluoroethylene-perfluoroalkylvinylether copolymer, PFA

$$-\!\!\left(\!CF_2\!-\!CF_2\!\right)_{\!n}\!\!\left(\!CF_2\!-\!CF\!\right)_{\!m}$$
$$CF_3$$

Tetrafluoroethylene-hexafluoropropylene copolymer, FEP

Figure 1 Chemical structure of PTFE, PFA, and FEP.

$$NC\!-\!CH_2CH_2CH_2\!-\!Si\!-\!(OCH_3)_3$$

3-cyanopropyltrimethoxysilane, CPS

Figure 2 Chemical structures of silanes used for surface modification.

tors, especially in the high-frequency current region. In this study, we investigated how to modify the PFA surface using four plasmas, argon, helium, oxygen, and hydrogen plasmas, to learn how introductory reactions for functional groups rival degradation reactions of the PFA surface. Furthermore, the surface-modification technique proposed in this study was for copper metallization of the PFA surface.

EXPERIMENTAL

Materials

PFA sheet (50 μm thickness), which was kindly provided by Daikin Industries, Ltd. (Japan; trade name, Neoflon-0050), was cut to a dimension of 12 mm wide $\times$ 75 mm long. The sheet was washed with acetone using an ultrasonic washer prior to the plasma treatment. 3-Cyanopropyl triethoxysilane (CPS) was purchased from Gelest Inc. (Tullytown, PA) and used without further purification as a reagent for the coupling reactions. The chemical structure of CPS is shown in Figure 2.

Surface Modification by Coupling Reactions

The surface modification of PFA sheets using CPS coupling reactions was carried out in two steps: (1) plasma treatment to form oxygenated functional groups on the PFA sheet surfaces and (2) coupling reactions between CPS and the oxygenated groups on the PFA sheets. First, the PFA surfaces were exposed to argon, helium, oxygen, and hydrogen plasmas for 10–180 s to form carbon radicals on the surfaces. These plasmas were operated at a constant pressure of 1.3 Pa at a constant discharge current of 30, 45, 60, and 75 mA, which corresponded to about 48, 73, 94, and 108 W, respectively. The details of the construction of the plasma reactor used for the plasma treatment and the operational procedures have been reported elsewhere.[5] Afterward, the plasma-treated PFA sheet surfaces were exposed to air for carbon radicals to be oxidized into oxygenated

functional groups. Subsequent to the plasma treatment, the sheets were dipped in a methanol solution (0.1–1.0 wt %) of CPS at room temperature for 10 min and then heated in an air oven at 110°C for 90 min to complete the coupling reactions. After the coupling reactions, the PFA sheets were washed with methanol using an ultrasonic washer and dried at 50°C under a vacuum.

Copper Metallization of PFA Sheet Surface

The surface of the CPS-modified PFA sheet was made electrically conductive by vacuum deposition of copper metal (100 nm thick) and then was electroplated with a copper metal layer of 20–40-μm thickness. The electroplating process was done at a constant dc current density of 3×10^4 A/m^2 and at 24°C in an aqueous sulfuric acid solution (90 g/L) containing copper sulfate (0.5M), hydrochloric acid (50 ppm), and a glossy reagent (5 mL) purchased from Nippon Rironal (Tokyo, Japan; trade name CLX-A). The electroplated PFA sheet was washed with water and dried at 80°C for 12 h in a vacuum.

Peel Strength of Copper Metal/PFA Sheet Systems

The T-peel strength (using 5-mm-wide strips) of copper metal/PFA systems was assessed at a peel rate of 10 mm/min using an Instron-type tensile strength tester (Shimadzu, Kyoto, Japan; Model AGS100-A). The peel strength was determined from an average of 10 specimens.

Contact Angle of Water on Plasma-treated PFA Sheet Surfaces

Using the sessile drop method,[6] contact angles of water on the PFA sheet surfaces were measured at 20°C using a contact angle meter with a goniometer (Erma Co. Ltd., Tokyo, Japan; Model G-1). An average contact angle was determined from 10 measurements with an experimental error of 3–4 degrees.

X-ray Photoelectron Spectroscopy

XPS spectra of PFA sheet surfaces were obtained on a Shimadzu (Japan) ESCA K1 spectrometer using a nonmonochromatic MgKα photon source. The anode voltage was 12 kV, the anode current was 20 mA, and the background pressure in the analytical chamber was 1.5×10^{-6} Pa. The size of the X-ray spot was 2 mm, and the take-off angle of

photoelectrons was 90° with respect to the sample surface. The spectra were decomposed by fitting a Gaussian–Lorentzian mixture function (80:20 ratio) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. The binding energies were corrected by referring the lowest binding energy component to 285.0 eV to eliminate charge effects. The sensitivity factors (S) for the core levels in the ESCAPAC were $S(C_{1s}) = 1.00$, $S(F_{1s}) = 4.26$, $S(O_{1s}) = 2.85$, $S(N_{1s}) = 1.77$, $S(Si_{2p}) = 0.87$, and $S(Cu_{2p3/2}) = 15.87$.

RESULTS AND DISCUSSION

Water Contact Angle on PFA Sheet Surface Modified by Plasmas

As described in the Introduction, when a polymer surface is exposed to plasma, two main reactions, introduction of functional groups and degradation of polymer chains, occur simultaneously on the polymer surface. To evaluate the formation of functional groups on the PFA sheet surface and degradation reactions of the PFA polymer chains by plasmas, two surfaces were used for the evaluation: One was the PFA surface that was just irradiated with the plasmas, and the other was the PFA surface that was irradiated with the plasmas and then rinsed with acetone. We refer here to the former as the surface before acetone-rinsing and to the latter as the surface after acetone-rinsing. If the plasma irradiation leads to the deposition of degradation products as well as to the formation of functional groups on the PFA surface, the acetone-rinsing procedure will remove the degradation products from the surface. As a result, there will be some difference in the water contact angle between the PFA surfaces before and after acetone-rinsing. From this viewpoint, the PFA sheet surfaces before and after acetone-rinsing were compared in regard to the water contact angle. Table I shows typical results regarding the water contact angle on the PFA surfaces before and after acetone-rinsing. Argon and hydrogen plasmas were used for the modification. The water contact angles in Table I are compared as functions of the plasma, discharge current, and plasma exposure time. All PFA surfaces before acetone-rinsing showed decreases in the water contact angle from 109° for the nonirradiated PFA surface to 94°–20°, the angles being strongly influenced by the discharge current and

Table I   Water Contact Angles on Plasma-treated PFA Sheet Surfaces

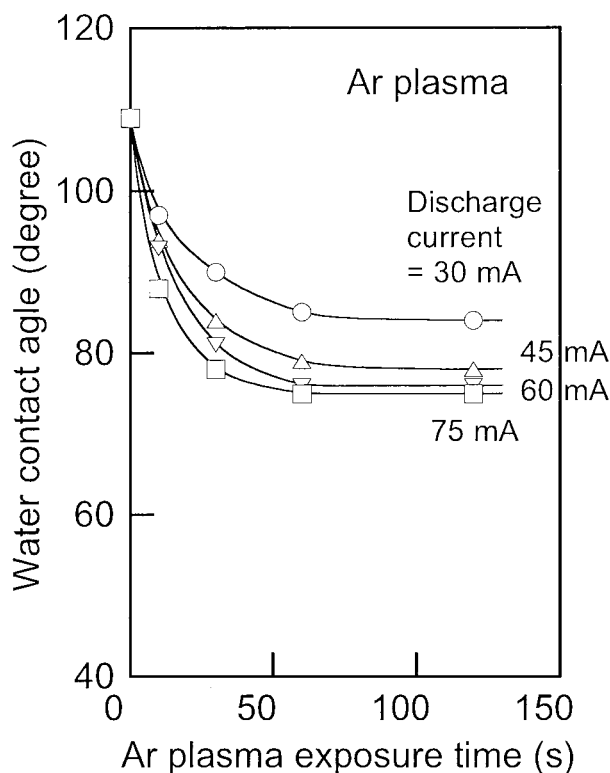| Plasma	Plasma Exposure Time (s)	Before Acetone-rinsing (Degree)	After Acetone-rinsing (Degree)	Difference
Plasma Treatment		Water Contact Angle on Plasma-treated PFA Surfaces		
None	—	109	109	0
Argon	10	94	94	0
At 45 mA	30	84	84	0
	60	79	79	0
	120	78	78	0
At 60 mA	10	94	93	−1
	30	83	81	−2
	60	73	76	3
	120	76	76	0
At 75 mA	10	91	97	6
	30	84	90	6
	60	75	85	10
	120	77	84	7
Hydrogen	10	104	104	0
At 45 mA	30	92	92	0
	60	80	80	0
	120	70	70	0
At 60 mA	10	82	94	12
	30	72	86	14
	60	69	71	2
	120	29	58	29
At 75 mA	10	81	87	6
	30	58	75	7
	60	31	60	29
	120	20	56	36

the plasma exposure time. Increase in the discharge current and the plasma exposure time, independently of the argon and hydrogen plasmas, led to a decrease in the water contact angle. For example, when exposed to the hydrogen plasma at discharge currents of 45 and 75 mA for 120 s, the PFA surface showed water contact angles of 70° and 20°, respectively. When the plasma exposure time (using the hydrogen plasma at a discharge current of 75 mA) was extended from 10 to 120 s, the water contact angle for the treated PFA surfaces decreased from 81° to 20°. Such a large decrease in the contact angle means that the argon and hydrogen plasmas have modifed the surface of the PFA sheet.

Once these modified PFA surfaces (surface before acetone-rinsing) were rinsed with acetone, the water contact angle for the rinsed PFA surface (surface after acetone-rinsing) was higher than that for the PFA surface before acetone-rinsing. Differences in the contact angle between
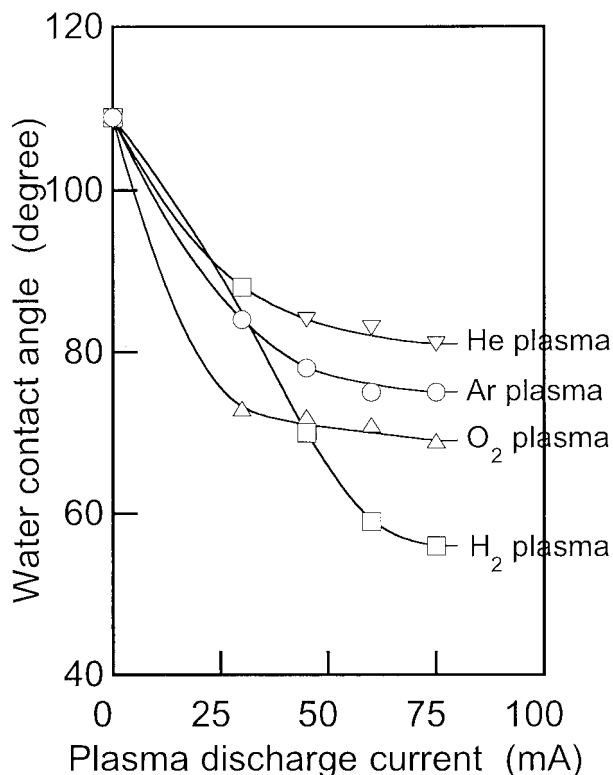
the PFA surfaces before and after acetone-rinsing are tabulated in Table I. The difference was strongly influenced by the discharge current rather than by the plasma exposure time. The argon and hydrogen plasmas, at a discharge current of 45 mA, as shown in Table I, showed no difference between the surfaces before and after acetone-rinsing, even when the exposure time was extended from 10 to 120 s. On the other hand, the argon and hydrogen plasmas at discharge currents of 60 and 75 mA made a large difference (up to 36°), indicating some change on the PFA surface by the acetone-rinsing. The change may be due to the removal of degradation products. We believe that the argon and hydrogen plasmas triggered degradation reactions of the PFA polymer chains and that degradation products were deposited on the PFA surface. The acetone-rinsing procedure removed these degradation products from the surfaces. Therefore, the difference in the water contact angle between the PFA surfaces before

and after acetone-rinsing is an indication of whether the plasma triggered degradation reactions. The plasma exposure at a discharge current of more than 60 mA caused both surface modification and degradation. While the plasma exposure at less than 45 mA also caused surface modification, it caused less degradation of the PFA polymer chains.

After acetone-rinsing, the water contact angle for the four plasmas (argon, helium, oxygen, and hydrogen) was strongly influenced by the exposure time, discharge current, and plasma. For example, the water contact angle in the case of the surface modification by the argon plasma, as shown in Figure 3, decreased with increasing exposure time. The decrease continued up to 60 s and leveled off at a plasma exposure time of 120 s. Therefore, the surface modification may be completed at an exposure time of 120 s. Similar effects of the exposure time on the water contact angle were observed in the modification by the other plasmas, H_2, He, and O_2. These figures are not shown here for the sake of brevity. Figure 4 shows the water contact angle as a function of the

Figure 4 Water contact angle as function of the discharge current and plasma.

discharge current and plasma. The discharge current, when increased from 30 to 75 mA, showed, in general, little effect on the water contact angle (as shown in Fig. 4). For example, in the case of the oxygen plasma treatment, the water contact angle was 73° and 69° at discharge currents of 30 and 75 mA, respectively. However, one of the plasmas showed a large effect on the water contact angle (Fig. 4). The hydrogen plasma led to the lowest contact angle (56° at a discharge current of 75 mA). The water contact angle at a discharge current of 75 mA was in the following order: hydrogen plasma (56°) < oxygen plasma (69°) < argon plasma (75°) < helium plasma (81°). From these results, we conclude following:

1. The argon, helium, oxygen, and hydrogen plasmas are able to surface-modify the PFA sheet.
2. Surface modification by the plasmas leads not only to changes in the water contact angle on the PFA surface but also to degradation of the PFA polymer chains. The plasma at a discharge current of more than 60 mA can both modify the surface and

Figure 3 Water contact angle as function of the plasma exposure time and discharge current in argon plasma.

Table II   Atom Composition of PFA Sheet Surfaces (After Acetone-rinsing) Exposed to Argon, Helium, Oxygen, and Hydrogen Plasmas

	Plasma Treatment		Atom Ratio		
Plasma	Discharge Current (mA)	Exposure Time (s)	F/C	O/C	Defluorination (%)
None			1.93	<0.05	0
Argon	30	120	1.07	0.14	45
	75	120	0.88	0.19	54
Helium	30	120	1.19	0.17	38
	75	120	0.97	0.17	50
Oxygen	30	120	1.08	0.16	44
	75	120	1.01	0.20	48
Hydrogen	30	120	1.03	0.17	47
	75	120	0.73	0.18	62

degrade the PFA polymer chains. On the other hand, the plasma at less than 45 mA can modify the surface but degrades less.

3. Efficiency of the plasmas in modification is hydrogen plasma > oxygen plasma > argon plasma > helium plasma.

Chemical Composition of PFA Sheet Surface Modified by Plasmas

The PFA sheet surfaces (after acetone-rinsing) treated with the four plasmas at discharge currents of 30 and 75 mA were analyzed by XPS. Results (F/C and O/C atom ratios) of the elemental analysis using XPS are shown in Table II. For the untreated PFA surface, the F/C and O/C atom ratios were 1.93 and <0.05, respectively. The four plasma treatments, as shown in Table II, led to some decrease in the F/C atom ratio (1.19–0.73) and increase in the O/C atom ratio (0.14–0.20), compared with those for the untreated PFA. These changes in the F/C and O/C atom ratios mean that defluorination and oxidation occurred on the PFA surfaces. Defluorination showed a strong dependence on the discharge current and the kind of plasma (Table II). Defluorination is defined by eq. (1):
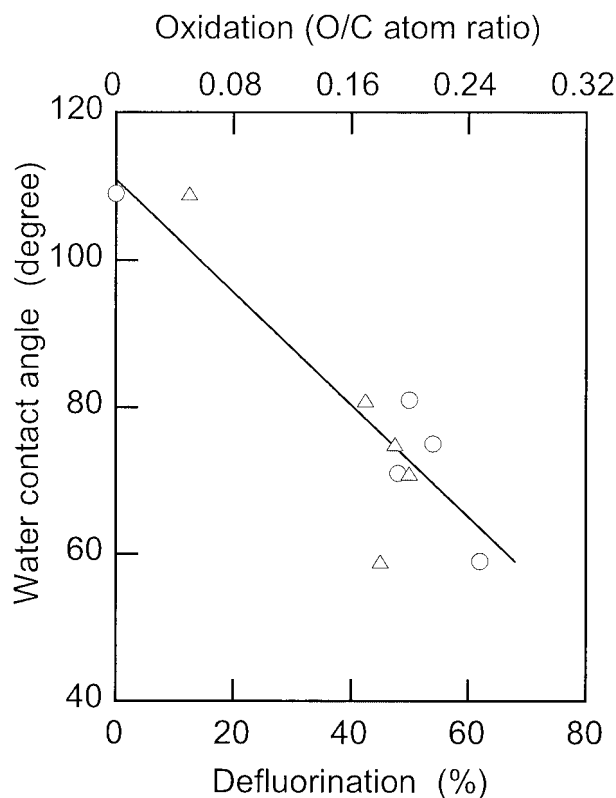
$$\text{Defluorination in } \% = \frac{F_0 - F_1}{F_0} \qquad (1)$$

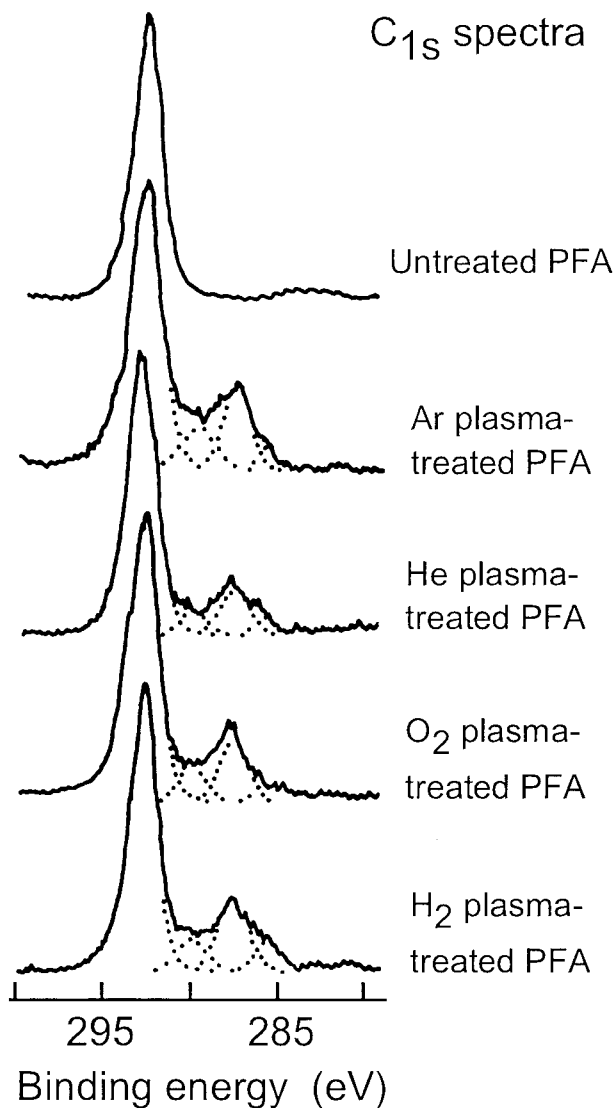where F_0 is the fluorine content in the untreated PFA, and F_1, the fluorine content in the plasma-treated PFA. The plasmas at a discharge current of 75 mA were more effective in defluorination than were those at 30 mA, because defluorination at 75 mA was 48–62%, while defluorination at 30 mA was 38–47%. The hydrogen plasma of the four plasmas showed the highest defluorination (62%). Defluorination by the other plasmas was 48–54%. The oxidation was not sensitive to the discharge current and the kind of plasma. The O/C atom ratio was less influenced by changing of the discharge current and the kind of plasma and was in the 0.14–0.20 range. It is reasonable that defluorination and oxidation may be closely related to the surface properties such as to the water contact angle. Figure 5 shows the water contact angles for the plasma-treated PFA surfaces as functions of defluorination and oxidation. The water contact angle showed a roughly linear relationship with both defluorination and oxidation. This reaffirms that the surface properties for the plasma-treated PFA may be related mainly to defluorination and oxidation on the PFA surfaces.

To account for details of defluorination and oxidation, the PFA sheet surfaces treated with the four plasmas were analyzed with XPS. Figure 6 shows typical C_{1s} spectra for the PFA sheet surfaces (after acetone-rinsing) treated with the four plasmas. Although the untreated PFA surface showed a simple peak at 292.8 eV, due to the CF_2 component, the plasma-treated PFA surfaces showed complex C_{1s} spectra. These C_{1s} spectra were decomposed into four components. The decomposed components are illustrated by dotted

lines in the figure. The four components appeared at 285.7–286.0, 287.5–287.8, 289.7–290.2, and 292.7–293.0 eV, which were assigned to the CH_2—CH_2—$\underline{C}HF$ groups (component 1); $\underline{C}HF$—CH_2—CF_2, CH_2—$\underline{C}HF$—CH_2, and O—$\underline{C}H_2$—CF_2 groups (component 2); CH_2—$\underline{C}HF$—CF_2, CHF—$\underline{C}HF$—CHF, and O—$\underline{C}HF$—CHF groups (component 3); and $\underline{C}HF$—CF_2—CF_2, CF_2—$\underline{C}F_2$—CF_2, and O—$\underline{C}F_2$—CF_2 groups (component 4), respectively. The underlined C in these groups means the objective carbon. These assignments were done from comparison with the binding energy estimated from the primary (2.9 eV) and secondary effects (0.7 eV) of fluorine atoms and the primary effect (1.54 eV) of the oxygen atom.[7–9] The decomposition in Figure 6 indicates that CF_2 carbons (component 4) were modified into CHF and CH_2 carbons (components 1, 2, and 3) and O—C carbons (O—CH_2 in component 2, O—CHF in component 3, and O—CF_2 in component 4) during the plasma exposure. Effects of the four plasmas and discharge current on these modifications are compared in Table III. The discharge current, rather than the kind of the plasma used, led to large effects on the modification. For exam-

Figure 6 XPS (C_{1s}) spectra for PFA surfaces treated with argon, helium, oxygen, and hydrogen plasmas at a discharge current of 30 mA for 120 s.

ple, when the plasmas used varied from argon to oxygen or hydrogen, the concentration of component 4 for the plasma-treated PFA surfaces was 68, 71, and 67%, respectively, not a large difference in the concentration of component 4. However, when the discharge current increased from 30 to 75 mA, there was a larger difference in the C_{1s} components. Concentration of component 4, as shown in Table III, is lower at a discharge current of 75 mA than at 35 mA, independent of the plasmas used. On the other hand, the concentration of components 1, 2, and 3 is higher at 75 mA than at 35 mA. This effect of the discharge current is concordant with the result from Figure

Figure 5 Water contact angle as function of (○) defluorination and (□) oxidation.

Table III C_{1s} Components of PFA Sheet Surfaces (After Acetone-rinsing) Exposed to Argon, Helium, Oxygen, and Hydrogen Plasmas

| | Plasma Treatment | | C_{1s} Components (mol %) | | | |
| | Discharge Current (mA) | Exposure Time (s) | | | | |
Plasma			Component 1	Component 2	Component 3	Component 4
None	—	—	0	0	0	100
Ar	30	120	4	17	11	68
	75	120	10	22	14	54
He	30	120	4	13	7	76
	75	120	10	14	11	65
O_2	30	120	4	16	9	71
	75	120	8	17	11	64
H_2	30	120	6	18	9	67
	75	120	10	12	10	68

Component 1, CH_2—CH_2—CHF; component 2, CHF—CH_2—CF_2, CHF—CHF—CHF, and O—CH_2—CF_2; component 3, CH_2—CHF—CF_2, CHF—CHF—CHF, and O—CHF—CHF; component 4, CHF—CF_2—CF_2, CF_2—CF_2—CF_2, and O—CF_2—CF_2.

6, where the discharge current led to a strong influence on the water contact angle for the plasma-treated PFA surfaces.

Analyses of the plasma-treated PFA sheet surfaces using XPS led to the following conclusions:

1. The plasma treatment leads to defluorination and oxidation of the PFA surfaces.
2. CF_2 carbons in the PFA surfaces are modified into CHF and CH_2 carbons by the plasma treatment. At the same time, C–O carbons such as O—CH_2, O—CHF, and O—CF_2 groups are formed by the plasma treatment.
3. Discharge current in the plasma rather than the kind of plasma used leads to large effects on the modification.

Copper Metallization of PFA Sheet Surfaces

The water contact angle measurement and XPS analysis showed that hydrogen plasma treatment is a good way to modify the PFA sheet surfaces to become water-wettable. Furthermore, oxygen functional groups, such as C—O groups, also are formed on the PFA surfaces. Accordingly, to achieve copper metallization of the PFA surfaces, cyano groups that could interact strongly with copper metal were introduced using coupling reactions. The PFA surfaces were first treated with hydrogen plasma to make oxygen functional groups and then were further treated with the silane coupling agent, CPS, at 110°C for 90 min.
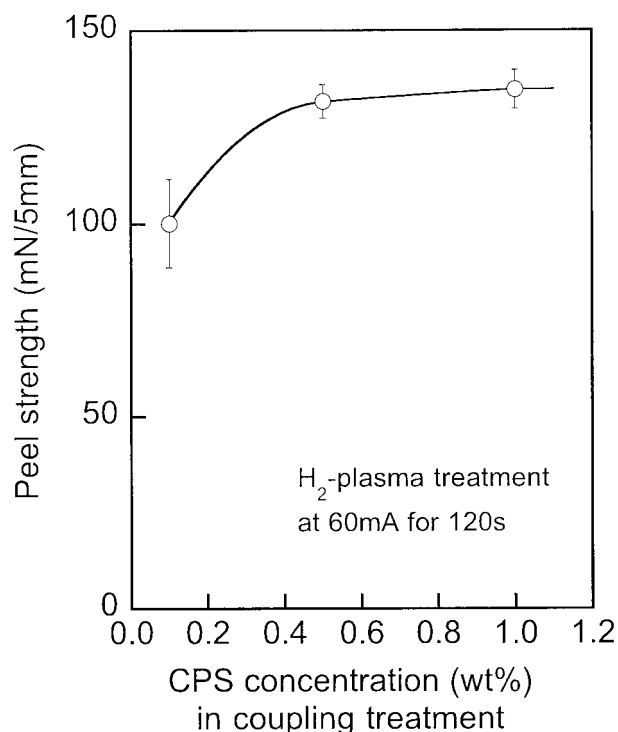
On the PFA sheet surfaces that were treated with hydrogen plasma and subsequently modified by the CPS coupling treatment, a copper metal layer of 20–40 μm thickness was deposited by a combination of evaporation and electroplating techniques. The effects of the surface modification, by the CPS coupling treatment, on the adhesion to copper metal were investigated.

The peel strength, between copper metal and the PFA sheet that was treated with the hydrogen plasma at 60 mA but not treated with CPS, was 66.5 mN/5mm. Modification with CPS made a large improvement in the peel strength. The peel strength for the Cu/PFA system was investigated as functions of the CPS concentration and discharge current in the hydrogen plasma. Figure 7 shows the peel strength of the Cu/PFA system as a function of the CPS concentration in the coupling treatment. The CPS concentration, when more than 0.5 wt %, showed less influence on the peel strength of the Cu/PFA system: The peel strength was in the 132–135 mN/5mm range. On the other hand, the discharge current in the hydrogen plasma greatly influenced the peel strength. Figure 8 shows the peel strength of the Cu/PFA system as a function of the discharge current. When the discharge current increased from 30 to 60 mA, the peel strength increased from 40 to 135 mN/5mm. Afterward, at a discharge current of 75 mA, the peel strength decreased largely to 48 mN/5mm. Therefore, suitable modification of the PFA sheet surfaces for copper metallization uses a combination of the
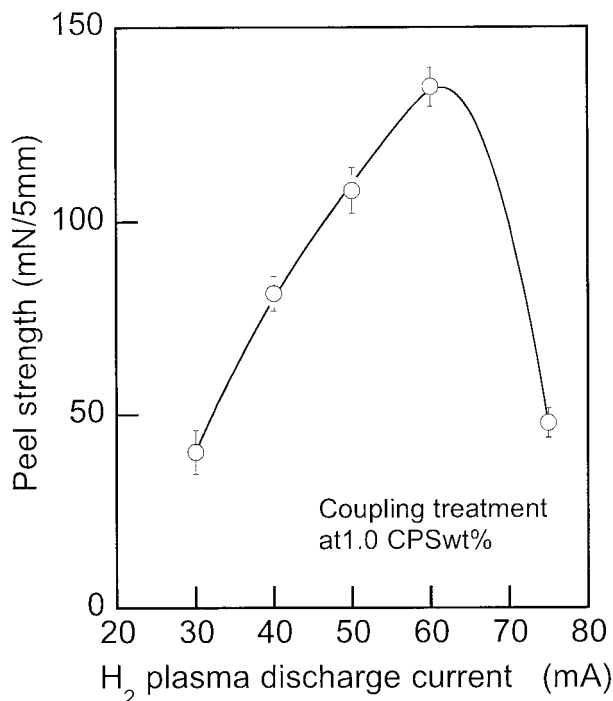
hydrogen plasma treatment at a discharge current of 60 mA for 120 s and the coupling treatment at a CPS concentration of 1 wt %. This conclusion was unexpected.

In our previous section on the water contact angle for PFA sheet surface modified by plasmas, we pointed out that plasma exposure leads not only to the introduction of functional groups on the PFA surface but also to degradation of the PFA polymer chains. Furthermore, we concluded, from the water contact angle measurements, that plasma exposure operating at a discharge current of more than 60 mA brings about introductory reactions with some degradation of the PFA polymer chains. On the other hand, the plasma exposure at less than 45 mA leads to introductory reactions with less degradation. From this viewpoint, we anticipated that the PFA surfaces, to improve the adhesion between the Cu/PFA system, should be modified without degradation (practically, the modification by the hydrogen plasma at a discharge current of less than 45 mA). Experiments (Fig. 4) showed, however, that the modification by hydrogen

Figure 8 Peel strength for adhesion between copper metal/PFA modified by a combination of hydrogen plasma treatment and silane coupling treatment as a function of the discharge current in hydrogen plasma.

plasma at discharge currents of 30 and 45 mA is no more effective in improving the peel strength of the Cu/PFA system than is that by hydrogen plasma at 50 and 60 mA: At discharge currents of 30 and 45 mA, the peel strengths were 40 and 81 mN/5mm, respectively. On the other hand, at 50 and 60 mA, the peel strength is 108 and 135 mN/5mm, respectively. This comparison indicates that modification at low discharge currents such as 30 and 45 mA is insufficient for improvement of the adhesion between copper metal and the PFA surface. However, this does not necessarily mean that heavy degradation of the PFA surface is indispensable for adhesion improvement, because the modification at a discharge current of 75 mA, where heavy degradation reactions occur on the PFA surface (as shown in Table I), led to a decrease in peel strength (48 mN/5mm).

Finally, we investigated, using XPS, where failure occurred when the Cu/PFA systems were peeled off. The specimen used for the investigation was the Cu/PFA system that showed a maximum (135 mN/5mm) in the peel strength. The PFA sheet surfaces were treated with hydrogen

Figure 7 Peel strength for adhesion between copper metal/PFA modified by a combination of hydrogen plasma treatment and silane coupling treatment as a function of the CPS concentration in the silane coupling treatment.

plasma at 60 mA for 120 s and then modified with CPS at 1 wt %. On the CPS-modified PFA surfaces, a copper layer (40 μm thick) was deposited using a combination of evaporation and electroplating. The Cu/CPS-modified PFA system was peeled off, and two surfaces peeled-off from the Cu/CPS-modified PFA system (the copper metal layer and PFA layer sides) were analyzed by XPS. The Cu/CPS-modified PFA system is composed of four layers and three interfaces: the copper metal layer, the CPS-modified layer, the hydrogen plasma-treated layer, and the original (unmodified) PFA layer. There are theoretically two possible modes in the failure for a laminated structure: failure within a layer (cohesive failure) or at the interface between two layers (interface failure). When a cohesive failure occurs, the two peeled-off surfaces show the same chemical composition. As a result, the surfaces must show the same XPS spectra. On the other hand, when interfacial failure occurs, the two peeled-off surfaces show different chemical compositions and the two surfaces must show distinctly different XPS spectra. Therefore, we can predict what failure mode occurred from a comparison of the two peeled-off surfaces in the XPS spectra.

The two surfaces peeled off from the Cu/CPS-modified PFA system showed no Si_{2p} and $Cu_{2p3/2}$ peaks, but showed different C_{1s} spectra. Figure 9 shows the C_{1s} spectra for the two peeled-off surfaces (copper metal layer and PFA layer sides). The C_{1s} spectrum for the copper metal layer side contained two main peaks at 285.4 and 292.6 eV, while the C_{1s} spectrum for the PFA layer side contained only a peak at 293.7 eV. This comparison shows that the two surfaces peeled off are essentially different in chemical composition and leads to the conclusion that cohesive failure did not occur but that adhesive failure did occur. A possible failure may be at the interface between the hydrogen plasma-treated PFA layer and the untreated PFA layer, because the C_{1s} spectrum for the copper metal layer side was similar to the C_{1s} spectrum for the untreated (original) PFA surface and the C_{1s} spectrum for the PFA layer side was similar to the C_{1s} spectrum for the hydrogen plasma-treated PFA surface. This conclusion points out an important aspect for adhesion improvement. The combination of hydrogen plasma treatment and silane coupling reactions with CPS is surely effective in improving the adhesion between copper metal and the PFA sheet. The PFA sheet surface-modified
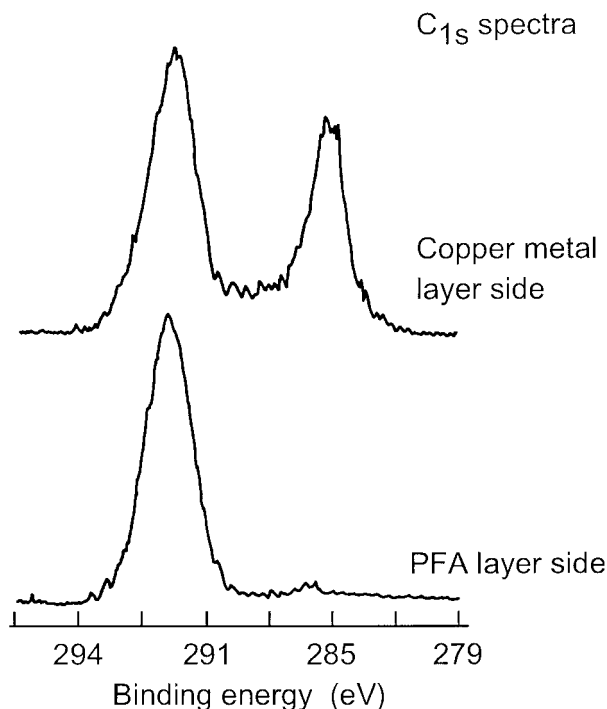
Figure 9   XPS spectra for the surfaces (copper metal layer side and PFA layer side) peeled off from copper metal/PFA system.

with CPS adheres completely to copper metal. Hydrogen plasma treatment makes a weak boundary layer near the PFA sheet surface. As a result, failure occurs at the interface between the hydrogen plasma-treated PFA layer and the untreated PFA layer. Therefore, a key to adhesion improvement is how to make sufficient modification of PFA surfaces with no degradation of the PFA surface.

CONCLUSIONS

PFA sheet surfaces were modified with four plasmas, argon, helium, oxygen, and hydrogen plasmas. How the four plasmas modified PFA sheet surfaces and how introductory reactions of functional groups rivaled degradation reactions were investigated. The surface-modification technique proposed in this study was applied for copper metallization of the PFA surface:

1. The argon, helium, oxygen, and hydrogen plasmas both modify and degrade the PFA sheet surfaces. The balance between the modification and degradation is strongly

influenced by the discharge current in the plasmas. The plasmas, at a discharge current of more than 60 mA, result in both surface modification and degradation. On the other hand, the plasmas at less than 45 mA result in surface modification, but not to degradation.

2. The relative efficiency of the plasmas in modification is hydrogen plasma > oxygen plasma > argon plasma > helium plasma.

3. The modification by the plasmas involves defluorination and oxidation of the PFA surfaces. CF_2 carbons in the PFA surfaces are modified into CHF and CH_2 carbons and, at the same time, C—O carbons such as O—CH_2, O—CHF, and O—CF_2 groups are formed.

4. A combination of a hydrogen plasma treatment and a silane coupling treatment with CPS is a useful technique for adhesion improvement between copper metal and the PFA sheet.

REFERENCES

1. Inagaki, N. Plasma Surface Modification and Plasma Polymerization; Technomic: Lancaster, PA, 1996; p 63.
2. Inagaki, N.; Tasaka, S.; Shimada, S. J Appl Polym Sci 2001, 79, 808.
3. Polymeric Materials Encyclopedia; Salamone, J. C., Ed.; CRC: Boca Raton, FL, 1996; Vol. 11, p 8293.
4. Negishi, A. Fluorine Chemistry; Maruzen: Tokyo, 1988; p 108.
5. Inagaki, N; Tasaka, S.; Masumoto, M. J Appl Polym Sci 1995, 56, 135; Macromolecules 1996, 29, 1642.
6. Garbassi, F.; Morra, M.; Occhiello, E. Polymer Surfaces: From Physics to Technology; Wiley: New York, 1994; p 155.
7. Clark, D. T.; Feast, W.-J. J Macromol Sci Rev Macromol Chem C 1975, 12, 191.
8. Polymer Surface, Elements and Applications; Ikada, Y., Ed.; Kagaku Dojin: Kyoto, Japan, 1986; p 69.
9. High Resolution XPS of Organic Polymers; Beamson, G; Briggs, D., Eds.; Wiley: New York, 1992.