Effects of Surface Modification by Remote Hydrogen Plasma on Adhesion in Poly(tetrafluoroethylene)/Copper Composites

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ABSTRACT: Poly(tetrafluoroethylene) (PTFE) sheet was modified with the remote hydrogen plasma, and the effect of the modification on adhesion between the PTFE sheet and copper metal was investigated. The remote hydrogen plasma was able to make PTFE surfaces hydrophilic without etching. In the modification process, defluorination and oxidation occurred on the PTFE surface. Reactivity of defluorination was 25% (estimated from the concentration of CF_2 component) -39% (estimated from the F/C atom ratio). Surface modification of PTFE surface by remote hydrogen plasma contributed to the adhesion between PTFE and copper metal. Peel strength was improved from 7.5 to 92 mN/5 mm by surface modification by a factor of 12. Failure of the PTFE/copper adhesive joint occurred at the interface between the PTFE and copper metal layers, rather than in the inner layer of the PTFE polymer or copper metal layers. Remote hydrogen plasma treatment is a preferable pretreatment of PTFE surface for the fabrication of PTFE and copper metal composites. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2191–2200, 1999

Key words: poly(tetrafluoroethylene); surface modification; adhesion; surface metallization; remote plasma treatment; peel strength

INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) is one of the most stable polymers with high-temperature resistance and chemical resistance, as well as hydrophobic properties. In addition to such excellent properties, PTFE also possesses outstanding properties, such as an electrical insulation material. Volume resistivity is $> 10^{19} \Omega$ -cm at dry atmosphere at 295.8 K and $> 10^{16} \Omega$ -cm at a relative humidity of 100% at 295.8 K.¹ Its dielectric constant is 2.1, in frequency ranges of 1 MHz to 1 GHz at 295.8 K, and its dissipation factor is < 1

 $\times~10^{-4}$ in frequency ranges of 1 MHz to 1 GHz frequency at 295.8 K.¹ Therefore, PTFE is expected to be one of the most suitable polymers for insulation from high-frequency electric currents (GHz), and to be used as printed wiring boards for integrated circuits and an insulator for coaxial cables. These electric materials are composites of PTFE and copper metal.

Copper metallization of polymeric materials is possible in many ways, such as electrolessplating, vacuum deposition, sputtering of copper metal, etc. Electrolessplating is a simple process to metallize polymer surfaces and requires no special equipment for the metallization. In the electrolessplating process, palladium metal particles, which act as catalysts for reduction reactions from copper ions to copper metal, are attached to

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the polymer surface. The polymer surface with the palladium metal particles is put in an electrolessplating solution containing copper ions. Copper metallization, which is reduction reactions of copper ions with formaldehyde over a palladium catalyst, and the deposition of the reduced copper metal, occurs on the surfaces of the palladium metal particles.² These are the essential reactions of copper metallization in the electrolessplating process. Therefore, how to attach the palladium metal particles on the polymer surface and how to operate strong interactions between the polymer surface and copper metal layer, which is deposited by electrolessplating, are important questions for successful metallization. On the other hand, in metallization by vacuum deposition and sputtering of copper metal, pretreatment of PTFE surface is a requisite process to get strong adhesion between the PTFE surface and copper metal layer before the metallization process. Pretreatment involves roughening the PTFE surface to provide strong adhesion by the anchor-lock effect. The excimer-laser radiation of KrF and ArF, and ion irradiation in the energy ranges of some keV to MeV are frequently used as the pretreatment process.^{3,4} Morphology of the PTFE surface is changed by these pretreatments, and adhesion between the PTFE and copper metal layer is improved by the anchor-lock effect.

In this study, we have focused on the copper metallization of the PTFE surface by electrolessplating, because of the easy process of the metallization. Before metallization of the PTFE surface, the surface of PTFE must be modified to become hydrophilic to well-wet its surface with an electrolessplating solution and to catch palladium metal particles on its surface. We have proposed a remote hydrogen plasma treatment as a hydrophilic surface modification process.⁵ Remote plasma treatment is different from the conventional plasma treatment with respect to relative distance of the sample position against the plasma zone. The sample in remote plasma treatment is positioned away from the plasma zone, and the sample in the conventional plasma treatment is positioned just in the plasma zone. We call conventional plasma treatment "the direct plasma treatment" to distinguish it from the remote plasma treatment.

Plasma is a mixture of electrons, ions, and radicals, which are able to initiate chemical reactions against polymer surfaces. Radicals in the plasma possess longer lifetime than electrons and ions. As a result, at a position far away from the plasma zone (in the remote plasma treatment), reactions with radicals occur predominantly, and reactions with electrons and ions scarcely occur. In the plasma zone (in the direct plasma treatment), reactions with electrons and ions, as well as radicals, occur simultaneously. This is an essential difference in plasma chemistry between the remote plasma and direct plasma treatments. Theoretical background of remote plasma treatment has been described elsewhere.⁶

From the viewpoint of special reactions in the remote plasma, we have investigated effects of remote hydrogen plasma treatment on the hydrophilicity of PTFE surfaces and on the adhesion between the PTFE sheet and the copper metal layer.

EXPERIMENTAL

Materials

The PTFE sheet, which was received from Nichias Co., Japan (Teflon 9001), in a form 300 mm wide and 50 mm thick, was cut to a dimension of 10 mm \times 30 mm and provided as a specimen for surface modification experiments. Before the experiment, the sheet was washed with acetone in an ultrasonic washer and dried at room temperature under a vacuum. Hydrogen and argon were pure grade, and purity was 99.995%.

Remote Hydrogen Plasma Treatment of the PTFE Sheet

A special reactor for the remote hydrogen plasma treatment of the PTFE sheet was used. The details of the reactor were described in a previous article.⁵ 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 radiofrequency (rf) power (13.56 MHz frequency). The stainless-steel chamber contains a Barocel pressure sensor (type 622, Edwards) and a vacuum system combination of a rotary pump (320 Lmin^{-1}) and a diffusion pump $(550 \text{ L} \text{ s}^{-1})$ (type YH-350A, Ulvac Co.). The Pyrex glass tube is joined with the chamber with a Viton O ring flange.

PTFE sheets were positioned at a constant distance of 800 mm from the center of the copper coil and were exposed to the hydrogen plasma. First, air in the reaction system was displaced with argon. Afterward, the reaction chamber was evacuated to $\sim 1.3 \times 10^{-2}$ Pa, and then hydrogen at a flow rate of 10 cm³ (STP) min⁻¹ was introduced into the Pyrex glass tube. Hydrogen plasma was operated at an rf power of 25, 50, 75, and 100 W at 13.56 MHz frequency, with a system pressure of 13.3 Pa for given times (10–300 s).

Contact Angle of Water

According to the sessile drop method,⁷ contact angles of water on the PTFE sheet surfaces treated with the remote hydrogen plasma were measured at 20°C using a contact angle meter with a goniometer (Erma Co. Ltd., Japan; model G-1). An average contact angle was determined from 10 measurements, with an experimental error of $3^{\circ}-4^{\circ}$.

X-ray Photoelectron Spectra (XPS)

The XPS spectra of the surface of the PTFE sheets treated with remote hydrogen plasma were obtained on a Shimadzu ESCA K1 using a nonmonochromatic MgK_a photon source. The anode voltage was 12 kV, the anode current 20 mA, and the background pressure in the analytical chamber 1.5×10^{-6} Pa. The size of the X-ray spot was 2 mm diameter, and the take-off angle of photoelectrons was 90° with respect to the sample surface. The XPS spectra were referenced with respect to the 690.0 eV fluorine 1-s core level to eliminate the charge effect. The smoothing procedure of the spectra was not done. The C_{1s} and O_{1s} spectra were decomposed by fitting a Gaussian-Lorentzian mixture function (mixture ratio: 80 : 20) to an experimental curve using a nonlinear, least-squares curve-fitting program, ESCAPAC, supplied by Shimadzu. The sensitivity factors (S)for the 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. An experimental error for estimating F/C and O/C atomic ratios from the relative F_{1s} , O_{1s} , and C_{1s} intensities were within 0.03.

Copper Metallization of the PTFE Surface

A combination of two processes, electrolessplating and electroplating, was conducted for copper metallization of the PTFE surface. Total thickness of the copper metal layer deposited by the electroless- and electroplatings was \sim 30 μ m (0.2 μ m thickness by the electrolessplating and 30 μ m

thickness by the electroplating). In the electrolessplating process, first, the PTFE sheets, of which surfaces were modified into hydrophilic by the remote hydrogen plasma treatment, were put 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, for 5 min at 25°C to attach the colloidal palladium-tin alloy particles on the PTFE surfaces. Then, the PTFE sheets were treated with a dilute sulfuric acid solution $(3.6M L^{-1})$ at 40°C for 5 min, to make surfaces of the colloidal particles palladium-rich by dissolving the tin component alone in the sulfuric acid solution. Afterward, PTFE sheets were put in a special electrolessplating solution (TMP, Okuno Chemical Industries Co.) at room temperature for 5 min to deposit copper metal on the PTFE surfaces.

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

Peel Strength of the Adhesive Joint between PTFE Sheet and Copper Metal

The T-type peel strength (5 mm wide) of the adhesive joint between the PTFE sheet and copper metal was evaluated at a peel rate of 10 mm \min^{-1} using an Instron-type tensile strength tester (Shimadzu AGS100-A). Peel strength was determined from an average of 10 measurements.

RESULTS AND DISCUSSION

Hydrophilic Modification of the PTFE Surface by Remote Hydrogen Plasma

Previously described surface modification of the PTFE sheets was conducted at an rf power of 25–100 W for 10–300 s. Figure 1 shows typical results of contact angle of water on the PTFE surfaces modified by remote hydrogen plasma at



Figure 1 Contact angle of water on PTFE surfaces treated with remote hydrogen plasma at 100 W as a function of plasma treatment time.

an rf power of 100 W, as a function of the plasma treatment time. The contact angle of water, as shown in Figure 1, decreases remarkably from 118° to 88° within a short plasma treatment time of 10 s, and the decrease continues up to 120 s. At a plasma treatment time of 120 s, the contact angle is 77°; afterward, the decrease in contact angle becomes negligible. This decrease in contact angle shows that the remote hydrogen plasma treatment within a short treatment time of 120 s can modify the PTFE surface from hydrophobic to hydrophilic. Figure 2 shows the contact angle of water on the PTFE surfaces treated with the remote hydrogen plasma for 120 s as a function of the rf power. The contact angle of water decreases linearly with increasing rf power. At an rf power of 100 W, the contact angle of water reaches 77°.

The remote hydrogen plasma treatment, as described in the Introduction, is distinguished from the conventional (direct) hydrogen plasma treatment in the viewpoint of the composition of active species in the plasma. In remote hydrogen plasma, hydrogen radicals, rather than electrons and hydrogen ions, are predominant species, and the hydrogen radicals chiefly will initiate hydrophilic modification reactions. On the other hand, in direct hydrogen plasma, electrons and hydrogen ions, as well as hydrogen radicals, exist together. In addition to the modification reactions by hydrogen radicals, reactions by electrons and hydrogen ions will occur simultaneously. Reactions by the electrons and ions may be mainly electron, and ion bombardments that initiate etching and degradation reactions. As a result, these reactions will lead to degradation products with low molecular weight on the PTFE surface. Such a PTFE surface will show a large difference in the contact angle before and after removing degradation products from the surface.

Using the same plasma reactor, remote and direct hydrogen plasma treatments were conducted in the same operational conditions (rf power, hydrogen flow rate, system pressure, etc.), except the sample position. In remote hydrogen plasma treatment, the PTFE sheets were put at a 80 cm distance from the plasma zone; and, in direct hydrogen plasma treatment, PTFE sheets were just put in the plasma zone. Water contact angles on the PTFE surfaces treated with remote and direct hydrogen plasmas were measured within a few minutes after finishing the plasma treatment. Successively, these PTFE surfaces were rinsed with acetone using an ultrasonic washer for 5 min to remove some degradation products formed by plasma irradiation; then, water contact angles on the acetone-rinsed PTFE surfaces were measured again. Table I shows the contact angles of water before and after the acetone-rinsing PTFE surfaces. The table shows essential differences in the water contact angle between the PTFE surfaces treated with remote and



Figure 2 Contact angle of water on PTFE surfaces treated with remote hydrogen plasma for 120 s as a function of rf power.

Plasma Treatment Time (s)	Plasma-Treated PTFE Surfaces (°)							
	Remote H	lydrogen Plasm	a Treatment	Direct Hydrogen Plasma Treatment				
	Before Rinsing	After Rinsing	Difference	Before Rinsing	After Rinsing	Difference		
0	118	118	0	118	118	0		
10	92	88	-4	62	90	+28		
20				67	84	+17		
40				67	84	+17		
60	87	83	-4	64	84	+20		
90	84	80	-4	67	86	+19		
120	78	77	-1	67	88	+21		

 Table I
 Contact Angle Changes on Remote and Direct Hydrogen Plasma-Treated PTFE Surfaces

 by Rinsing with Acetone
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Contact Angle of Water on Direct or Remote Hydrogen,

direct hydrogen plasmas. For PTFE surfaces treated with the remote hydrogen plasma, there is less difference in the water contact angle before and after acetone-rinsing. No change in the water contact angle indicates that no degradation product was formed on the PTFE surface by remote hydrogen plasma treatment. On the other hand, for the PTFE surfaces treated with direct hydrogen plasma, there are large differences in the water contact angle before and after acetone-rinsing. Although the contact angle $(62^\circ - 67^\circ)$ for the PTFE surfaces treated with the direct hydrogen plasma is smaller than that for those treated with remote hydrogen plasma (78°-87°), once the PTFE surfaces were rinsed with acetone, the water contact angles increases from 62°-67° to 84°-90°, which is higher than that for the PTFE surfaces treated with remote hydrogen plasma. This increase in water contact angle by acetone-rinsing may be due to removal of some degradation products from treated PTFE surface. From these results, we believe that remote hydrogen plasma treatment is essentially different from the direct hydrogen plasma treatment. The remote hydrogen plasma treatment can make the PTFE surface hydrophilic without formation of degradation products.

Scanning electron microscopic (SEM) micrographs show the essential difference between remote and direct hydrogen plasma treatments (Fig. 3). PTFE surfaces that were treated with remote and direct hydrogen plasmas at 100 W for 120 and 30 s, respectively, and then were rinsed with acetone for 5 min in an ultrasonic washer served as specimens for SEM observation. The PTFE surface treated with remote hydrogen plasma, as shown in Figure 3(b), shows a scabrous surface that contains many micropores of 0.2–0.4 μ m wide and 1–2 μ m long. This SEM micrograph shows similar surface morphology to the original PTFE sheet [Fig. 3(a)]. On the other hand, the PTFE surface treated with direct hydrogen plasma is distinctly different in the surface morphology from the remote hydrogen, plasma-treated PTFE surface. The PTFE surface treated with direct hydrogen plasma [Fig. 3(c)] is rougher than the remote hydrogen, plasmatreated PTFE surface. The dimension of micropores is $1-2 \ \mu m$ wide and $3-7 \ \mu m$ long. This roughened surface indicates that heavy etching reactions in the direct hydrogen plasma occurred on the PTFE surface.

From these results, we conclude that less etching reaction occurs in the remote hydrogen plasma treatment, and heavy etching reactions occur in direct hydrogen plasma. Remote hydrogen plasma treatment may be preferable for the pretreatment of PTFE surface because there is no formation of degradation products.

Chemical Composition of the PTFE Surface Modified by Remote Hydrogen Plasma

The PTFE surface that was treated with remote hydrogen plasma at 100 W for 120 s and rinsed with acetone was analyzed by XPS (C_{1s} , F_{1s} , and O_{1s} core-level spectra). Table II shows the F/C and O/C atom ratios on the plasma-treated PTFE surface, as well as the original PTFE surface, which was estimated from the relative intensities of the







(c)

Figure 3 SEM micrographs of PTFE surfaces treated with remote and direct plasma. (a) Original PTFE. (b) Treated with remote hydrogen plasma at 100 W for 120 s. (c) Treated with direct hydrogen plasma at 100 W for 30 s.

 C_{1s} , F_{1s} , and O_{1s} core-level spectra. The F/C atom ratio for the plasma-treated PTFE surface is 1.1, which is lower than that of the original PTFE (1.8), and its O/C atom ratio is 0.09, which is higher than the original PTFE (< 0.03). These changes in atom ratios indicate that defluorination and oxidation occurred in the remote hydrogen plasma treatment process. The reactivity of the defluorination by the remote hydrogen plasma (at 100 W for 120 s) is estimated to be 39% from decreases in the F/C atom ratio.

To analyze chemical composition of the PTFE surface treated by remote hydrogen plasma, the C_{1s} spectrum [Fig. 4(b)] is decomposed into four components that are illustrated in a dotted line in Fig. 4. The four components appear at 285.6, 287.7, 290.0, and 292.5 eV, which are assigned <u>CH</u>₂—CF_n, <u>C</u>HF and O—<u>C</u>H—CF_n, <u>C</u>HF—CF_n and O=<u>C</u>—CF_n, and <u>C</u>F₂ groups, respectively.^{8,9} The underlined carbons in Table II mean objective carbons. The relative concentration of these components was estimated from the relative peak area, and results of the estimation are listed in Table II. The carbons in CH—O and C=O groups in nonfluorinated compounds appear in general at 286.5-286.7 and 287.9-289.0 eV, respectively; but, the binding energy of the corresponding carbons in the fluorinated compounds is shifted to higher level of the binding energy (287.7 and 290.0 eV) by the strong electron-withdrawing effects of fluorine atoms.⁸ Table II shows that 25%of the total CF_2 units in PTFE were defluorinated by remote hydrogen plasma treatment and were modified into CH₂, CHF, CHO, and C(O) groups. The increase from <0.03 to 0.09 in the O/C atom ratio by remote hydrogen plasma treatment means that some oxygen functional groups were formed simultaneously with the defluorination process. These oxygen functional groups may correspond to the components at 287.7 and 290.0 eV, which are assigned O—<u>C</u>H—CF_n, as well as CHF, and $O=\underline{C}-\overline{CF_n}$, as well as $\underline{C}HF-\overline{CF_n}$ groups, respectively. It is explicable that oxygen functional groups, such as $O-\underline{C}H-CF_n$ and $O=\underline{C}-CF_n$ groups, were formed on the PTFE surface treated with remote hydrogen plasma, although oxygen was never used in the plasma treatment process. We can speculate on a mechanism with regard to the formation of these oxidized groups. Hydrogen radicals in remote hydrogen plasma abstract fluorine atoms from PTFE surface to form carbon radicals. Carbon radicals recombine with other hydrogen radicals in the hydrogen plasma to form C-H bonds. This is the defluorination mecha-

	Atom Ratio		Relative Concentration of $\rm C_{1s}$ Components (mol %)				
Sample	F/C	O/C	CH ₂ —CF _n	$\begin{array}{c} \text{CHF} \\ \text{O}\text{CH}_2\text{CF}_n \end{array}$	$\begin{array}{c} CHF - CF_n \\ O = C - CF_n \end{array}$	CF_2	$\begin{array}{c} F_{1s} \ Spectrum \\ (eV) \end{array}$
Original PTFE	1.8	< 0.03				100	690.0
PTFE treated with remote hydrogen plasma at 100 W for 120 s	1.1	0.09	9	8	8	75	689.7

Table II Chemical Composition of PTFE Surface Treated with Remote Hydrogen Plasma

nism by remote hydrogen plasma. However, all carbon radicals that are formed by hydrogen abstraction do not recombine with hydrogen radicals; but, a part of the carbon radicals remains on the PTFE surface even after finishing remote hydrogen plasma treatment. The remaining radicals react with oxygen and water in air to form peroxide groups as soon as the PTFE sheet is taken out from the plasma reactor; then, peroxide groups are modified into oxygen functional groups, such as hydroxyl and carbonyl groups. This is a mechanism of the formation of oxygen functional groups.

From these results, we conclude that remote hydrogen plasma treatment causes defluorination and oxidation of the PTFE surface. Reactivity of defluorination is 25% (estimated from concentration of the CF_2 component) to 39% (estimated from the F/C atom ratio). Oxidation of carbon



Figure 4 C_{1s} and F_{1s} spectra of the PTFE surface treated with remote hydrogen plasma at 100 W for 120 s. (a) Original PTFE. (b) Treated with remote hydrogen plasma at 100 W for 120 s.

radicals forms oxygen functional groups, such as C—O and C—O groups. Oxidation may be due to postreactions of the plasma treatment process. We expect that these oxygen functional groups would act as sites that catch the colloidal palladium catalysts and copper metallization would have success.

Copper Metallization of the PTFE Surface by Copper Electrolessplating

Effects of surface modification by remote hydrogen plasma on adhesion between the PTFE sheet and copper metal layer were investigated using T-type peel strength. First, the PTFE sheets used for metallization were treated with remote hydrogen plasma at 100 W for 120 s; then, on the PTFE surfaces, a copper metal layer (0.2 μ m thickness) was deposited by electrolessplating. Furthermore, a copper metal layer (30 μ m thickness) was deposited by electroplating. Table III shows the peel strength for adhesive joint between the plasma-treated PTFE sheet and copper metal layer. Peel strength for the adhesive joint between the original PTFE sheet and copper metal layer is 7.5 mN/5 mm. The copper metal layer deposited on the original PTFE surface is easily peeled off by rubbing with the fingers. On the other hand, peel strength for the adhesive joint between the plasma-treated PTFE sheet and copper metal layer is increased by increasing the plasma treatment time, and reaches a maximum of 92 mN/5 mm at a plasma treatment time of 120 s, which is higher by ~ 12 times that for the original PTFE sheet. Longer plasma treatment than 120 s, as shown in Table III, disturbs the adhesion, and peel strength falls down from 81 to 69 mN/5 mm.

Wang and colleagues³ reported ion irradiation effects on the adhesion between the PTFE sheet and copper metal. The T-type peel strength was

Kind of Plasma	Plasma Treatment Time (s)	Peel Strength of Plasma-Treated PTFE/Copper Metal Adhesive Joint (mN/5 mm)
Untreated		7.5 ± 0.3
Remote hydrogen plasma	10	36 ± 3.7
	60	62 ± 4.1
	90	75 ± 2.9
	120	92 ± 7.0
	150	81 ± 3.1
	300	69 ± 8.9

Table IIIPeel Strength for Adhesive Joint between Hydrogen Plasma-Treated PTFE andCopper Metal

improved from 3 g mm⁻¹ to 30 g mm⁻¹ (which corresponded to 14.7 mN/5 mm) by the Bi²⁴⁺ ion irradiation. A combination of the Bi²⁴⁺ ion irradiation and heat treatment at 250°C led to further improvement in the peel strength by a factor of 1.5 (\sim 22 mN/5 mm). By comparing Wang's results with our results (the maximum peel strength is 92 mN/5 mm), it is obvious that the remote hydrogen plasma treatment is superior as a pretreatment process to the Bi²⁴⁺ ion irradiation and the combination of Bi²⁴⁺ ion irradiation and heat treatment.

To investigate where the failure of the adhesive joint occurred, the surfaces of failed parts were observed using SEM and XPS. Figure 5 shows typical SEM pictures of two layers (PTFE polymer and copper metal sides) peeled-off from adhesive joints. The PTFE polymer layer peeled-off from the original PTFE/copper adhesive joint, as shown in Figure 5, shows a different surface from that of the copper metal layer. The surface shows micropores similar to the original PTFE, and many fibrils that might be formed by stretching the PTFE polymer. The copper metal layer shows a complicated surface with many parallel lines and particles of $\sim 1 \ \mu m$ diameter. Parallel lines appearing on the copper metal surface may be a molded copy of the PTFE surface. The original PTFE surface also shows similar parallel lines that may be formed in the perpendicular direction against the rolling direction by rolling in the PTFE film fabrication process. On the other hand, the PTFE polymer layer peeled-off from the plasma-treated PTFE/copper adhesive joint shows a flat, but pitted, surface. The copper metal layer shows a similar surface to the copper metal layer peeled-off from the original PTFE/copper adhesive joint. On the surface of the copper metal side, many parallel lines and particles of $\sim 1 \ \mu m$ diameter appear. From these SEM pictures, we cannot

conclude confidently where the failure occurred, but we believe that the failure occurred possibly at the interface between the PTFE and copper metal layers.

XPS analyses can answer the question where the failure occurred. Two typical adhesive joints [the original (untreated) PTFE/copper metal adhesive joint and the remote hydrogen, plasmatreated (at 100 W for 120 s) PTFE/copper adhesive joint] were used as the specimens for the XPS analyses. Surfaces peeled-off from the two adhesive joints were analyzed with XPS (Figs. 6 and 7). Peel strength for the PTFE/copper metal adhesive joint is 7.5 mN/5 mm, and that for the remote hydrogen, plasma-treated PTFE/copper adhesive joint is 92 mN/5 mm. Although the two adhesive joints show large differences in peel strength (a factor of 12), the surfaces peeled off from the two adhesive joints show similar XPS spectra. Figures 6 and 7 show XPS (C_{1s} and $Cu_{2p3/2}$) spectra for four layer surfaces peeled-off from two adhesive joints. We call the two layers peeled-off from the adhesive joint "PTFE polymer and copper metal layers." The PTFE polymer layer means the layer based on the PTFE sheet, and the copper metal layer means the layer based on the copper metal film. The PTFE polymer layers peeled-off from PTFE/copper and the plasmatreated PTFE adhesive joints, as shown in Figure 6, show different C_{1s} spectra from the copper metal layers. For the PTFE polymer layer, the peak appears at 292.5 eV, which is assigned to the CF_2 groups. Peak intensity is strong. On the other hand, for the copper metal layers, the C_{1s} spectra distribute widely from 290 to 297 eV, and the peak intensity is weak. The C_{1s} spectra, as illustrated in dotted lines in Figure 6, are decomposed into two components: CF₂ and CF₃ groups.



Figure 5 SEM micrographs of PTFE and copper metal layers peeled-off from PTFE/ copper adhesive joints. (a) Peeled off from the original PTFE/copper adhesive joint. (b) Peeled off from the plasma-treated PTFE/copper adhesive joint.

In the $Cu_{2p3/2}$ spectra, there is no essential difference between the two PTFE polymer layers peeled off from the PTFE/copper and the plasmatreated PTFE adhesive joints; but, there are large differences between the PTFE polymer layer and copper metal layer. The PTFE polymer layers show no $Cu_{2p3/2}$ spectrum, and the copper metal layers show strong $Cu_{2p3/2}$ spectra at 932.2 eV, which is assigned copper oxide.¹⁰

From these comparisons, we summarize that the PTFE polymer layers are different in XPS spectra from the copper metal layers. The PTFE polymer layer surfaces are composed mainly of CF_2 units (PTFE polymer). The copper metal layer surfaces are composed mainly of copper oxide and are soiled with fluorinated carbon compounds. This summary indicates that the failure occurs at the interface between the PTFE and copper metal layers rather than in the inner layer of the PTFE polymer or copper metal layers.

CONCLUSIONS

The PTFE sheet was modified with remote hydrogen plasma, and the effects of modification on adhesion between the PTFE sheet and copper metal were investigated. Results are summarized as follows.

- 1. Remote hydrogen plasma is able to make PTFE surfaces hydrophilic without etching. Direct hydrogen plasma also makes PTFE surfaces hydrophilic, but heavy etching reactions occur.
- 2. In the remote hydrogen plasma treatment process, defluorination and oxidation occur on the PTFE surface. Reactivity of defluorination is 25% (estimated from the concentration of CF_2 component) to 39% (estimated from the F/C atom ratio). Oxidation of carbon radicals forms oxygen functional groups, such as C—O and C=O groups. Oxidation may be due to postreactions of the plasma treatment process.
- Surface modification of PTFE by remote hydrogen plasma contributes to the adhesion between PTFE and copper metal. Peel strength is improved from 7.5 to 92 mN/5 mm by surface modification by a factor of 12.
- 4. Failure of the PTFE/copper adhesive joint occurs at the interface between PTFE and copper metal layers rather than in the inner layer of the PTFE polymer or copper metal layers.



Figure 6 C_{1s} spectra of PTFE and copper (Cu) metal layers peeled off from PTFE/copper adhesive joints. (a) Peeled off from the original PTFE/copper adhesive joint. (b) Peeled off from the plasma-treated PTFE/copper adhesive joint.



Figure 7 $Cu_{2p3/2}$ spectra of PTFE and copper (Cu) metal layers peeled off from PTFE/copper adhesive joints. (a) Peeled off from the original PTFE/copper adhesive joint. (b) Peeled off from the plasma-treated PTFE/copper adhesive joint.

From these results, we conclude that remote hydrogen plasma treatment may be a preferable pretreatment of PTFE surface for the fabrication of PTFE and copper metal composites.

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