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Surface Modification of Tetrafluoroethylene−Perfluoroalkyl Vinyl Ether Copolymer (PFA) by Remote Hydrogen Plasma and Surface Metallization with Electroless Plating of Copper Metal

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ABSTRACT: PFA sheets were modified with remote hydrogen plasma, and effects of the modification on the adhesion between copper layer and FEP were investigated. Remote hydrogen plasma treatment for a short time of 30 s is able to make the PFA surface hydrophilic. The remote hydrogen plasma treatment causes defluorination and oxidation of PFA surface. The extent of the defluorination is 42−48%, and the oxidation reaches 9−13% of the total carbon atoms. The modification of the PFA surface by the remote hydrogen plasma is effective in the adhesion to copper metal. The peel strength for the copper metal/PFA system is improved from 0 to 101 mN/5 mm by the surface modification. The failure mode of the copper metal/PFA system is an inner layer of the plasma-treated PFA layer. The remote hydrogen plasma treatment is the preferable pretreatment of the PFA surface for adhesion with copper metal.

Introduction

A copolymer of tetrafluoroethylene and perfluoroalkyl vinyl ether, PFA, which is similar to poly(tetrafluoroethylene), PTFE, shows notable physical and chemical properties such as high-temperature resistance and chemical resistance as well as hydrophobic properties. In addition to these notable properties, PFA as well as PTFE shows excellent electrical properties, which include a high resistivity of more than 10^{18} Ω cm, a low dielectric constant of 2.1, and a low dissipation factor of less than 3×10^{-4}. Furthermore, PFA can be fabricated easily in conventional melt processes because of its amorphous structure.[1,2] From this aspect, we believe that PFA may be an outstanding insulator of electrical currents with high frequencies (GHz); for example, PFA could be used for a printed wiring board for integrated circuits and an insulator for electrical wires. For these applications, a composite of PFA and copper metal is required.

In this study, we have focused on the composite of PFA and copper metal by means of a combination of electroless- and electroplatings. To make a composite with copper metal, the PFA surface has to be modified because of its poor adhesion with copper metal. An effective modification on the PFA surfaces is the introduction of special groups or polymer chains that can interact strongly with copper metal.[3−11] The plasma graft copolymerization of vinylimidazole and the deposition of the plasma polymer of acrylonitrile are examples of such a surface modification.[12,13] With regard to the surface modification, we should take notice that the introduction of such polymer chains on the PFA surface debases the electrical properties of PFA, because of increases in the dielectric constant and the dissipation factor. The introduction of the polymer chains in abundance is not always a good surface modification for the electrical insulators. From this concept, we chose a remote hydrogen plasma treatment as a surface modification of PFA to obtain a copper metal/PFA composite. The remote plasma treatment is different from the conventional plasma treatment with respect to the relative distance of the sample position from the plasma zone. In the remote plasma treatment, the PFA sample is positioned away from the plasma zone, whereas in the conventional plasma treatment, the PFA sample is positioned just in the plasma zone. We call the conventional plasma treatment “the direct plasma treatment” to distinguish it from the remote plasma treatment. Plasma involves electrons, ions, and radicals, which are able to play as active species in surface modification reactions. Radicals possess a longer lifetime than electrons and ions. As a result, at a position far away from the plasma zone (in the remote plasma treatment), radicals will become a predominant species and will play an important role in surface modification reactions. In the plasma zone (in the direct plasma treatment), electrons and ions as well as radicals will play a part in surface modification reactions. In addition to the surface modification, etching reactions due to electrons and ions will occur on the polymer surface. This is an essential difference in the plasma chemistry between the remote- and direct-plasma treatments. The theoretical aspects of the remote plasma treatment have been described elsewhere.[14]

To make a composite of PFA and copper metal, the following procedures were designed.

Procedure 1: The PFA surface was modified into a hydrophilic surface by the remote hydrogen plasma. Such a hydrophilic surface will become wet with an electroless plating solution, and palladium catalysts will deposit on the PFA surface.

Procedure 2: On the plasma-treated PFA surfaces, copper metal was deposited by a combination of electroless- and electroplatings.

In the electrolessplating process, reduction reactions of copper ions into copper metal with formaldehyde occur with the assistance of palladium catalysts that are deposited on the PFA surface.[15] This is the essential reaction of the copper metallization in the electroless

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plating process. Therefore, important factors for surface metallization are how to deposit the palladium catalyst to the PFA surface and how to make a strong adhesion between the copper metal layer deposited by the electroless plating and the PFA surface. In this study, we have investigated how the surface modification of PFA by the remote hydrogen plasma contributes to the adhesion with copper metal.

Experimental Section

Materials. Tetrafluoroethylene−perfluoroalkyl vinyl ether copolymer, PFA, sheet received from Daikin Industries, Ltd., Japan (trade name, Neoflon AF-0050) in a form of 300 mm wide and 50 μm thick was cut to a dimension of 12 mm × 90 mm, and used as specimens for surface modification experiments. Prior to the surface modification experiment, the PFA sheets were washed with acetone in an ultrasonic washer and dried at room temperature under vacuum. Hydrogen and argon were pure grade (99.995%).

Remote Hydrogen Plasma Treatment of PFA Sheets. A special reactor was used for the remote hydrogen plasma treatment of the PFA sheets. Details of the reactor have been described in a previous paper.[14] The reactor consists of a cylindrical Pyrex glass tube (45 mm diameter, 1000 mm long) and a columnar stainless steel chamber (300 mm diameter, 300 mm height). The Pyrex glass tube has two gas inlets for the injection of hydrogen and argon gases and a copper coil of nine turns for the energy input of rf power (13.56 MHz frequency). The stainless steel chamber contains a Barocel pressure sensor (type 622, Edwards) and a vacuum system composed of a combination of a rotary pump (320 L/min) and a diffusion pump (550 L/s) (type YH-350A, Ulvac Co.). The Pyrex glass tube is joined with the chamber by a Viton O ring flange.

The PFA sheets were positioned at a constant distance of 800 mm from the center of the copper coil and exposed to the hydrogen plasma. First, the air in the reactor was displaced with argon. Afterward, the reactor was evacuated to approximately 1.3×10^{-2} Pa, and then hydrogen, whose flow rate was adjusted to 10 cm^3 (STP)/min by a mass flow controller, was introduced into the Pyrex glass tube. The hydrogen plasma was operated at rf powers of 50−110 W at 13.56 MHz frequency at a system pressure of 13.3 Pa for given times (10−300 s).

Contact Angle of Water. Using the sessile drop method,[16] contact angles of water on the PFA surfaces treated with the remote hydrogen plasma were measured at 20 °C using a contact angle meter with a goniometer (Erma Co., Ltd.; model G-1). An average contact angle was determined from 10 measurements with an experimental error of 3−4°.

X-ray Photoelectron Spectra. XPS spectra for PFA surfaces treated with the remote hydrogen plasma were obtained on a Shimadzu ESCA K1 spectrometer using a nonmonochromatic Mg Kα photon source at an anode voltage of 12 kV, an anode current of 20 mA, and a pressure in the analytical chamber of 1.5×10^{-6} Pa. The XPS spectra were referenced with respect to the 690.0 eV fluorine 1s core level to eliminate charging effects. The spectra were not modified by the smoothing procedure. The C_{1s} and O_{1s} spectra were deconvoluted by fitting a Gaussian−Lorentzian mixture function (the mixture ratio was 80:20) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. Sensitivity factors (S) for the C_{1s}, O_{1s}, F_{1s}, and $Cu_{2p3/2}$ core levels were $S(C_{1s}) = 1.00$, $S(O_{1s}) = 2.85$, $S(F_{1s}) = 4.26$, and $S(Cu_{2p3/2}) = 15.87$. The F/C and O/C atomic ratios were calculated from the F_{1s}, O_{1s}, and C_{1s} intensities, and their experimental error was within 0.03.

Copper Metallization of the PFA Surface. PFA surfaces were metallized by electroless plating, and then the copper layer deposited on the PFA surface was thickened by electroplating. The total thickness of the deposited copper metal was about 30 μm (0.2 μm thickness by the electrolessplating and 30 μm thickness by the electroplating). In the electrolessplating process, the PFA sheets whose surfaces were modified by the remote hydrogen plasma treatment were placed in a special solution (a mixture of OPC-80 and OPC-SAL, Okuno Chemical Industries Co. Ltd., Japan) containing colloidal palladium−tin alloy particles, which acted as a catalyst for reduction reactions from copper ions to copper metal, and kept in the solution at 25 °C for 5 min in order to deposit the colloidal palladium−tin alloy particles on the PFA surfaces. Then, the PFA sheets were treated with a dilute sulfuric acid solution (3.6 M/L) at 40 °C for 5 min, to make surfaces of the colloidal particles palladium-rich by dissolving only the tin component in the sulfuric acid solution. Afterward, the PFA sheets were dipped in a special electroless plating solution (aqueous solution including copper ion and formaldehyde) (TMP, Okuno Chemical Industries Co., Ltd.) at room temperature for 5 min to deposit copper metal on the PFA surfaces.

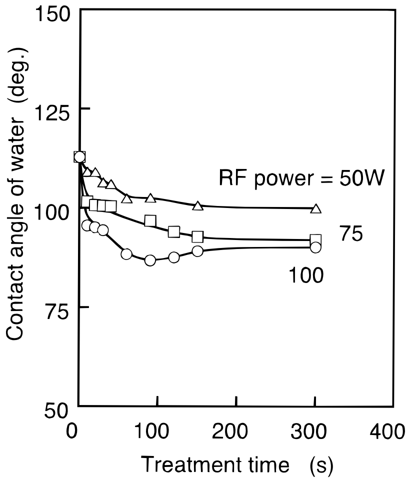


Figure 1. Contact angle of water on PFA surfaces treated with remote hydrogen plasma as functions of rf power and plasma treatment time.

The PFA sheets whose surfaces had been made electrically conductive by the electrolessplating process were electroplated with copper to a thickness of 30 μm. The electroplating procedure was carried out at a constant current of 10 A (current density of 300 A/m^3) and at a constant volt of 8 V at 24 °C for 1 h in a sulfuric acid solution (190 g/L) containing copper sulfate (75 g/L), hydrogen chloride (50 ppm), and a glossy reagent (Nippon Rironal Co. Ltd.; PCM, 5 mL). Finally, the PFA sheets were washed with water and dried at 80 °C for 12 h under vacuum.

Peel Strength of the Copper/PFA System. The T-type peel strength (5 mm wide) of the copper/PFA system was evaluated at a peel rate of 10 mm/min using an Instron-type tensile strength tester (Shimadzu AGS100-A). The peel strength was determined from an average of 10 measurements.

Results and Discussion

Modification of the PFA Surface by Remote Hydrogen Plasma. Figure 1 shows typical results for the contact angle of water on PFA surfaces modified by the remote hydrogen plasma as functions of the plasma treatment time and rf power. The contact angle of water, as shown in Figure 1, showed a large decrease within a short treatment time of about 120 s. At treatment times longer than 120 s, the decrease became negligibly small. The contact angle at 120 s was 102−87°, which depended on the magnitude of the rf power. Figure 2 shows effects of the rf power in the remote hydrogen plasma treatment for 90 s on the contact angle of water on the treated PFA surfaces. The contact angle decreased linearly with increasing the rf power. At a rf power of 100 W, the contact angle reached 87°. These results show that the remote hydrogen plasma treat-

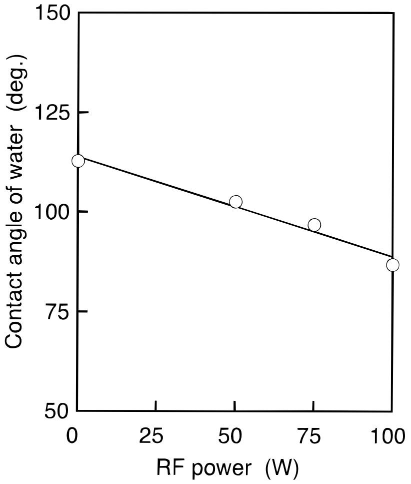


Figure 2. Contact angle of water on PFA surfaces treated with remote hydrogen plasma for 90 s as a function of rf power.

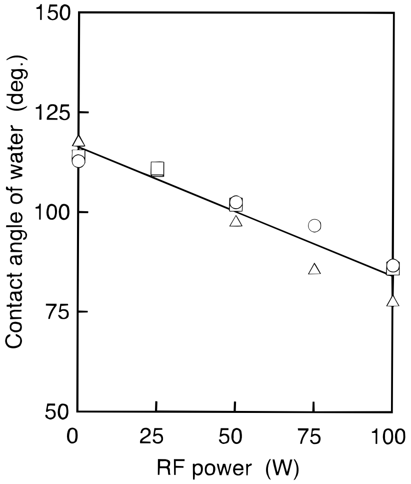


Figure 3. Contact angle of water on PFA (○), PTFE (△), and FEP (□) surfaces treated with remote hydrogen plasma for 90 s as a function of the rf power.

ment is able to make the PFA surface relatively hydrophilic.

Figure 3 compares other fluoropolymers besides PFA with regard to the hydrophilic modification by the remote hydrogen plasma. The fluoropolymers are poly(tetrafluoroethylene), PTFE, and tetrafluoroethylene−hexafluoropropylene copolymer, FEP, which are similar in chemical and physical properties to FAP. The surface modification of PTFE and FEP sheets by the remote hydrogen plasma was carried out using the same plasma reactor and operational plasma conditions as used for PFA. Contact angle data for the PTFE and FEP surfaces are duplicated from previous papers.[3,4] The water contact angle for the three fluoropolymers, PFA, PTFE, and FEP, as shown in Figure 3, decreased linearly with increasing the rf power. The common dependence on the rf power among the PFA, PTFE, and FEP surfaces indicates a similar susceptibility to the hydrogen plasma. This commonality may be due to a similarity of the chemical composition among PFA, PTFE, and FEP. PFA, PTFE, and FEP are mainly composed of CF_2-CF_2 units. PFA and FEP contain amounts of perfluoroalkyl vinyl ether and hexafluoropropyl units with a few percentages of each other.

Table 1. Atomic Composition of PFA, PTFE, and FEP Surfaces Treated with Remote Hydrogen Plasma at 100 W

fluoropolymer	plasma treatment time (s)	atomic composition: F/C atom ratio	atomic composition: O/C atom ratio	defluorination (%)
PFA	0	2.01	<0.03	
	30	1.04	0.13	48
	45	1.15	0.09	43
	60	1.15	0.13	43
	90	1.17	0.13	42
PTFE	60	1.06	0.09	47
FEP	60	1.63	0.11	16

The PFA surfaces treated with the remote hydrogen plasma at 100 W for 30−90 s were analyzed by XPS (C_{1s}, F_{1s}, and O_{1s} core level spectra), and the atomic composition (F/C and O/C atom ratios) was estimated from the signal intensities. Table 1 shows the F/C and O/C atom ratios for the plasma-treated PFA surfaces as a function of the plasma treatment time. The F/C atom ratio decreased from 2.01 to 1.17−1.04 and the O/C atom ratio increased from <0.03 to 0.09−013. These changes in the F/C and O/C atom ratios indicate that defluorination and oxidation occurred simultaneously in the procedure of the remote hydrogen plasma treatment. Why did oxidation reactions occur on the PFA surface, although oxygen was never used in the surface modification procedure? We can speculate on a mechanism for the oxidation reactions as follows. Hydrogen radicals in the remote hydrogen plasma remove fluorine atoms from PFA surface, leaving behind carbon radicals on the surface. The carbon radicals recombine with other hydrogen radicals in the hydrogen plasma to form C−H bonds. This is a mechanism of the defluorination by the remote hydrogen plasma. However, all carbon radicals that are formed by the hydrogen plasma do not recombine with hydrogen radicals, but part of the carbon radicals remains on the PFA surface even after the remote hydrogen plasma treatment is finished. The remaining radicals react with oxygen and water in air to form peroxide groups when the plasma treatment is finished and the PFA sheet is taken out from the plasma reactor. Accordingly, the peroxide groups are modified into oxygen functional groups such as hydroxyl and carbonyl groups. This is one possible mechanism for the oxidation reactions.

The degree of defluorination, as shown in Table 1, was estimated to be 42−48% from decreases in the F/C atom ratio. For other fluoropolymers, the degree of defluorination was 47 and 16% for PTFE and FEP, respectively (Table 1). We cannot interpret at present why PFA and PTFE showed higher defluorinations than FEP, since there are minor differences in the chemical composition among the three fluoropolymers.

To investigate the chemical composition of the PFA surfaces treated by the remote hydrogen plasma treatment, C_{1s}, O_{1s}, and F_{1s} spectra were analyzed. There were large changes in C_{1s} and O_{1s} spectra for the PFA surfaces by the remote hydrogen plasma treatment, but there was no change in the F_{1s} spectrum. Figure 4 shows typical C_{1s} and O_{1s} spectra for the PFA surface treated with the remote hydrogen plasma for 60 s. The C_{1s} spectrum for the untreated PFA was symmetrical (The full width at half-maximum, fwhm, was 1.86 eV), and the peak appears at 292.9 eV, which is assigned to CF_2 groups. The O_{1s} spectrum was noisy and very weak in signal intensity. For the plasma-treated PFA, the C_{1s} and O_{1s} spectra were completely different from those

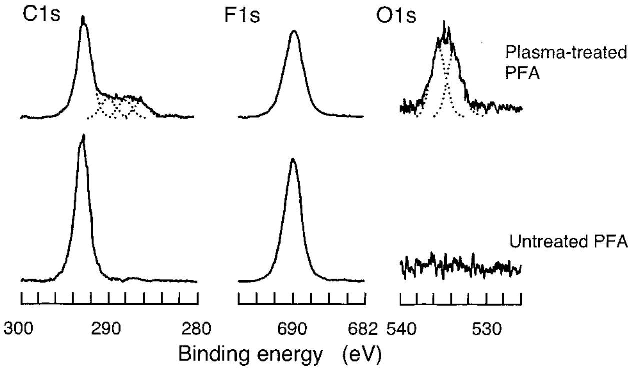


Figure 4. XPS (C_{1s}, F_{1s}, O_{1s}) spectra for PFA surfaces untreated and treated with the remote hydrogen plasma at 100 W for 60 s.

for the untreated PFA. The C_{1s} spectrum for the plasma-treated PFA was deconvoluted into four components, which appeared at 286.4, 288.2, 290.1, and 292.8 eV. The deconvoluted components are shown in dotted lines in Figure 4. The four components in the order of binding energy are assigned to *C*H$_2$−CF$_n$ and O-*C*H−CF$_n$, *C*HF−CF$_n$ and O*C*H−CF$_n$, O−*C*F−CF$_n$ and O═*C*−CF$_n$, and *C*F$_2$ groups, respectively.[17,18] The underlined C is the objective carbon atom for the assignment. The O_{1s} spectrum, as shown in Figure 4, was deconvoluted into two components, which appeared at 533.6 and 535.5 eV. The two O_{1s} components shifted to higher binding energy field than regular oxygen compounds (531−533 eV).[17,18] This shift may be due to the electron-withdrawing effect of fluorine atoms. Therefore, the two O_{1s} components at 533.6 and 535.5 eV are assigned to fluorinated *O*═C and *O*−C groups, respectively. Other PFA surfaces treated with the remote hydrogen plasma for 30 and 90 s also showed similar C_{1s} and O_{1s} spectra. Results of the deconvolution are summarized in Table 2. There is no change with regard to the kind of components that composed the C_{1s} and O_{1s} spectra and their concentrations even when the plasma treatment time was altered from 30 to 90 s. The C_{1s} spectra were composed of four components, *C*H$_2$−CF$_n$ and O−*C*H−CF$_n$, *C*HF−CF$_n$ and O*C*H−CF$_n$, O−*C*F−CF$_n$ and O═*C*−CF$_n$, and *C*F$_2$ groups, and the O_{1s} spectra were composed of two components, fluorinated *O*═C and *O*−C groups. Such unchanged C_{1s} and O_{1s} spectra indicate that the modification reactions might be completed in a short time, within 30 s.

In conclusion, the remote hydrogen plasma treatment results in defluorination and oxidation of PFA surface. The degree of defluorination is 42−48%, and the oxidation reaches 9−13% of the total carbon atoms. We expect that such oxidized groups could act as sites on which the colloidal palladium catalyst deposit and the copper metallization would start from the catalyst-deposited sites.

Copper Metallization of PFA Surface by a Combination of Electroless- and Electroplating. Effects of the surface modification by the remote hydrogen plasma on adhesion between copper metal and PFA were investigated using a T-type peel test. The PFA sheets were treated with the remote hydrogen plasma at 50−110 W for 10−300 s, and then on the plasma-treated PFA surfaces, a copper metal layer (30.2 μm thick) was deposited by a combination of electroless- and electroplatings. Figure 5 shows the peel strength for the copper metal/PFA system as a function of the plasma treatment time at an rf power of 100 W. The untreated PFA showed no adhesion with the copper metal layer, and the peel strength for the copper metal/PFA system was zero. The surface modification of the PFA sheets by the remote hydrogen plasma led to a large improvement in adhesion with copper metal. The peel strength, as shown in Figure 5, was increased with increasing plasma treatment time and reached a maximum of 101 mN/5 mm at a treatment time of 60 s. Afterward, the peel strength was decreased with increasing treatment time, and the decrease continued up to 300 s. This decrease in the peel strength may be due to the formation of a surface layer injured by the plasma (weak boundary layer). On the other hand, the direct hydrogen plasma was not effective in the adhesion improvement, although PFA surfaces were modified effectively. PFA surfaces treated with the direct hydrogen plasma at 100 W for 30−300 s showed a constant F/C atom ratio of 0.70 whose defluorination was estimated to be 65%. This defluorination is higher than that by the remote hydrogen plasma (42−48% shown in Table 1). PFA surfaces were modified by the direct hydrogen plasma, and were metallized with copper metal using a combination of electroless- and electroplatings. The peel strength for the copper metal/PFA system was evaluated as a function of the plasma treatment time (Figure 5). The peel strength was improved from 0 to 24 mN/5 mm by direct hydrogen plasma treatment for 10 s, but a further increase in peel strength was never seen even when the plasma treatment time was increased from 10 up to 300 s. This figure shows that the surface modification by the direct plasma treatment leads to improvement of the peel strength, but the improvement (from 0 to 24 mN/5 mm) is inferior to that by the remote hydrogen plasma (from 0 to 101 mN/5 mm). Therefore, the direct hydrogen plasma treatment is not an adequate method for improvement of the adhesion between copper metal and PFA surface. The comparison between the direct and remote hydrogen plasma treatments points out an important concept that heavy surface modification is not always effective in the adhesion. In the direct plasma treatment, the PFA surfaces are always in the plasma zone and are exposed to energetic electrons, ions, and radicals. As a result, heavy degradation as well as defluorination will occur on the PFA surfaces. In the remote hydrogen plasma treatment, the PFA surfaces are kept from the energetic plasma and will be modified mildly with less heavy degradation. This is one of the main differences in surface modification between direct and remote hydrogen plasma treatments.

Figure 6 shows effects of the rf power in the remote hydrogen plasma treatment process on the peel strength for the copper metal/PFA system. The remote hydrogen plasma at a rf power of less than 25 W did not contribute to the adhesion. The peel strength, as shown in Figure 6, increased linearly from 46 mN/5 mm at a rf power of 50 W to 105 mN/5 mm at 110 W with increasing rf power.

To investigate one of the mechanisms of failure for the copper metal/PFA system, two surfaces (PFA polymer and copper metal layers) from the system that failed were observed using XPS. PFA sheets treated with remote hydrogen plasmas at 100 W for 60 s were used for the adhesive joints. Figure 7 shows XPS (C_{1s}, F_{1s}, and $Cu_{2p3/2}$) spectra for the PFA polymer and copper metal layers peeled-off from the copper metal/PFA system. The PFA polymer and copper metal layers, as

Table 2. C_{1s} and O_{1s} Components for PFA Surfaces Treated with Remote Hydrogen Plasma at 100 W

sample	plasma treatment time (s)	peak position in eV (relative concentration in %)					
		C_{1s} components				O_{1s} components	
		no. 1	no. 2	no. 3	no. 4	no. 1	no. 2
original PFA	0				292.9 (100%)	-	-
plasma-treated PFA	30	286.9 (25%)	288.9 (9%)	290.5 (9%)	292.9 (57%)	533.5 (46%)	535.1 (54%)
	60	286.4 (10%)	288.2 (12%)	290.1 (13%)	292.8 (65%)	533.6 (49%)	535.5 (51%)
	90	286.3 (13%)	288.1 (12%)	290.3 (12%)	293.1 (63%)	533.5 (49%)	535.4 (51%)

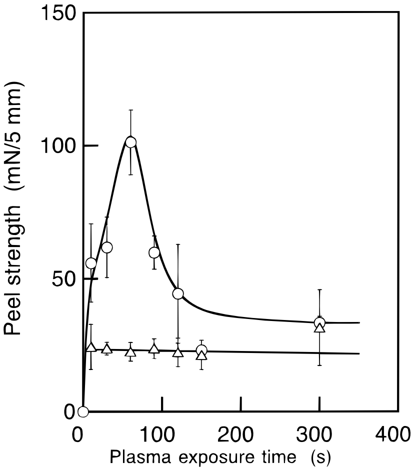


Figure 5. Peel strength for copper metal/PFA system as a function of plasma treatment time at a rf power of 100 W. Key: remote hydrogen plasma-treated PFA (○); direct hydrogen plasma-treated PFA (△).

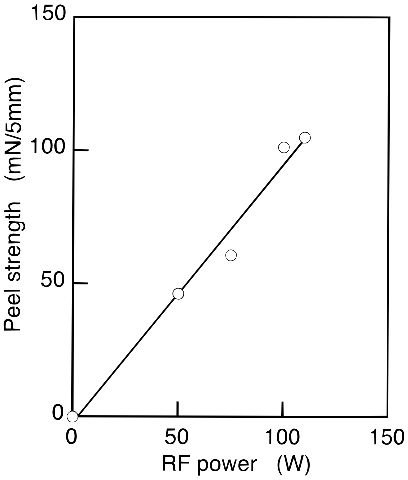


Figure 6. Peel strength for copper metal/PFA system as a function of the rf power for 60 s.

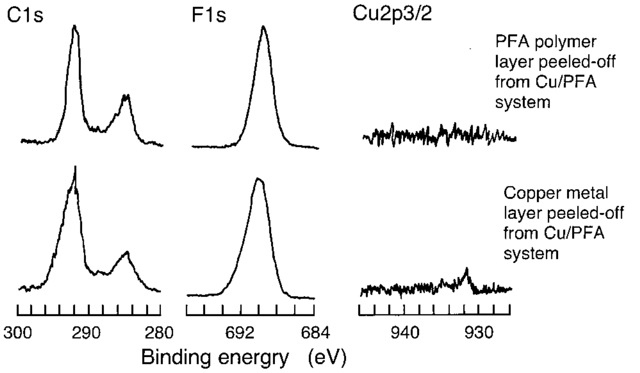
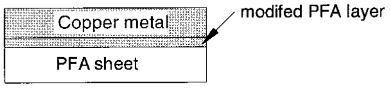
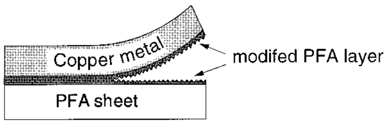


Figure 7. XPS (C_{1s}, F_{1s}, and $Cu_{2p3/2}$) spectra for the PFA polymer and copper metal layers peeled-off from the copper metal/PFA system (plasma-treated at 100 W for 60 s).



Structure of copper metal/PFA system



Failure mode of copper metal/PFA system

Figure 8. A failure mode of the copper metal/PFA system.

shown in Figure 7, showed similar C_{1s} and F_{1s} spectra, and no $Cu_{2p3/2}$ spectrum. The C_{1s} spectra contained an intense and sharp peak at 292.8 eV and a small but widely distributed peak at 287−284 eV. The F_{1s} spectra contained a symmetrical peak at 690 eV. From these XPS spectra, the F/C, O/C, and Cu/C atom ratios for the two layers were calculated. The F/C, O/C, and Cu/C atom ratios for the PFA polymer layer were 1.06 and 0.11, and <0.03, respectively. The F/C, O/C, and Cu/C atom ratios for the copper metal layer were 1.14, 0.12, and <0.03, respectively. These comparisons show the two layers are similar in chemical composition (F/C, O/C, and Cu/C atom ratios) to each other. Furthermore, the two layers resemble in the atomic composition the PFA surface just modified by the remote hydrogen plasma. The F/C and OC atom ratios for the PFA polymer layer were 1.06 and 0.11, respectively; and the F/C and OC atom ratios for the copper metal layer were 1.14 and 0.12, respectively. On the other hand, the F/C and O/C atom ratios for the PFA surface treated with the remote hydrogen plasma were 1.15 and 0.13, respectively (see in Table 1). From these results, we conclude that the copper metal/PFA polymer system was not peeled-off from the interface between the copper metal and PFA surface but was peeled off from an inner layer of a part of the plasma-treated PFA polymers. Figure 8 represents schematically one of the failure modes of the copper metal/PFA system.

In conclusion, the modification of the PFA surface by the remote hydrogen plasma can contribute effectively to improvement of adhesion with copper metal. The peel strength for the copper metal/PFA system is improved from 0 to 101 mN/5 mm by the surface modification using the remote hydrogen plasma. The failure mode of the copper metal/PFA system is an inner layer of the plasma-treated PFA polymer layer.

Conclusion

PFA sheets were modified with the remote hydrogen plasma and effects of the modification on the adhesion between copper layer and FEP was investigated. The remote hydrogen plasma treatment is a preferable surface modification for copper metal/PFA system. The results are summarized as follows.

(1) Remote hydrogen plasma treatment for a short time of 30 s is able to make the PFA surface relatively hydrophilic.

(2) Remote hydrogen plasma treatment causes defluorination and oxidation of the PFA surface. The extent of the defluorination is 42−48%, and the oxidation reaches 9−13% of the total carbon atoms.

(3) The modification of the PFA surface by the remote hydrogen plasma is effective in the adhesion to copper metal. The peel strength for the copper metal/PFA system is improved from 0 to 101 mN/5 mm by the surface modification.

(4) The failure mode of the copper metal/PFA system is an inner layer of the plasma-treated PFA layer.

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