

# Improved Adhesion Property and Electromagnetic Interference Shielding Effectiveness of Electroless Cu-Plated Layer on Poly(ethylene terephthalate) by Plasma Treatment

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Received 10 February 2001; accepted 29 July 2001

**ABSTRACT:** To develop high-quality electromagnetic interference (EMI) shielding materials, the effect of plasma pretreatment with various gases prior to Cu plating was investigated. Plasma treatment increased the surface roughness in the decreasing order of Ar > O<sub>2</sub> > NH<sub>3</sub>, but adhesion of the Cu layer on poly(ethylene terephthalate) (PET) film increased in the following order of O<sub>2</sub> < Ar < NH<sub>3</sub>, indicating that the appropriate surface roughness and introduction of an affinitive functional group to Pd on the surface of the PET film were key factors for improving adhesion of the Cu layer. As investigated by XPS analysis, plasma treatment with NH<sub>3</sub> produced N atoms on the PET film, which enhances the chemisorption of Pd<sup>2+</sup> on PET film, resulting in improved adhesion and shielding effectiveness of the Cu layer deposited on the Pd-catalyzed surface, because of the high affinity of Pd<sup>2+</sup> for nitrogen. Comparatively, O<sub>2</sub> plasma treatment allowed the chemisorption of more Sn<sup>2+</sup> than of Pd<sup>2+</sup> due to a lack in the affinity of Pd<sup>2+</sup> for oxygen, resulting in the lowest Pd<sub>3d</sub>/Sn<sub>3d</sub> ratio; thereby, the lowest EMI-shielding effectiveness (SE) value was obtained. In addition, fairly low adhesion was obtained with Ar plasma-treated PET, even though the PET surface was significantly etched with Ar plasma, due to introduced oxygen groups on the PET surface. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1369–1379, 2002; DOI 10.1002/app.10272

**Key words:** adhesion; poly(ethylene terephthalate); plasma treatment

## INTRODUCTION

Recently, the metallization of polymer materials has attracted more and more attention. Many polymer films, fibers, and plastics are metallized for extensive applications in food packaging, mi-

croelectronics, computer technology, and the automotive industry to provide an electromagnetic shielding property.<sup>1–6</sup> Metal foil and laminates, conductive paints and lacquers, sputter-coating, vacuum deposition, flame and arc spraying, and electroless metal plating are recently developed metal-coating techniques. Among them, electroless metal plating is probably a preferred way to produce metal-coated materials. Because electroless plating has advantages in terms of coherent metal deposition, excellent conductivity and shielding effectiveness, and applicability to com-

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Contract grant sponsor: Korea Research Foundation; Contract grant number: KRF-99-041-D00480.

*Journal of Applied Polymer Science*, Vol. 84, 1369–1379 (2002)  
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plicated-shaped materials or nonconductors, it can be applied to almost all polymer substrates.<sup>1,2</sup>

The electroless plating process has been ascribed to occur due to a combination of partial electrode oxidation and reduction processes. The driving forces for these reactions arise from the potential difference that exists between the metal-solution interface and the equilibrium electrode potential for these (cathodic and anodic) half-reactions. In a typical non-electromagnetic deposition system, copper reduction and formaldehyde oxidation are the cathodic and anodic reactions, respectively. This deposition will continue to occur as long as a positive driving force exists for both of these reactions, and the rate of the reaction will decrease by the reduction of these two reactions.<sup>7</sup>

A number of studies have taken into account the mechanism and kinetics of electroless Cu plating on various substrates, determining the quality of the deposited Cu layer and the plating rate as a function of various solution components and conditions.<sup>1,2,5-10</sup> Generally, plating is initiated upon the catalyzed surface, and the plating reaction is sustained by the catalytic nature of the plated metal surface itself, so that understanding and improving the electromagnetic interference (EMI) shielding effectiveness (SE) and adhesion at metal/polymer interfaces are recognized to be of prime technological importance.

Since the surface activity of the polymer substrate is generally low with metals, to enhance the adhesion, the polymer surface must be formed of a suitable irregularity for a mechanical anchorage between the catalyst and polymer surface and the introduced functional groups for an affinity with the catalyst.<sup>3,11</sup> In this research, therefore, plasma surface treatment was applied on the PET film to improve the surface adhesion and to increase the amount of the chemisorbed catalyst, thereby increasing the EMI-SE and the adhesion of the metal layer.<sup>12</sup> Many authors<sup>13-16</sup> have shown that low-temperature reactive gas-plasma treatment is highly efficient for increasing the surface energy and reactivity without altering the substrate bulk properties. Among various gases, oxygen, argon, and ammonia gases were used on the PET film to improve the adhesion and deposition of catalyst in this study. Surface characteristics of the plasma-treated PET films were analyzed by X-ray photoelectron spectroscopy. The effects of plasma pretreatment and the catalyza-tion condition on the EMI-SE and adhesion prop-

erties of electroless Cu-plated PET film were investigated to obtain high-quality EMI shielding materials.

## EXPERIMENTAL

### Materials

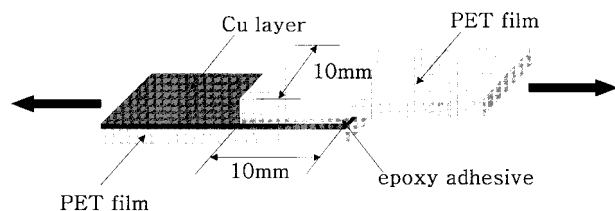
PET film of 100  $\mu\text{m}$  thickness, obtained from the SKC Co., was used as a polymer substrate. Oxygen, ammonia, and argon gases were used for the plasma treatment of the PET film. For surface catalyza-tion, tin(II) chloride ( $\text{SnCl}_2$ , Junsei Chemical Co.) and palladium(II) chloride ( $\text{PdCl}_2$ , Kojima Chemical Co.) were used as a catalyst and a catalyst activator, respectively. The bath pH was adjusted with NaOH. The mixture solution of cupric sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), Rochelle salt [potassium sodium tartrate,  $\text{KOOCC}(\text{OH})\text{CH}(\text{OH})\text{COONa} \cdot 4\text{H}_2\text{O}$ ], formaldehyde ( $\text{HCOH}$ ), and NaOH was used for the electroless copper plating. The mixture of citric acid [ $\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 \cdot \text{H}_2\text{O}$ ] and sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ) was used as a posttreatment solution.

### Electroless Cu Plating

For even deposition of the Cu layer on the PET film, electroless Cu plating was conducted by multistep processes.<sup>17,18</sup> All processing steps were performed at room temperature. Prior to the surface-etching process (plasma treatment), the PET film was cleaned with ethanol in an ultrasonic washer for 30 min and dried at 60°C. The PET films were then etched by plasma treatment with various gases ( $\text{O}_2$ , Ar, and  $\text{NH}_3$  gases) at different rf power (50, 75, and 100 W) for various treatment times. The plasma-treated PET films were directly dipped in a catalyza-tion solution of pH 12.4 containing  $\text{SnCl}_2$ ,  $\text{PdCl}_2$ , and HCl at room temperature for 10 min. The catalyzed PET films were then rinsed in a large volume of distilled water to prevent the plating bath from being contaminated. The acceleration step was performed to remove  $\text{Sn}^{2+}$  ions over the catalytic Pd nuclei with the HCl solution. They were then immersed in a bath containing the mixture of cupric sulfate, Rochelle salt, formaldehyde, and NaOH. Plated samples were then treated in a posttreatment solution.

### X-ray Photoelectron Spectra Analysis

Surface characteristics of plasma-treated PET films with various gases were analyzed by X-ray



**Figure 1** Scheme of lap-shear sample preparation and testing.

photoelectron spectroscopy (XPS) (SSI 2803). This spectrometer, from VG Microtech Ltd., was equipped with an  $AlK\alpha$  X-ray source. The X-ray source was 12 kV and 20 mA. All core-level spectra were obtained at a photoelectron take-off angle of  $35^\circ$  with respect to the sample surface. To compensate for the surface-changing effect, all binding energies were referenced to the  $C_{1s}$  neutral carbon peak at 285 eV.

XPS spectra for the catalyzed surface with plasma treatment after activation or an acceleration step were obtained on a Kratos AXIS HS spectrometer using a nonmonochromatic  $MgK\alpha$  photon source (1253.6 eV). The X-ray source was 10 kV and 10 mA. All spectra were recorded at a take-off angle of  $25^\circ$  with respect to the sample surface and referenced to the  $C_{1s}$  signal at a binding energy of 285 eV.

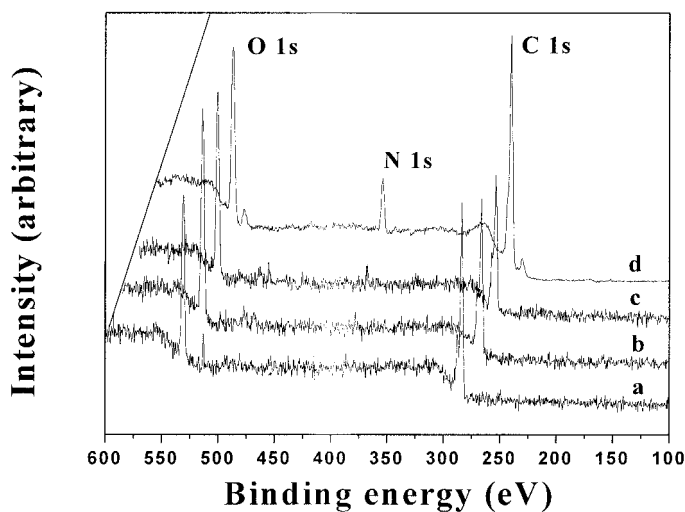
### Surface Morphology and Element Analysis

The effect of etching on plasma-treated PET film with various gases was investigated with

an atomic force microscope (AFM), AP-0109 Model (PSI Co.). All AFM images were examined using the contact mode with the force applied between the tip and the polymer surface. An Ultra lever tip was used in this measurement. The amount of palladium and tin deposits after catalyzation was analyzed quantitatively using an energy dispersive X-ray spectrometer in FE-SEM.

### Lap-shear Test

For measuring the adhesion between the Cu layer and the PET film, modified lap-shear samples were prepared by following ASTM F 1044. The preparation and testing method of the lap-shear sample are schemed in Figure 1. The epoxy adhesive was applied between the Cu layer and the upper PET film as a supporter. The epoxy was degassed for 3 min and cured for 48 h at room temperature since the epoxy adhesive was a room-temperature curing-type commercial adhesive, Araldite manufactured by Ciba. Fracture from the applied force only could happen at the interface of the Cu layer and the PET base film. Adhesion of the Cu layer at the PET base film is much lower than that of epoxy and the upper PET film. Using an Instron Model No 4465, the lap-shear strength of the prepared samples were measured at a crosshead speed of 30 mm/min and determined from an average of five measurements.



**Figure 2** XPS survey spectra of control and plasma-treated PET films at rf power of 75 W for 20 min with various gases: (a) control; (b)  $O_2$ ; (c) Ar; (d)  $NH_3$ .

**Table I Atomic Composition Ratio of Control and Plasma-Treated PET Film Surfaces**

Treatment	C <sub>1s</sub>	N <sub>1s</sub>	O <sub>1s</sub>	N <sub>1s</sub> /C <sub>1s</sub>	O <sub>1s</sub> /C <sub>1s</sub>
Control	75.0	0	25.0	0	0.33
O <sub>2</sub> plasma	66.3	0	33.7	0	0.51
Ar plasma	65.2	4.9	30.0	0.07	0.46
NH <sub>3</sub> plasma	70.0	9.0	20.9	0.13	0.30

### EMI-SE

The EMI-SE of electroless Cu-plated PET film was evaluated with an impedance analyzer (HP4291A, Hewlett Packard Co.). SE was estimated by calculating the reflection loss with the ratio of wave impedance (377Ω in the air) to the characteristic impedance of the material at a wide range of frequency levels between 100 MHz and 1 GHz.<sup>19,20</sup>

## RESULTS AND DISCUSSION

### Characteristics of Plasma-treated PET Films

Organic polymer films have so low an affinity with metals that they have to be treated by either chemical or mechanical etching, which increased the interface area and, simultaneously, chemical activation improved. These steps may change the topography and/or surface chemistry of the substrate significantly. In previous studies,<sup>17,21</sup> we found that the acid mixture of HCl and HNO<sub>3</sub> solutions was a better etching medium than were other chemical baths for PET. However, the wet pretreatment process requires additional rinsing and drying steps, using more water, energy, and time consumption. Therefore, in this study, we tried to determine the feasibility of using plasma to replace this chemical-etching process.

Plasma treatment is a useful way to modify the surface of a polymer to improve the adhesion of electroless-plated metals, with the surface properties of plasma-treated PET highly dependent on the selection of treatment gases.<sup>12</sup> After selecting the type of treatment gases, oxygen, ammonia, and argon, plasma surface treatments were performed on the PET films.

XPS spectra of an ethanol degreased control PET film and plasma-treated PET film with O<sub>2</sub>, Ar, and NH<sub>3</sub> are shown in Figure 2. Atomic composition ratios of nitrogen or oxygen to carbon, which were obtained from the plasma-treated

PET surface, were calculated from the XPS data and are presented in Table I.

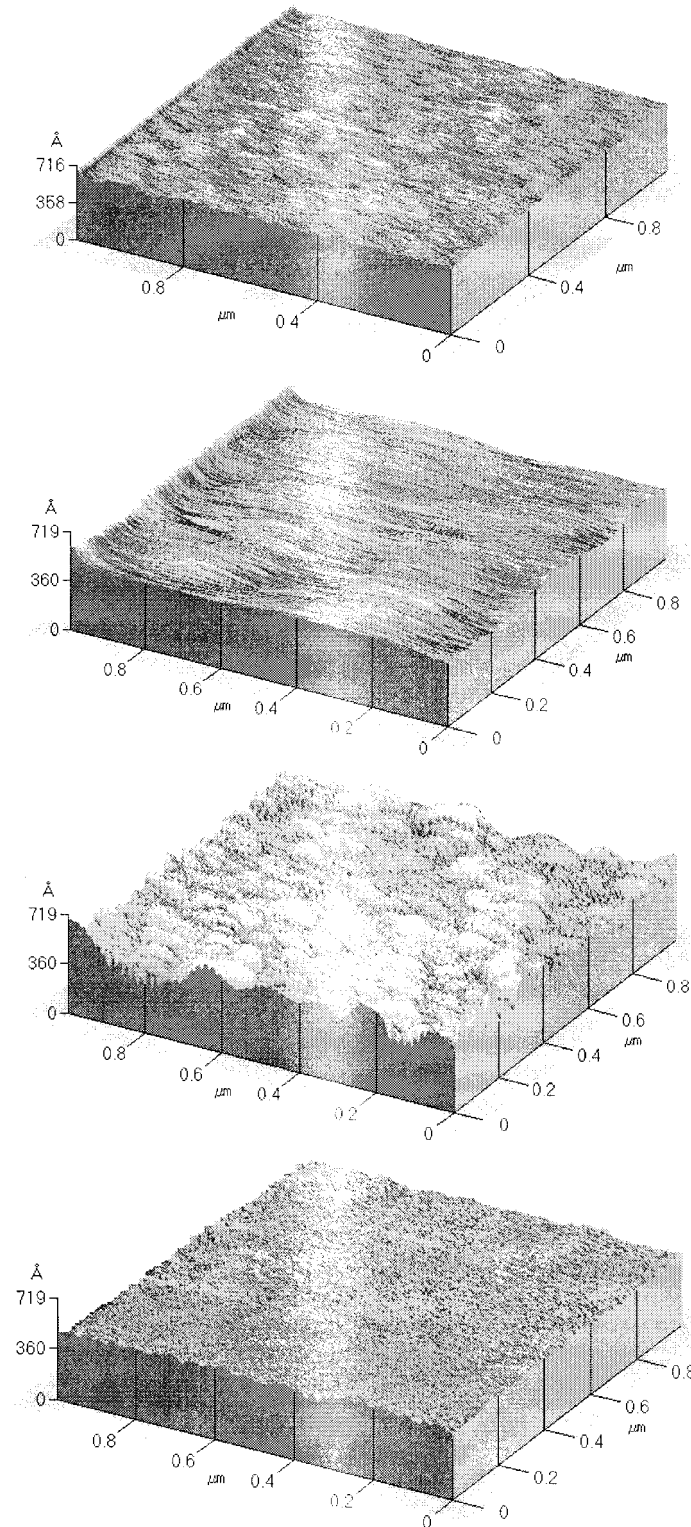
The fiber surface treated by NH<sub>3</sub> plasma had more nitrogen species, whose relative N<sub>1s</sub>/C<sub>1s</sub> core-level intensity was 0.13. This value is much higher than those of the control and O<sub>2</sub> plasma-treated PET. On the other hand, more oxygen species were introduced onto PET surface by both O<sub>2</sub> and Ar plasma treatments. The relative O<sub>1s</sub>/C<sub>1s</sub> core-level intensity of the control film was 0.33, and those of O<sub>2</sub> and Ar plasma-treated PET film were 0.51 and 0.46, respectively. Similar to the NH<sub>3</sub> plasma-treated PET film, the relative N<sub>1s</sub>/C<sub>1s</sub> core level was slightly increased to 0.07 with the Ar plasma treatment, whereas no nitrogen was found in O<sub>2</sub> plasma-treated PET.

Changes in the surface morphology and roughness of the control and plasma-treated PET film with various gases were more accurately observed by AFM as shown in Figure 3. Surface roughness data were calculated from AFM images and are presented in Figure 4. RMS roughness data indicated that plasma treatment increased the surface roughness in the decreasing order of Ar > O<sub>2</sub> > NH<sub>3</sub>. The roughness of the PET film treated by Ar plasma was increased about four times greater than that of the control film.

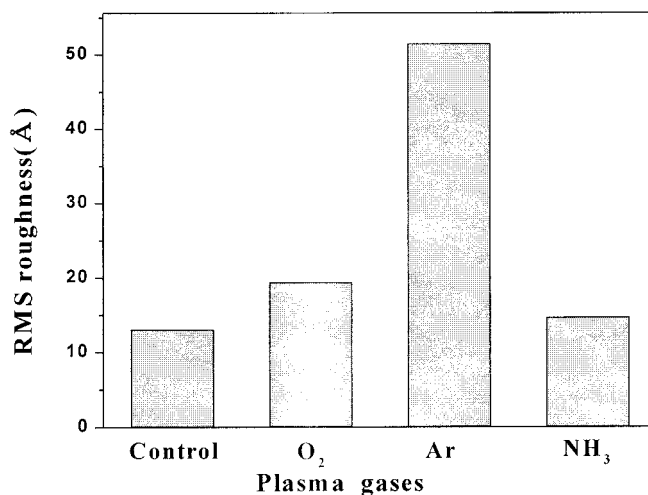
### Effect of Plasma Treatment on Cu Adhesion and EMI-SE

Surface roughness brings about an increase in adhesion corresponding to mechanical anchorage. Moreover, the introduction onto the polymer surface of the functionality was found to give a marked improvement in adsorption and adhesion.<sup>22</sup> Accordingly, the effects of various plasma-treatment conditions on the adhesion and EMI-SE properties of electroless Cu-plated PET film were investigated.

Electroless Cu plating was performed on the PET films which had been plasma-treated at 75 W for 20 min with various gases and catalyzed at



**Figure 3** AFM images of PET films prepared by various etching conditions: (a) control; (b) O<sub>2</sub> plasma; (c) Ar plasma; (d) NH<sub>3</sub> plasma.

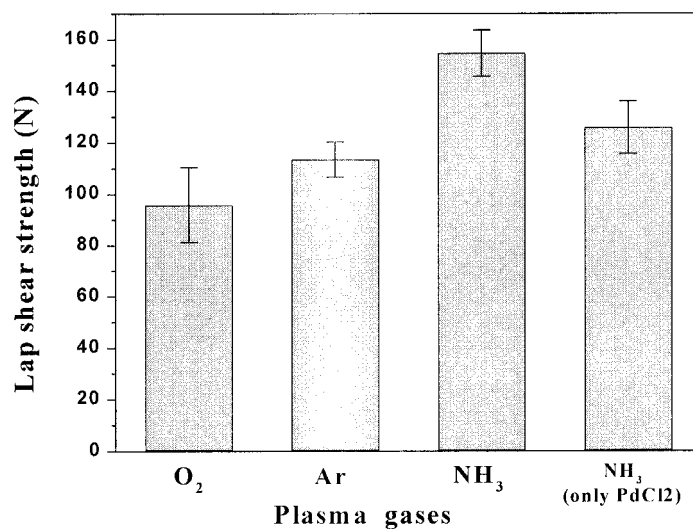


**Figure 4** RMS roughness of control and plasma-treated PET film as a function of various plasma gases.

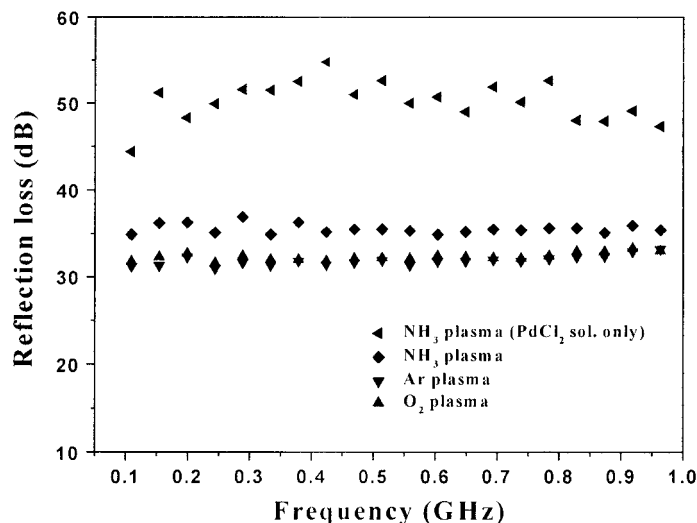
a 1 : 16 molar ratio of a PdCl<sub>2</sub>/SnCl<sub>2</sub> mixed solution. The adhesion of the deposited Cu layer on the PET film was evaluated by its lap-shear strength as shown in Figure 5. As a result, in spite of the low surface roughness of the NH<sub>3</sub> plasma-treated PET film as compared with the others, the adhesion strength of the deposited Cu layer was the highest. It is probably because the introduced N atoms on the PET film by NH<sub>3</sub> plasma treatment enhances the direct chemisorption of Pd<sup>2+</sup> on the PET surface. Since nitrogen atoms give their electron pair to Pd<sup>2+</sup> and form a

polar bond, it is possible to improve the adhesion of Pd. Thereby, the adhesion of the Cu layer on the Pd-catalyzed surface can also be increased.<sup>23</sup>

On the other hand, the lap-shear strength of the oxygen plasma-treated PET is the lowest, which might be because the introduced oxygen disturbed the direct deposition of the Pd<sup>2+</sup> ion. Charbonnier et al.<sup>23</sup> proposed that Sn<sup>2+</sup> ions fix selectively onto oxygen atoms because of their strong electronegativity and form a polar bond; then, Pd<sup>2+</sup> ions can be chemisorbed onto Sn<sup>2+</sup> ions through Cl<sup>-</sup> ions. Accordingly, adhesion of



**Figure 5** Lap-shear strength of copper-plated PET film as a function of plasma-treatment gases.



**Figure 6** Effect of plasma surface treatment on reflection loss of PET film; rf power of 75 W for 20 min with 1 : 16 molar ratio of PdCl<sub>2</sub> : SnCl<sub>2</sub> catalyst.

Pd<sup>2+</sup> ions to the substrate is very low, resulting in that the adhesion strength of Cu deposited on the PdCl<sub>2</sub>/SnCl<sub>2</sub>-catalyzed PET film is reduced.

We also found that the adhesion of the Cu layer on the Ar plasma-treated PET was fairly low, even though the PET surface was significantly etched with the Ar plasma (Fig. 4), which is explainable by the effect of the introduced oxygen groups on the substrate. On the other hand, since copper was hardly deposited on the control PET film without plasma treatment, its lap-shear strength was about zero. The overall results indicated that both the surface roughness and type of introduced functional groups played important roles to improve the metal adhesion on the polymer surface.

Furthermore, the introduced N atoms on the PET film by the NH<sub>3</sub> plasma treatment make it possible to plate Cu onto the PET surface without helping SnCl<sub>2</sub>. This single catalyst system cannot be applied to O<sub>2</sub> or Ar plasma-treated ones. As shown in Figure 5, we obtained a good adhesion property with this sample which had been NH<sub>3</sub> plasma-treated and treated with a PdCl<sub>2</sub> single catalyst, as compared those of O<sub>2</sub> or Ar plasma-treated and catalyzed with the PdCl<sub>2</sub>/SnCl<sub>2</sub> mixture.

The EMI-SE of electroless Cu-plated PET film was estimated by the reflection loss calculated from the ratio of the wave impedance in the air (377Ω) to the characteristic impedance of the material.<sup>19,20</sup> The EMI-SE of the material was de-

termined from the sum of the reflection loss and the absorption loss. For the conductive materials, the dominant shield mechanism is predicted to be a reflection loss, which shows an increasing function of electrical conductivity.<sup>19</sup> As shown in Figure 6, in the case of O<sub>2</sub> or Ar plasma-treated PET film, the reflection loss value was about 30 dB. However, NH<sub>3</sub> plasma-treated film was above 35 dB at the all frequency levels. As mentioned above, the introduced N atoms on the PET film surfaces enhanced the chemisorption of the Pd catalyst for inducing the Cu deposition; thereby, EMI-SE was increased with increasing conductivities owing to the even deposition of Cu particles on the plasma-treated surfaces. Also, electroless Cu-plated PET film activated with a single PdCl<sub>2</sub> catalyst after NH<sub>3</sub> plasma treatment was shown to have the highest value of reflection loss, indicating the highest EMI-SE, because there was a very low Sn<sup>2+</sup> content that might have acted as impurities on the plated surface.

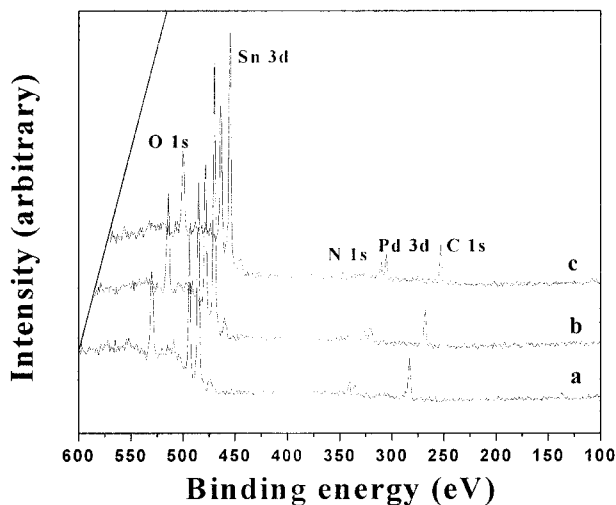
#### Characteristics of Catalyzed PET Film

To confirm the reason why the adhesion property was affected by various plasma treatments, an XPS survey spectra of the catalyzed PET film was done. Also, the atomic composition ratio of the catalyzed PET film was analyzed by both XPS and energy dispersive X-ray spectroscopy (EDX) in FE-SEM. The escape depth of the X-ray is limited to only a few angstroms (about 5–20 Å) with XPS,

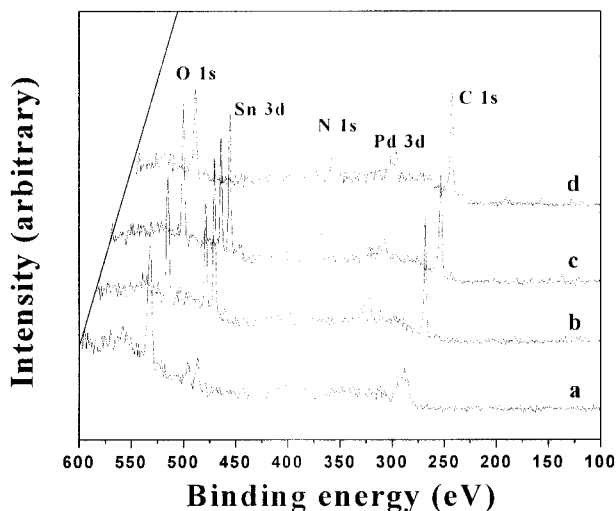
since an X-ray of a narrower band width is employed to enhance the resolution. Thus, information on the elements in the outermost layer of the surface can be obtained. On the other hand, we can obtain better information on the total amount of elements on the PET surface with EDX analysis, since the elements in the deeper location from the surface (about 1000 to 2000 Å) over the wider range of area could be detected. Figure 7(A) corresponds to the XPS spectra of PET films catalyzed by dipping in the PdCl<sub>2</sub>/SnCl<sub>2</sub> mixed solution after plasma-treated with (a) O<sub>2</sub>, (b) Ar, and gases (c) NH<sub>3</sub>. As compared to the other plasma-treated ones, the Pd<sub>3d</sub> core level was significantly high for the NH<sub>3</sub> plasma-treated film, indicating that the greater amount of Pd<sup>2+</sup> ions were deposited. In general, many Sn<sup>2+</sup> ions were detected on the surface of the film before the acceleration step as shown in Tables II and III. Since the catalyzing nuclei deposited are protective colloids which consist of a Pd–Sn alloy core with a stabilizing Sn(II) ion layer, the relative atomic composition ratio of Pd/Sn is significantly low in the XPS data as compared with those detected by EDX.

Figure 7(B) shows XPS spectra of the same plasma-treated samples as presented in Figure 7(A), but they were accelerated for 3 min with 1M of the HCl solution after being activated by the mixed PdCl<sub>2</sub>/SnCl<sub>2</sub> solution. After accelerating the catalyzed samples with the HCl solution, the Sn core-level intensities of those samples were more decreased than were those of Pd, leading to an increase in the Pd/Sn ratio as shown in Tables II and III. Among them, the PET film that has graft-nitrogenated functions by the NH<sub>3</sub> plasma treatment provides the highest Pd/Sn core-level intensity after acceleration. This is probably related to the greater affinity of palladium for nitrogen. Comparatively, O<sub>2</sub> and Ar plasma treatment allows chemisorption of more tin than of palladium due to a lack of affinity of palladium for oxygen, resulting in a low Pd/Sn ratio.

As mentioned above, introducing N atoms having good affinity for Pd atoms enhances the chemical bonding with the polymer substrate. During the acceleration, some Pd–Sn bonds are broken and Sn<sup>2+</sup> ions that are not directly attached to the PET film are easily eliminated. Charbonnier et al.<sup>23</sup> proposed that, when nitrogenated groups were grafted onto the substrate in parallel with oxygenated functions, the Sn<sup>2+</sup> ions did not bond to the oxygen of the surface because of the inhibition exercised by the nitro-



(A)



(B)

**Figure 7** (A) XPS spectra of PET samples: (a) O<sub>2</sub>, (b) Ar, and (c) NH<sub>3</sub> plasma-treated, then catalyzed with a PdCl<sub>2</sub>/SnCl<sub>2</sub> mixed-catalyst solution. (B) After accelerating the (A-a–c) samples by an HCl solution. (d) is the XPS spectrum after NH<sub>3</sub> plasma-treated, then catalyzed with a PdCl<sub>2</sub> single catalyst, and rinsed.

gen. In consequence, many Sn<sup>2+</sup> ions which were not bonded directly to the surface of NH<sub>3</sub> plasma-treated PET film were easily eliminated during the acceleration process. The PET film surface treated by O<sub>2</sub> and Ar plasma had more Sn atoms, whose relative Pd/Sn core-level in-



**Table II Atomic Composition Ratio of PET Films Subjected to the Catalyzation and (or) Acceleration Step After Plasma Treatment with Various Gases (XPS Analysis)**

Surface Treatment <sup>a</sup>	C <sub>1s</sub> (%)	O <sub>1s</sub> (%)	N <sub>1s</sub> (%)	Pd <sub>3d</sub> /C <sub>1s</sub>	Sn <sub>3d</sub> /C <sub>1s</sub>	O <sub>1s</sub> /C <sub>1s</sub>	N <sub>1s</sub> /C <sub>1s</sub>	Pd/Sn
O <sub>2</sub> plasma + A	41.28	45.38	0	0.028	0.295	1.099	0	0.095
O <sub>2</sub> plasma + B	46.46	51.03	0	0.008	0.046	1.098	0	0.174
Ar plasma + A	35.96	46.65	3.22	0.039	0.355	1.297	0.090	0.110
Ar plasma + B	52.92	35.03	6.12	0.017	0.096	0.662	0.116	0.177
NH <sub>3</sub> plasma + A	34.91	44.6	5.62	0.048	0.378	1.278	0.161	0.127
NH <sub>3</sub> plasma + B	50.59	33.59	10.98	0.017	0.079	0.664	0.217	0.215
NH <sub>3</sub> plasma + C	54.78	28.58	15.63	0.018	0	0.522	0.285	0

<sup>a</sup> A: Samples were catalyzed with PdCl<sub>2</sub>/SnCl<sub>2</sub> after plasma treatment. B: Samples were catalyzed with PdCl<sub>2</sub>/SnCl<sub>2</sub> and accelerated with an HCl solution after plasma treatment. C: The sample was catalyzed with single PdCl<sub>2</sub> solution after plasma treatment.

tensity was 0.167 and 0.172 after acceleration, which were lower than that of the NH<sub>3</sub> plasma-treated one. It indicated that introduced oxygen groups on the PET surface inhibit direct Pd adsorption. In addition, Figure 7(B-d) shows the XPS spectrum after NH<sub>3</sub> was plasma-treated, catalyzed with a PdCl<sub>2</sub> single catalyst, and rinsed. The relative N<sub>1s</sub>/C<sub>1s</sub> core-level intensity of this PET film was 0.285, which is higher than that of NH<sub>3</sub> plasma-treated and catalyzed with a mixed catalyst solution.

#### Effect of Plasma-treatment Conditions on Cu Adhesion

As the plasma power and treatment time were changed, the effect of the plasma conditions on the adhesion of the Cu layer were investigated to optimize the plasma condition. Lap-shear test re-

sults with various powers of plasma treatment are shown in Figure 8. As the plasma power was increased, adhesion of the deposited Cu layer on the PET film increased. However, an application of excessive RF power causes the film to turn yellow with little effect on the adhesion. Therefore, we fixed the RF power at 70 W and changed the treatment time. Changes in the lap-shear strength for Cu-plated PET film was measured and the result is shown in Figure 9. Regardless of the treatment gases, the adhesion of the Cu layer was increased as the plasma treatment time elapsed. However, there was no significant increment of adhesion as the plasma-treatment time elapsed from 20 to 30 min.

## CONCLUSIONS

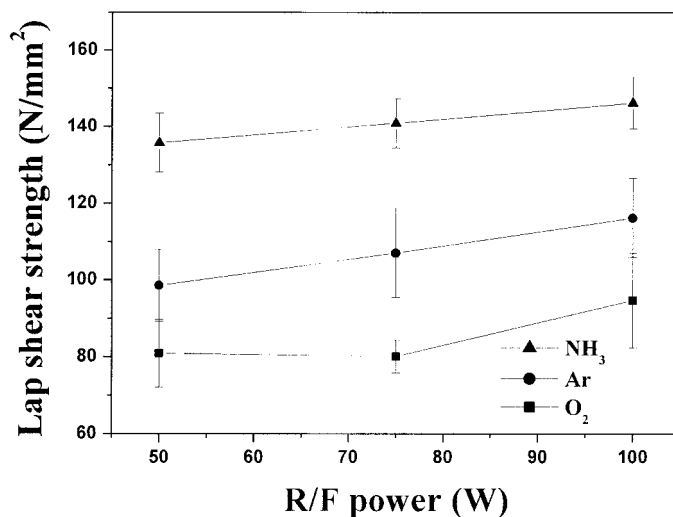
Copper-coated PET films were prepared by the electroless-plating method. To improve the adhesion between the Cu layer and the PET film and to develop high-quality EMI shielding materials, Pd chemisorption was employed to establish strong chemical bonds between the nonconductive substrate and the copper layer. The effects of the PET film-activation process through plasma etching and catalyzation on the adhesion of the Cu layer and the EMI-SE of the treated PET were investigated.

From the AFM and XPS studies, we concluded that both the surface roughness and type of introduced functional group played important roles for improving the metal adhesion on the polymer surface. Plasma pretreatment increased the surface roughness in the decreasing order of Ar > O<sub>2</sub>

**Table III Atomic Composition Ratio of Pd and Sn Deposits on PET Film Surfaces Subjected to Catalyzation and (or) Acceleration Step After Plasma Treatment with Various Gases (EDX Analysis)**

Pretreatment Condition <sup>a</sup>	Pd (%)	Sn (%)	Pd/Sn
O <sub>2</sub> plasma + A	32.3	67.7	0.476
O <sub>2</sub> plasma + B	33.6	66.5	0.505
Ar plasma + A	12.6	87.4	0.145
Ar plasma + B	44.1	55.9	0.788
NH <sub>3</sub> plasma + A	36.6	63.4	0.577
NH <sub>3</sub> plasma + B	70.4	29.6	2.376

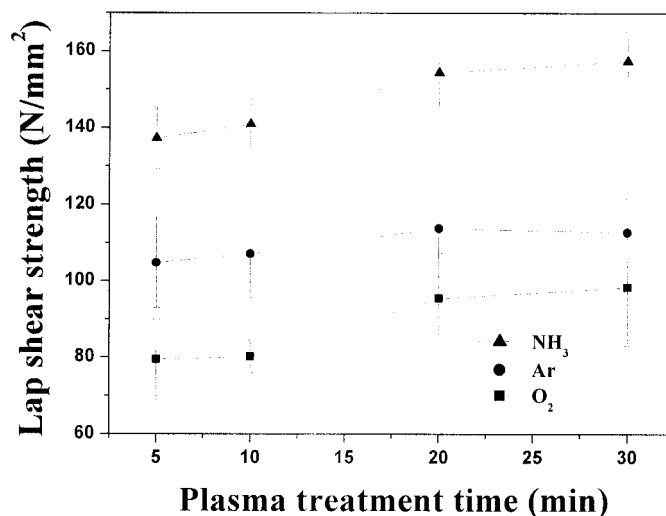
<sup>a</sup> See footnote to Table II.



**Figure 8** Lap-shear strength of copper-plated PET film as a function of rf power. Samples were plasma-treated for 10 min with various gases, then catalyzed with a PdCl<sub>2</sub>/SnCl<sub>2</sub> mixed solution of 1 : 16 molar ratio.

> NH<sub>3</sub>. Plasma treatment with NH<sub>3</sub> produced N atoms on the PET film, which enhances the chemisorption of Pd<sup>2+</sup> on PET, resulting in improved adhesion of the Cu layer deposited on the Pd-catalyzed surface. On the contrary, adhesion of the Cu layer on the oxygen plasma-treated PET was low due to a lack of affinity of Pd<sup>2+</sup> for oxygen. Moreover, the introduced oxygen groups on the Ar plasma-treated PET substrate inhibit direct Pd<sup>2+</sup> adsorption, hence, leading to low adhe-

sion of the Cu layer in spite of the high surface roughness. In the O<sub>2</sub> and Ar plasma cases, Pd<sup>2+</sup> ions chemisorb onto the Sn<sup>2+</sup> ions through Cl<sup>-</sup> ions, thereby decreasing adhesion of the Cu layer. High EMI-SE of the PET film over a wide range of frequency levels was obtained under optimum conditions. We found that the NH<sub>3</sub> plasma was the most effective etching medium, and the optimum plasma condition was when the rf power was 75 W and the reaction time was 20 min.



**Figure 9** Lap-shear strength of copper-plated PET film as a function of plasma-treatment time. Samples were plasma-treated at rf power of 75 W with various gases, then catalyzed with a PdCl<sub>2</sub>/SnCl<sub>2</sub> mixed solution of 1 : 16 molar ratio.

This work was supported by a Korea Research Foundation Grant (KRF-99-041-D00480).

## REFERENCES

1. Deckert, C. A. *Plat Surf Finish* 1995, Feb., 48.
2. Deckert, C. A. *Plat Surf Finish* 1995, Mar., 58.
3. Manenq, F.; Carlotti, S.; Mas, A. *Angew Makromol Chem* 1999, 271, 11.
4. Inagaki, N.; Tasaka, S.; Narushima, K.; Mochizuki, K. *Macromolecules* 1999, 32, 8566.
5. Sun, R. D.; Tryk, D. A.; Hashimoto, K.; Fujishima, A. *J Electrochem Soc* 1998, 145, 3378.
6. Chu, S. Z.; Sakairi, M.; Takahashi, H.; Qiu, Z. X. *J Electrochem Soc* 1999, 146, 537.
7. Karmalkar, S.; Banerjee, J. *J Electrochem Soc* 1999, 146, 580.
8. Ramasubramanian, M.; Popov, B. N.; White, R. E.; Chen, K. S. *J Electrochem Soc* 1999, 146, 111.
9. Yang, C. H.; Wang, Y. Y.; Wan, C. C.; Chen, C. J. *J Electrochem Soc* 1996, 143, 3521.
10. Meek, R. L. *J Electrochem Soc* 1975, 122, 1478.
11. Kim, E. Y.; Kong, J. S.; Lee, G. H.; Kim, H. D. *J Kor Fiber Soc* 2000, 37, 11.
12. Yasuda, H. *Plasma Polymerization*; Academic: New York, 1985.
13. Liston, E. M.; Martinu, L.; Wertheimer, J. *Adhes Sci Technol* 1993, 7, 1090.
14. Chin, J. W.; Wightman, J. P. *J Adhesion* 1991, 36, 25.
15. Gerenser, L. J. *J Adhes Sci Technol* 1993, 7, 1019.
16. Oh, K. H.; Kim, S. H.; Kim, E. A. *J Appl Polym Sci*, in press.
17. Han, E. K.; Kim, E. A.; Oh, K. W. *J Kor Fiber Soc* 1998, 35, 515.
18. Kim, E. A.; Han, E. G.; Oh, K. W.; Na, J. G. *J Appl Phys* 2000, 87, 4984.
19. Kim, Y. S.; Choi, I. K.; Kim, S. S. *Kor J Mater Res* 1999, 9, 913.
20. Kim, Y. S.; Jeon, Y. S.; Kim, S. S. *Kor J Mater Res* 1999, 9, 1055.
21. Oh, K. H.; Kim, D. J.; Kim, S. H. *Polymer (Korea)*, in press.
22. Minjer, C. H.; Boom, R. P. J. *J Electrochem Soc* 1973, 120, 1644.
23. Charbonnier, M.; Alami, M.; Romand, M. *J Electrochem Soc* 1996, 143, 472.