# Improved Adhesion Between Kapton Film and Copper Metal by Silane-Coupling Reactions

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**ABSTRACT:** Kapton film, poly[(*N*,*N'*-oxydiphenylene)pyromellitimide], was modified by silane-coupling reactions using 3'(trimethoxysilyl)propoxy-2-hydroxypro-pyl-1,3-diazole (Si-imidazole) to improve the adhesion with copper metal. The Kapton film surface was first treated with argon plasma for 30 s, then dipped into a methanol solution of Si-imidazole (0.01 wt %), followed by heating at 110°C for 90 min. The Kapton surfaces, modified by the argon plasma and Si-imizadole coupling reactions, were analyzed by water contact-angle measurement, atomic force microscopy, and XPS. The Si-imidazole modification showed a large increase in adhesion between the copper metal and the Kapton film. The peel strength of the copper metal/Kapton film joint increased from 0.94 to 2.4 N/5 mm. The failure occurred at the interface between the Si-imidazole and the Kapton film layer. We conclude that the Si-imidazole modification is an effective treatment for improvement of the adhesion between copper metal and Kapton film. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1645–1654, 1999

**Key words:** Kapton film; copper metal; silane-coupling reactions; adhesion; surface modification; peel strength

# INTRODUCTION

Poly[(N,N'-oxydiphenylene)pyromellitimide], which is well known as Kapton (a trade name of E. I. du Pont de Nemours & Co), is used in large quantities as an insulating material in the field of microelectronics technology due to its excellent properties of a low dielectric constant, hightemperature resistance, etc. A practical usage of Kapton in the microelectronics technology is as a flexible printed circuit board (FPC), which is a lamination of Kapton film and copper metal foil. Because of poor adhesion between Kapton film and copper metal, the lamination in the populargrade FPC is done with the assistance of adhesives such as epoxy or polyimide resins.<sup>1</sup> If the adhesion between Kapton film and copper metal can be improved, the direct deposition of copper metal onto the Kapton film surface will be possible for manufacturing FPC without an adhesive. Vacuum evaporation, sputtering, ion plating, electroless plating, etc., will be used for the copper deposition.

Many investigators have undertaken experiments for improvement of the adhesion between Kapton film and copper metal from two viewpoints: One is the synthesis of new polyimides having good adhesion with copper metal. Chen and co-workers<sup>2</sup> and Lee and co-workers,<sup>3</sup> separately, synthesized new polyimides containing imidazole or triazole functional groups in the main chains. Imidazole and triazole functional groups in the polyimides formed a complex with copper atoms, and the adhesion with copper metal was improved effectively. The other viewpoint is

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3'-(trimethoxysilyl)propoxy-2-hydroxypropyl-1,3-diazole (Si-Imidazole)

**Figure 1** Chemical structure of 3'(trimethoxysilyl)-propoxy-2-hydroxypropyl-1,3-diazole (Si-imidazole).

the surface modification of Kapton film to introduce special functional groups onto the film surface. The introduced functional groups have to interact with copper atoms to effect a strong adhesion with copper metal. We chose an imidazole residue as a functional group and plasma graftcopolymerized vinylimidazole onto the Kapton film surface.<sup>4,5</sup> The graft-copolymerized Kapton film made a charge-transfer complex with the copper atoms and showed good adhesion with the copper metal. Recently, Ang and co-workers<sup>6</sup> reported similar modification of Kapton film by the graft copolymerization of vinylimidazole.

Tsuchida et al.<sup>7</sup> reported on a special reagent, 3'(trimethoxysilyl)propoxy-2-hydroxypropyl-1,3diazole, for rust proofing copper metal. The chemical structure of 3'(trimethoxysilyl)propoxy-2hydroxypropyl-1,3-diazole is shown in Figure 1, and, hereafter, the reagent is abbreviated as Siimidazole. Si-imidazole contains imidazole functional groups for the formation of a complex with copper metal and methoxy silvl groups for the formation of siloxane polymers by polycondensation. Therefore, the siloxane polymers are formed on the copper metal surface and adhere strongly to the copper metal surface by complexes between the copper atoms and imidazole functional groups in the polymers. As a result, the siloxane polymers act as an excellent barrier to water vapor and liquid. This is the mechanism of rust proofing by Si-imidazole.

We have been interested in Si-imidazole from the viewpoint of the surface modification of Kapton film. Si-imidazole may be easily attached onto the Kapton film surface if silane-coupling reactions occur on the Kapton film surface. The Si-imidazole-coupled Kapton film will show good adhesion with copper metal. In this study, we investigated the surface modification with Si–imidazole to improve the adhesion between Kapton film and copper metal.

# **EXPERIMENTAL**

## **Materials**

The polyimide film used in this study was poly[(N,N'-oxydiphenylene)pyromellitimide], Kapton<sup>®</sup> 200H (508 mm wide and 50  $\mu$ m thick), which was kindly provided by the Toray du Pont Co. The film was washed with acetone using an ultrasonic washer prior to the plasma treatment experiment. 3'-(Trimethoxysilyl)propoxy-2-hydroxypropyl-1,3-diazole (Si-imidazole) was kindly provided by the Japan Energy Co. and was used without further purification as a reagent for the surface modification by coupling reactions.

#### Surface Modification by Coupling Reactions

The surface modification of the Kapton films by Si-imidazole was carried out in two steps: (1) formation of reactive sites on the Kapton film surface by argon plasma treatment and (2) coupling reactions with Si-imidazole. In the reactivesite formation step, the Kapton film surfaces were exposed to argon plasma for 5-60 s to form carbon radicals on the surfaces and then exposed to air for carbon radicals to be oxidized into oxygen functional groups on the surfaces. The argon plasma was operated at a constant discharge current of 30-80 mA at a pressure of 1.3 Pa. Details of the construction of the plasma reactor used for the plasma treatment and the operational procedures were reported elsewhere.<sup>8</sup> In the couplingreaction step, the plasma-treated Kapton films were dipped into the methanol solution (0.01 wt %) of Si-imidazole at room temperature for 10 min and then were heated in an air oven at 110°C for 90 min to effect the coupling reactions. After the coupling reaction, the Kapton films were washed with methanol using an ultrasonic washer and dried at 50°C under a vacuum.

#### **Copper Metallization of Kapton Film Surface**

The surface of the Si–imidazole-modified Kapton film was modified to become electrically conductive by the vacuum deposition of a copper metal (100 nm thickness) and then was electroplated at a layer of 40- $\mu$ m thickness with copper. The plat-

Argon Plasma Treatment (s)	Before Met	hanol Rinse	After Meth	anol Rinse	Difference Between Before and After Mathanol Binse		
	Advancing Contact Angle of Water (degree)	Receding Contact Angle of Water (degree)	Advancing Contact Angle of Water (degree)	Receding Contact Angle of Water (degree)	Advancing Contact Angle (degree)	Receding Contact Angle (degree)	
0	82	67	82	67	0	0	
10	18	6	56	24	48	18	
20	16	6	52	27	46	21	
60	23	10	64	28	41	14	

Table I Contact Angle on Water on Argon Plasma-Treated Kapton Film Surfaces

ing process was done at a constant dc current density of  $3 \times 10^4$  A/m<sup>2</sup> and at 24°C in a sulfuric acid aqueous solution (90 g/L) containing copper sulfate (0.5*M*), hydrogen chloride (50 ppm), and a glossy reagent (Nippon Rironal, Japan, CLX-A, 5 mL). The plated Kapton film was washed with water and dried at 80°C for 12 h in a vacuum.

# Peel Strength of Adhesive Joint Between Copper Metal and Kapton Film

The T-type peel strength (5 mm wide) of the adhesive joints between the copper metal and the Kapton film was evaluated at a peel rate of 10 mm/min using an Instron-type tensile strength tester (Shimadzu, Japan, AGS100-A). The peel strength was determined from an average of 10 specimens.

# Contact Angle of Water Against Plasma-treated Kapton Film Surfaces

Using the sessile drop method,<sup>9</sup> contact angles of water on the plasma-treated Kapton film surfaces 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 3-4 degrees.

#### **Atomic Force Microscopy**

The argon plasma-treated and the argon plasmatreated and methanol-rinsed Kapton films were scanned with atomic force microscopy (AFM) (Seiko Instrument, Japan, SFA-300) to observe their surface configuration. A triangular-pyramidal silicon nitride tip was used as a probe, and an area of  $2 \times 2$ -µm square was scanned under a probe pressure of  $8.7 \times 10^{-11}$  N/m<sup>2</sup>. An arithmetic mean of the surface roughness  $(R_a)$  was calculated from the roughness profile determined by AFM.

#### X-ray Photoelectron (XPS) Spectroscopy

XPS spectra of the argon and oxygen plasmatreated Kapton films were obtained on a Shimadzu (Japan) ESCA K1 using a nonmonochromatic  $MgK_{\alpha}$  photon source. The anode voltage was 12 kV; the anode current, 20 mA; and the background pressure in the analytical chamber,  $1.5 \times 10^{-6}$  Pa. The size of the X-ray spot was 2 mm $\Phi$ , and the take-off angle of the photoelectrons was 90° with respect to the sample surface. A smoothing procedure of the spectra was not done. The C1s, N1s, O1s, and Cu2p spectra were decomposed by fitting a Gasussian–Lorentzian mixture function (80 : 20 mixture ratio) to an experimental curve using a nonlinear, least-squares curvefitting program, ESCAPAC, supplied by Shimadzu. The binding energy was corrected by referring the lowest binding energy component to 285.0 eV for eliminating a charge effect. The sensitivity factors (S) for the core levels were S(C1s)= 1.00, S(N1s) = 1.77, S(O1s) = 2.85, and S(Cu2p3/2) = 15.87.

# **RESULTS AND DISCUSSION**

# Surface Modification by Combination of Plasma Treatment and Silane-Coupling Reactions

For execution of successful coupling reactions with Si-imidazole, the Kapton film surface was modified by an argon plasma treatment to become wettable and to form oxygen functional groups, which could immobilize Si-imidazole on its film surface through silane-coupling reactions. Table I shows the advancing and receding water contact angles on the plasma-treated Kapton surfaces as a function of the argon plasma treatment time. The argon plasma treatment for such a short time of 10 s gave a large decrease in the advancing and receding water contact angles from 82° to 18° and from 67° to 6°, respectively. Other plasma treatments for a longer time of up to 60 s also showed small advancing  $(16^\circ-23^\circ)$  and receding water contact angles  $(6^\circ-10^\circ)$ . From these results, there is no doubt that the argon plasma treatment could modify the Kapton film surface from water-repellent to wettable.

Although the Kapton film surface, just after finishing the argon plasma treatment, was wettable, the surface lost wettability once the surface was rinsed with methanol. Table I compares the advancing and the receding water contact angles on the argon plasma-treated Kapton film surfaces before and after the methanol rinse. For the Kapton film plasma-treated for 10 s, as shown in Table I, the advancing and receding contact angles increased from 18° to 56° and from 6° to 24°, respectively, after the methanol rinse. For other plasma-treated Kapton films also, large increases in the advancing  $(41^\circ - 48^\circ)$  and receding contact angles (14°-21°) occurred. These increases indicate that the wettability was decreased by the methanol rinse. There are two possible mechanisms to interpret the wettability decrease: One is the removal of hydrophilic groups from the surface by the methanol rinsing, and the other is the modification of hydrophilic groups into hydrophobic groups by reactions with methanol. The removal of hydrophilic groups from the surface rather than the modification of hydrophilic groups into hydrophobic groups may be a reliable mechanism, because of less reactivity of hydrophilic groups such as carbonyl and ether groups against methanol. We infer a mechanism for the wettability decrease as follows: The argon plasma treatment formed hydrophilic groups on the Kapton film surface and, at the same time, initiated degradation reactions of Kapton polymers on the surface to yield hydrophilic fragments from the Kapton polymers on the surface. The hydrophilic fragments were removed from the surface by the methanol rinse, and as a result, the wettability decreased.

There appeared a large hysteresis in the water contact angle on the methanol-rinsed Kapton film surfaces (Table I). For the argon plasma-treated and methanol-rinsed Kapton film surfaces, the

difference between the advancing and the receding contact angles was 25°-37°. Meanwhile, for the argon plasma-treated Kapton film surfaces without the methanol rinse, the difference was 10°-13°. The large hysteresis in the contact angle indicates some changes in the surface properties such as surface configuration (surface roughness) and the mobility of functional groups. Figure 2 shows AFM pictures of three Kapton films: the untreated Kapton film, the Argon plasma-treated (at a discharge current of 60 mA for 30 s) Kapton film, and the Argon plasma-treated and successively methanol-rinsed film. From the AFM pictures, the surface roughness  $(R_a \text{ in nm})$  was estimated and is listed in Table II. The  $R_a$  value was 0.4 nm for the untreated Kapton film, 0.6 nm for the argon plasma-treated Kapton film, and 0.4 nm for the argon plasma-treated and methanolrinsed film. This comparison indicates that the difference in  $R_a$  among the three film surfaces is as small as the experimental error (0.2-0.3 nm). Accordingly, the argon plasma treatment led to no change in the configuration of the Kapton film surface, although degradation reactions occurred on the surface. Therefore, a configuration change of the Kapton surface is not a main factor of the increased hysteresis, but may be due to the mobility of functional groups. However, we do not yet have reliable experimental evidence to interpret a mechanism for the increased hysteresis.

The argon plasma-treated and successively methanol-rinsed Kapton film surfaces were analyzed with XPS to characterize the modification by the argon plasma. Specimens used for the XPS analyses were Kapton films treated with the argon plasma at a discharge current of 60 mA for 30 s and rinsed with methanol. Table III compares the argon plasma-treated and the untreated Kapton films in O/C and N/C atom ratios. For the untreated Kapton film, the O/C and N/C atom ratios were 0.19 and 0.10, respectively, which correspond to those calculated from the repeating unit of the Kapton polymer (the O/C atom ratio is 0.23 and the N/C atom ratio 0.09). The argon plasma-treated and methanol-rinsed Kapton film showed large changes in the O/C and N/C atom ratios: The O/C atom ratio increased from 0.19 to 0.31, and the N/C atom ratio increased from 0.10 to 0.14. Such a high O/C atom ratio indicates that the argon plasma-treated Kapton film surface contains many oxygen groups even after the methanol rinse. Oxygen groups on the Kapton film surface might be formed by post-



Untreated Kapton film Ra = 0.4 nm

Ar plasma-treated Kapton film Ra = 0.6 nm



Ar plasma-treated and methanol-rinsed Kapton film Ra = 0.4 nm

Figure 2 AFM pictures of argon plasma-treated, argon plasma-treated, and methanol-rinsed Kapton films.

reactions of carbon radicals with oxygen in air after finishing the argon plasma treatment.

Figure 3 shows C1s, O1s, and N1s spectra for the argon plasma-treated Kapton film. The C1s spectrum for the untreated Kapton film was composed of five components due to CH, CH-N and <u>CH</u>—C(O), <u>C</u>—O, and <u>C</u>(O) groups and a  $\pi$ – $\pi^*$ shake-up satellite whose peaks appeared at 285.0, 286.0, 286.8, 289.0, and 291.5 eV, respectively.<sup>10</sup> Here, the underlined carbons are objec-

Table II	Surface	Roughness	of Argon
Plasma-T	reated K	apton Film	s

Argon Plasma Treatment	Methanol Rinse	Surface Roughness $(R_a)$ (nm)			
No	No	0.4			
Yes	No	0.6			
Yes	Yes	0.4			

Ar Plasma Treatment	Coupling Reaction	Atom Ratio		C1s Component (%)				O1s Component (%)			
		O/C	N/C	Si/C	СН	C—N CH—C(O)	С—О	C=0	0=C	0—Si	0—Si
No	No	0.19	0.10	0.00	46	30	9	15	75		25
Yes	No	0.31	0.14	0.00	54	18	7	21	63		37
Yes	Yes	0.27	0.13	< 0.03	44	33	7	16	52	27	21
Yes											
(O2)	No	0.29	0.13	0.00	52	18	9	21	60		40
Yes											
(O2)	Yes	0.30	0.11	0.05	44	29	11	16	50	26	24

Table III XPS Spectra of Argon Plasma-Treated and Si-Imidazole-Coupled Kapton Film Surfaces

tive atoms. The relative concentration of the former four components was estimated from the relative peak area to be 46, 30, 9, and 15%, respectively. Their estimated concentration corresponds well to the concentration calculated from the repeating unit of the Kapton film. The calculated concentration is 45.5% (CH groups), 27.2% [C-N and CH-C(O) groups], 9.1% (C-O groups), and 18.2% [C(O) groups], respectively. The O1s spectrum for the untreated Kapton film was composed of two components due to O=C (at 532.5 eV) and O—C groups (at 534.0 eV)<sup>10</sup> whose concentrations were 75 and 25%, respectively. The N1s spectrum was composed of a simple component at 400.9 eV with a small full width at half-maximum (fwhm) of 1.4 eV. On the other hand, the argon plasma-treated Kapton film, as seen in Figure 3, showed a similar C1s spectrum which was composed of five components [CH, C—N and CH—C(O), C—O, and C(O) groups and a  $\pi - \pi^*$  shake-up satellite) whose concentration

was 54% (CH groups), 18% [CH-N and CH-C(O) groups], 7% (C-O groups), and 21% (C=O groups). The concentration of the C-N and CH-C(O) groups were decreased by the argon plasma treatment, and that of the C(O) groups increased. The O1s spectrum contained two components due to O=C (63%) and O-C (37%) groups. The concentration of the O=C groups was decreased by the argon plasma treatment, and that of the O-C groups increased. On the N1s spectrum, there was no change by the argon plasma treatment. The N1s spectrum for the argon plasma-treated Kapton film appeared at 400.6 eV with a small fwhm of 1.6 eV. From the XPS results, we conclude that the argon plasma treatment formed oxygen functional groups such as hydroxyl and carbonyl groups on the Kapton film surface.

Subsequently, the argon plasma-treated Kapton film surface was modified by silane-coupling reactions with Si–imidazole to introduce imidazole groups onto the film surface. The modified film



Figure 3 XPS (C1s, N1s, and O1s) spectra of argon plasma-treated Kapton film.



**Figure 4** (a) XPS (C1s and N1s) spectra of Si-imidazole-modified Kapton film. (b) XPS (O1s and Si2p) spectra of Si-imidazole-modified Kapton film.

was analyzed with XPS (C1s, N1s, O1s, and Si2p) to make certain successful coupling reactions. The specimen used for the XPS analysis was the Kapton film that was treated with the argon plasma at a discharge current of 60 mA for 30 s and then reacted with Si-imidazole at 110°C for 90 min. Finally, the Kapton film was rinsed with methanol and dried under a vacuum. C1s, N1s, O1s, and Si2p spectra for the modified Kapton film are shown in Figure 4(a,b). For the sake of comparison, Figure 4(a,b) contains the duplication of the C1s, N1s, and O1s spectra for the argon plasma-treated Kapton. The C1s and O1s spectra were decomposed into five to three components, and the decomposed components are tabulated in Table III. The Si-imidazole-modified Kapton film showed large differences in the C1s, O1s, and Si2p spectra from the argon plasma-treated Kapton film. First, a Si2*p* spectrum appeared, but the spectrum intensity was weak. Second, the relative concentration of the CH component on the C1s spectrum decreased by the Si-imidazole modification, and that of the C—N and CH—C(O)component increased. Third, a new component due to O—Si groups (at 533.1 eV) appeared on the O1s spectrum. These differences indicate that silane-coupling reactions may have occurred on the argon plasma-treated Kapton film surface. If the silane-coupling reactions occurred, there must be some change in the N1s spectrum. However, the N1s spectrum did not show reliable evidence that imidazole groups were incorporated onto the Kapton film surface. This may be due to less difference in the chemical shift between nitrogen atoms in the imidazole groups in Si-imidazole and imino groups in the Kapton. The N1s spectrum for the Si-imidazole-modified Kapton film appeared at 400.7 eV with an fwhm of 1.5 eV, and that for the argon plasma-treated Kapton film appeared at 400.6 eV with an fwhm of 1.6 eV. From these results, we conclude that the Kapton film surface may have been modified with Si-imidazole and imidazole groups may have been incorporated onto the Kapton film surface.

# Copper Metallization of Kapton Film Surface and Adhesion Between Copper Metal and Kapton Film

On the argon plasma-treated and successively Siimidazole-modified Kapton film surfaces, a copper metal layer (40.1- $\mu$ m thickness) was deposited by a combination of vacuum deposition (100-nm thickness) and electroplating (40- $\mu$ m thickness). To discuss whether the Si-imidazole modification was effective in improving the adhesion between the copper metal and the Kapton film, factors



**Figure 5** Influence of Si–imidazole concentration in silane-coupling reaction on peel strength of copper metal/Kapton film joint.



**Figure 6** Effects of argon plasma-treatment time on peel strength of copper metal/Kapton film joint.

related to the Si-imidazole modification process, that is, the Si-imidazole concentration in the silane-coupling reaction process, and the treatment time and the discharge current in the argon plasma-treatment process were investigated. Figure 5 shows the peel strength (in N/5-mm width) of the copper metal/Kapton film joints as a function of the Si-imidazole concentration (in methanol solution) in the silane-coupling process. The peel strength, as shown in Figure 5, increased from 0.94 N/5 mm (for the untreated Kapton film) to 2.1 N/5 mm by the Si-imidazole modification. A constant peel strength of 2.1 N/5 mm continued in the ranges of the Si-imidazole concentration from 0.01 to 10 wt %. Therefore, the peel strength was independent of the Si-imidazole concentration within 0.01-10 wt %. Hereafter, we used a Siimidazole concentration of 0.01 wt % for the silane-coupling reaction process. Figure 6 shows the peel strength of the copper metal/Kapton film joints as a function of the argon plasma-treatment time. The peel strength increased with increasing the treatment time and reached a maximum (2.4 N/5 mm) at a treatment time of 30 s. Finally, the effects of the discharge current on the peel strength were investigated. Figure 7 shows the peel strength of the copper metal/Kapton film joints as a function of the discharge current. The peel strength increased with increasing the discharge current and reached a maximum (2.4 N/5 mm) at 60 mA and, afterward, decreased.

From these results, we conclude that the Siimidazole modification is able to improve the adhesion between the copper metal and Kapton film. The peel strength of the copper metal/Kapton film joints increased from 0.94 to 2.4 N/5 mm (2.5 times higher).

We believe that imidazole groups incorporated by the Si-imidazole modification may have contributed to the adhesion of the copper metal/Kapton film joints. Oxygen functional groups, which were formed by the argon plasma treatment on the Kapton film surface, may play an important role in the incorporation of imidazole groups onto the surface. If an oxygen plasma, instead of the argon plasma, is used for the formation of oxygen functional groups, how will the oxygen plasma treatment improve the adhesion? The Kapton films were treated with oxygen plasmas at a discharge current of 10-70 mA for 30 s and modified with the Si-imidazole. Figure 7 shows the peel strength of the copper metal/oxygen plasmatreated Kapton film joints as a function of the discharge current in the oxygen plasma treatment. The peel strength, as shown in Figure 7, increased monotonously with increasing the discharge current. At a discharge current of 70 mA, the peel strength reached 1.5 N/5 mm, but the peel strength is somewhat lower than that for the argon plasma-treated Kapton film (2.4 N/5 mm). This comparison shows that the argon plasma treatment is more effective as a pretreatment for silane-coupling reactions than is the oxygen plasma treatment. The oxygen plasma treatment may have impaired the Kapton film to form a weak boundary layer near the surface.

We have accomplished the plasma graft copolymerization of vinylimidazole onto the Kapton film surfaces.<sup>5</sup> The plasma graft copolymerization led to large increases in the peel strength (3.4 N/5 mm) of the copper metal/Kapton film joint. As to the adhesion improvement, the plasma graft copolymerization is superior to the Si-imidazole



**Figure 7** Effects of discharge current in argon plasma treatment on peel strength of copper metal/Kapton film joint.



**Figure 8** (a) XPS (C1s, N1s, and O1s) spectra of peeled-off layers from copper metal/Kapton film joint. (b) XPS (Si2p, and Cu2p3/2) spectra of peeled-off layers from copper metal/Kapton film joint.

modification. However, in practical usage, the Siimidazole modification is a convenient process without the intricacy of reactions such as graft copolymerization.

# Analysis of Peeled Layers from Copper Metal/Kapton Film Joints

The Si-imidazole-modified Kapton film, as described in a previous section, showed good adhesion with copper metal. There is no doubt that the Si-imidazole modification contributed to improving the adhesion. How did the Si-imidazole modification improve the adhesion? The question is an essential item in adhesion science. To answer the question, we investigated where the failure occurred when the copper metal/Si-imidazole-modified Kapton film joint was peeled-off. Two layers (polymer and metal layer sides) peeled-off from the copper metal/Si-imidazole-modified Kapton film joint were analyzed by XPS. Figure 8(a,b) shows XPS (C1s, N1s, O1s, Si2p, and Cu2p3/2) spectra for the polymer and metal layer sides peeled-off from the adhesive joint which showed a peel strength of 2.4 N/5 mm. The polymer layer side showed strong and sharp C1s, N1s, and O1s spectra, but no Si2p and Cu2p3/2 spectra. The C1s, N1s, and O1s spectra were similar to those of the untreated Kapton film. Meanwhile, the metal layer side showed strong C1s, O1s, Si2p, and Cu2p3/2 spectra, but a weak N1s spectrum. Therefore, the polymer-layer and metal-layer sides are completely different in chemical composition from each other.

When a sandwich structure composed of A and B layers is peeled-off, three possible failure patterns will occur ideally, that is, the failure within the A or B layer (inner-layer failure) and failure at the interface between the A and B layers (interface failure). If the inner-layer failure occurs, two layers peeled-off from the adhesive joint will show homogeneity in the chemical composition, whereas if the interface failure occurs, two peeled-off layers will show heterogeneity in the chemical composition. Therefore, where the failure occurred can be easily determined from chemical inspection of the peeled-off layers. In practice, the ideal failure never occurs, but complicated failure (combination of inner-layer and interface failures) occurs. From the above viewpoint, chemical analysis of the peeled-off layer surfaces gives reliable information on where the failure occurred. The peeled-off layers (the polymer-layer and metal-layer sides) from the copper metal/ Kapton film joint, as shown in Figure 8(a,b), are completely different in chemical composition from each other. The polymer-side layer shows similar C1s, N1s, and O1s spectra to the original Kapton film, and no Si and Cu atoms appear on the layer surface, whereas the metal-side layer shows different C1s and N1s spectra from the original Kapton film and many Si and Cu atoms appear on the layer surface. This indicates that the failure occurs at an interface rather than within layers in the sandwich structure of the adhesive joint. The interface may be between the Si-imidazole and Kapton film layers. This suggests that the bonding between Si-imidazole and the Kapton film surface may not be strong enough to adhere copper metal to Kapton film surface. To obtain larger peel strength, the Si-imidazole and the Kapton film surface must be bonded as tightly as the Si-imidazole or Kapton film layer itself is broken down.

#### CONCLUSIONS

The Kapton film was modified by silane-coupling reactions using Si-imidazole to improve the adhesion with copper metal. The Kapton film surface was first treated with argon plasma for 30 s, dipped into a methanol solution of Siimidazole (0.01 wt %), and heated at 110°C for 90 min. The Si-imidazole modification showed a large increase in adhesion between copper metal and the Kapton film. The peel strength of the copper metal/Kapton film joint increased from 0.94 to 2.4 N/5 mm. The failure occurred at the interface between Si-imidazole and the Kapton film layer. We conclude that the Siimidazole modification is an effective treatment for improvement of the adhesion between copper metal and the Kapton film.

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