



# Effects of titania content and plasma treatment on the interfacial adhesion mechanism of nano titania-hybridized polyimide and copper system

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Received 8 December 2003; received in revised form 5 April 2004; accepted 9 April 2004

## Abstract

Nano-titania (TiO<sub>2</sub>) incorporated into polyimide (PI) matrix can significantly enhance the adhesion strength for PI/TiO<sub>2</sub> hybrid film and copper system. Surface modifications by various plasma treatments (Ar, Ar/N<sub>2</sub> and Ar/O<sub>2</sub>) were also applied in this study to improve the adhesion strength. The Ar/N<sub>2</sub> plasma treatment is regarded as the more effective way in promoting the adhesion strength. The maximum adhesion value of 9.53 N/cm was obtained for the PI/TiO<sub>2</sub>–1 wt% hybrid film with Ar/N<sub>2</sub> plasma treatment. It is enhanced about 10 times as large as pristine PI. Furthermore, by Ar/O<sub>2</sub> plasma treatment, a weak boundary of copper oxide was formed at the interlayer between PI/TiO<sub>2</sub> hybrid film and copper which decreases the adhesion strength. The effects of plasma treatment and content of nanosized TiO<sub>2</sub> on the adhesion strength between PI/TiO<sub>2</sub> hybrid film and copper system were studied. Atomic force microscope and contact angle analyses were used to measure the changes in surface morphology and surface energy as a result of plasma treatment. Besides, the interfacial states of peeled-off polymer side and copper side were investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Based on the result of XPS spectra, the peeled-off failure mode between PI/TiO<sub>2</sub> hybrid film and copper was proposed in this study.

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**Keywords:** Polyimide; Titania; Plasma treatment

## 1. Introduction

Polyimide (PI), a low dielectric material with high temperature stability, is known to be one of the most widely used polymers in the electronic industry [1,2]. A typical example is the flexible printed circuits (FPC) which is used in electronic products such as cell phones, printers, cameras and their peripherals. In some applications, the adhesion between PI and copper can be classified by two-layer or three-layer types. For the three-layer type, a thin passivation/adhesion promoting layer of metals such as Cr, Ni and Ta were pre-coated to improve the adhesion between PI and copper as well as to prevent the formation of copper oxide in the interface [3–7]. However, to meet the demand of highly miniaturized electronic devices, two-layer type directly metallized without any adhesive layer between PI and copper is required. Although there were some previous studies reported, a thin metal buffer layer could enhance the

adhesion strength between PI and copper [8,9]. However, the process is still not simple and cost effective because it contains metal capping step on the PI. Therefore, a number of methods devoted directly to the surface modification of PI for adhesion improvement have been developed.

Earlier studies have shown that the adhesion strength of PI and copper could be significantly enhanced through the surface modification of plasma treatment [7,10–14]. One of the main reasons is the formation of new chemical species that create bonds to link the metal film and polymer substrate. The other reason is modifying the surface morphology of PI to take mechanical interlocking effect. Besides, there are few references mentioned that metal-containing PI could improve the adhesion strength between PI and copper because the metal can serve as active sites on the PI surface [15–17]. In this study, the plasma treatment method was applied to the PI/TiO<sub>2</sub> nano hybrid film which our laboratory has successfully prepared [18,19]. The interfacial adhesion strength between PI/TiO<sub>2</sub> nano hybrid film and copper system was investigated. The objective here is to study the correlation of the amount of nanosized TiO<sub>2</sub>

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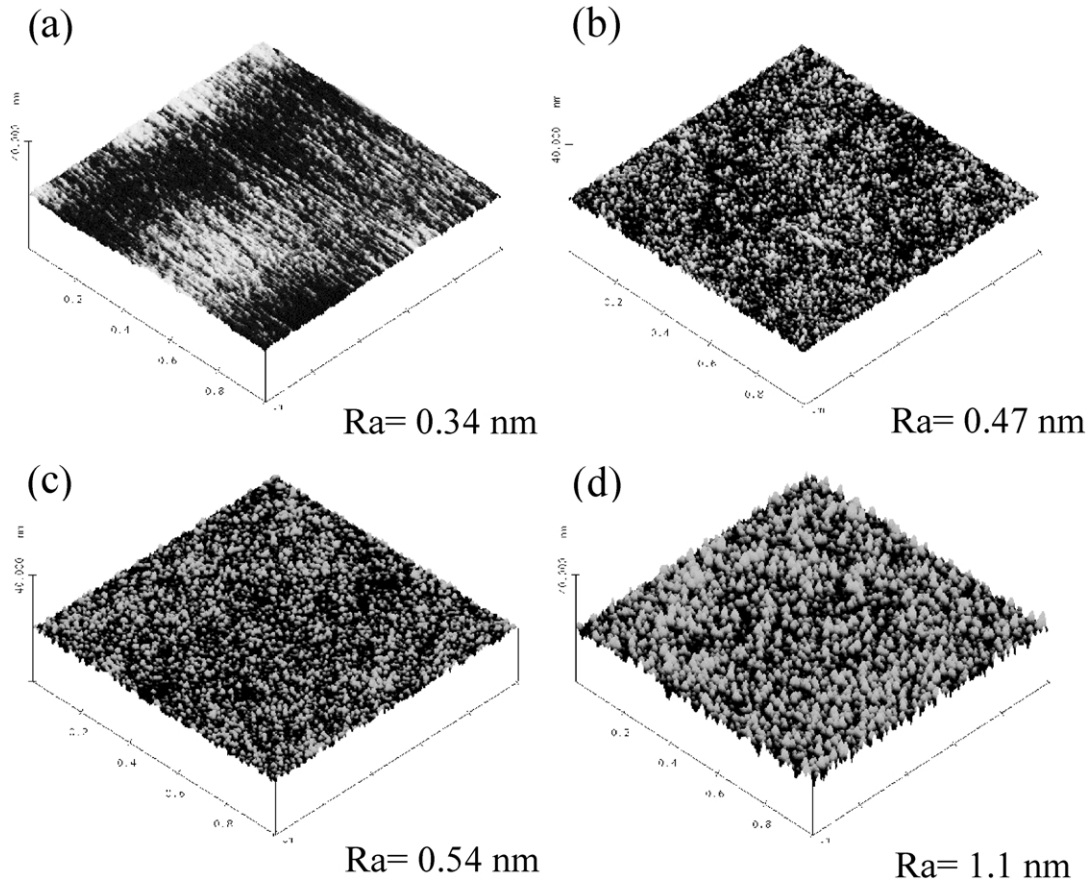


Fig. 1. AFM images of PI/TiO<sub>2</sub>-1 wt% hybrid film after various plasma treatments. (a) No plasma, (b) Ar plasma, (c) Ar/N<sub>2</sub> plasma and (d) Ar/O<sub>2</sub> plasma.

on adhesion promotion and the interfacial states such as adhesion strength, chemical state and surface morphology. In addition, the difference on the adhesion strength among the effects of Ar, Ar/N<sub>2</sub> and Ar/O<sub>2</sub> plasma treatments is further discussed to elucidate which is strongly correlated with the enhanced adhesion strength. Based on the X-ray photoelectron spectroscopy (XPS) experimental results, the peeled-off failure mode between PI/TiO<sub>2</sub> hybrid film and copper is also discussed.

## 2. Experiment

PI used in this study was 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride-oxydianiline (BTDA-ODA). The detail synthesis procedures of PI/TiO<sub>2</sub> nano hybrid film can be seen elsewhere and not reiterated here [18,19]. The concentration of TiO<sub>2</sub> in hybrid film was approximately 1, 3, 5, 7, 9 wt%, respectively, and the thickness of PI/TiO<sub>2</sub> hybrid film was 35–40 μm. Metallization processes were sequentially proceeded with the following steps. First, the PI/TiO<sub>2</sub> hybrid film was dried in an oven at 250 °C for 2 h to remove water absorbed by the film. Second, four conditions of plasma treatment by radio-frequency (RF) generator were used to pre-activate hybrid film surface before deposition of copper. They were (i) no plasma treatment; (ii) only Ar

plasma treatment; (iii) after Ar plasma treated followed by N<sub>2</sub> plasma treatment; and (iv) after Ar plasma treated followed by O<sub>2</sub> plasma treatment. For the sake of brief notation, Ar, Ar/N<sub>2</sub> and Ar/O<sub>2</sub> represent each condition of the plasma treatments used in this paper. The plasma was controlled by three parameters: a power of RF generator at 250 W, a system pressure of 20 mTorr and a treatment time of 180 s in each step of plasma treatment. The flow rates of Ar, N<sub>2</sub> and O<sub>2</sub> were 50, 80, 80 sccm/min, respectively. After plasma treatment, 400 nm thickness of copper was deposited by Ar in sputtering system with a DC power of 1600 W for 600 s without breaking the vacuum. The base pressure was below 10<sup>-6</sup> Torr and the pressure during Cu sputtering was maintained at 20 mTorr. In this study, Ar is employed in the sputtering system due to its inertness, larger ion mass and high sputtering yield. Finally, in order to measure the adhesion of the samples by using a 90° peel test method (Model HT-8116 Hung TA), 30 μm thick copper was electroplated and strips of 10 × 80 mm<sup>2</sup> were made. The peel rate was 50.8 cm/min and the experimental value was obtained from the average of at least four measurements that were performed.

The surface morphology change of PI/TiO<sub>2</sub> hybrid film after plasma treatment was analyzed by atomic force microscope (AFM) of Digital Instrument NS3a controller with D3100 stage. In each case, a certain area of

Table 1  
Surface roughness of PI/TiO<sub>2</sub> hybrid films after plasma treatment

Plasma treatment	Surface roughness (nm)					
	Pure PI	1 wt%	3 wt%	5 wt%	7 wt%	9 wt%
No plasma	0.28	0.34	0.38	0.51	0.57	0.63
Ar plasma	0.36	0.47	0.63	0.86	1.56	2.12
Ar/N <sub>2</sub> plasma	0.48	0.54	0.82	1.12	1.78	2.34
Ar/O <sub>2</sub> plasma	0.71	1.10	1.97	2.46	3.74	4.89

1  $\mu\text{m} \times 1 \mu\text{m}$  was scanned by tapping mode. Scanning electron microscope (SEM) was used to observe the peeled-off surface of polymer side. The apparatus used was JEOL JSM-6500F and specimens were pre-coated with a thin layer of gold to eliminate electron charging effect. For interface analysis, X-ray photoelectron spectroscopy (XPS) spectra were obtained by using a ESCA PHI 1600 spectrometer working in the constant analyzer energy mode with a pass energy of 50 eV and Mg K $\alpha$  (1253.6 eV) radiation as the excitation source. XPS analysis was done at room temperature and below  $10^{-10}$  Torr. The take-off angle used in the XPS measurements was 90°. Surface energy was measured and calculated by Dynamic Contact Angle Analyzer FTA-200 from a contact angle test using two standard liquids: H<sub>2</sub>O and CH<sub>2</sub>I<sub>2</sub>.

### 3. Results and discussion

Nanosized TiO<sub>2</sub> is incorporated into PI matrix as the polymer substrate in this study. The change in surface topography of the PI/TiO<sub>2</sub> hybrid film before and after plasma treatment was investigated by atomic force microscopy (AFM). Fig. 1(a)–(d) shows the AFM images of the pristine PI/TiO<sub>2</sub>–1 wt% hybrid film surface and after plasma modified surface. The root mean square surface roughness ( $R_a$ ) of the pristine PI/TiO<sub>2</sub>–1 wt% hybrid film is 0.34 nm (Fig. 1(a)). After plasma treatment, the surface topography has changed considerably. The  $R_a$  values increase to 0.47, 0.54 and 1.1 nm for Ar, Ar/N<sub>2</sub> and Ar/O<sub>2</sub>

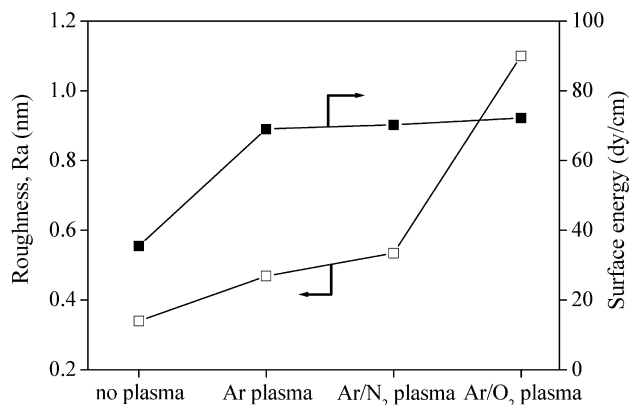


Fig. 2. The surface roughness and surface energy of PI/TiO<sub>2</sub>–1 wt% hybrid film after various plasma treatments.

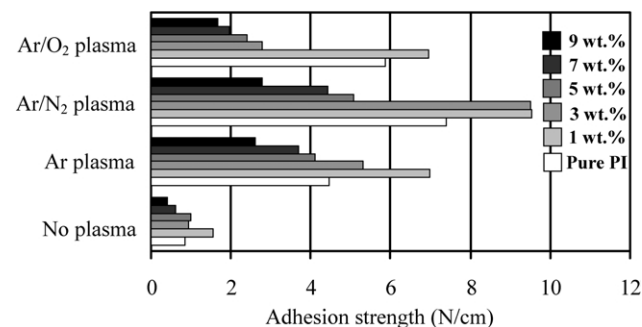


Fig. 3. Adhesion strengths of PI/TiO<sub>2</sub> hybrid films and Cu with various plasma treatments.

plasma treatment, respectively. It is suggested that oxygen is a much more active gas than nitrogen and thus the oxygen plasma is likely to produce rougher surface as compared with nitrogen plasma. As shown in Table 1, the similar tendency of increasing roughness for the other PI/TiO<sub>2</sub> hybrid film is observed. Surface roughness is also related with the content of TiO<sub>2</sub>. The more TiO<sub>2</sub> is contained, the more rugged surface is shown and that will facilitate the mechanical interlocking effect during Cu sputtering.

The surface energy and surface roughness of PI/TiO<sub>2</sub>–1 wt% hybrid films after plasma treatment are plotted in Fig. 2. The pristine hybrid film (no plasma treatment) showed a low surface energy value, indicating a poor wettability. However, the plasma-treated surface produced noticeable increase in surface energy (i.e. high wettability) and the surface energy values were close in spite of what kind of plasma was used. The surface energies of pure PI and PI/TiO<sub>2</sub> hybrid films with various TiO<sub>2</sub> contents without plasma treatment are in the range of 31.11–36.33 dy/cm. Once using plasma treatment, the surface energies of pure PI and all PI/TiO<sub>2</sub> hybrid films vary from 60.63 to 72.2 dy/cm. The change in surface energy after plasma treatment could be ascribed to the modifications of surface roughness and surface chemistry [10]. Besides, it should be noted that the hybrid film surface after plasma treatment by RF generator not exactly represented the one during Cu sputtering because the process of Cu sputtering is always accompanied by Ar plasma treatment with DC power. Therefore, ‘no plasma’ sample for contact angle and AFM experiment is different from no plasma sample for adhesion test. To distinguish one from the other, we assumed that the sample without plasma treatment by RF is regarded as no plasma sample in this study. However, the results of surface energy and AFM could be provided as reference materials.

Adhesion strength of PI/TiO<sub>2</sub> hybrid film and Cu was estimated by 90° peel test to investigate the effects of nanosized TiO<sub>2</sub> content and plasma treatment. Fig. 3 shows the peel strength between PI/TiO<sub>2</sub> hybrid films and Cu under various plasma treatments. The adhesion strength of the hybrid film without plasma treatment is below 1.5 N/cm, while the adhesion strength of the Ar plasma-treated hybrid film is 2.6–6.97 N/cm. The Ar/N<sub>2</sub> and Ar/O<sub>2</sub> plasma

Table 2

The component percentage and atomic ratios of PI/TiO<sub>2</sub>-9 wt% hybrid film after plasma treatment

Plasma treatment	Component percentage (%)				Atomic ratio		
	C	N	O	Ti	[O]/[C]	[N]/[C]	[O]/[N]
No plasma	78.78	3.22	17.48	0.52	0.222	0.040	5.429
Ar plasma	61.17	2.53	30.6	5.7	0.500	0.041	12.095
Ar/N <sub>2</sub> plasma	54.98	2.99	33.34	8.69	0.606	0.054	11.151
Ar/O <sub>2</sub> plasma	54.67	2.62	33.98	8.73	0.622	0.048	12.969

treatment are much more effective in improving the adhesion strength. In particular, the Ar/N<sub>2</sub> treatment causes a large increase in the adhesion strength from 2.78 to 9.53 N/cm. The adhesion strength is promoted about 10-fold larger than pristine PI (0.86 N/cm).

A tendency (see Fig. 3) that adhesion strength can be greatly improved by adding small amount of TiO<sub>2</sub> could be resulted from the existence of TiO<sub>2</sub> on the hybrid film surface which reduces the surface resistivity of hybrid film [18]. The more TiO<sub>2</sub> is contained on the hybrid film surface, the higher conductivity is expected and easier for Cu to adhere to hybrid film. However, for the hybrid film with high TiO<sub>2</sub> content, the sample cracked in polymer substrate not fail at the interface or Cu layer during the peel test. This is resulted from that incorporation of TiO<sub>2</sub> into PI matrix makes a loss in flexibility of hybrid film. Therefore, the

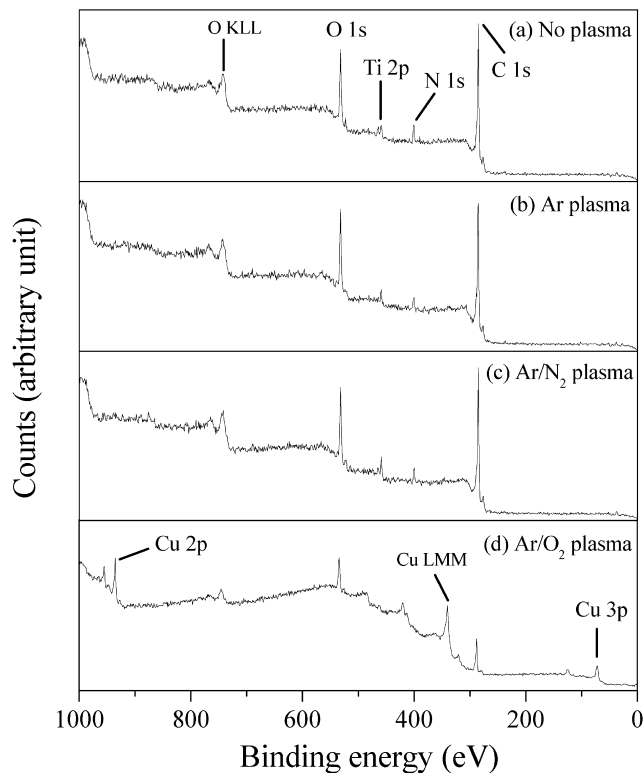


Fig. 4. XPS spectra of PI/TiO<sub>2</sub>-9 wt% hybrid films modified by various plasma treatments after peel test.

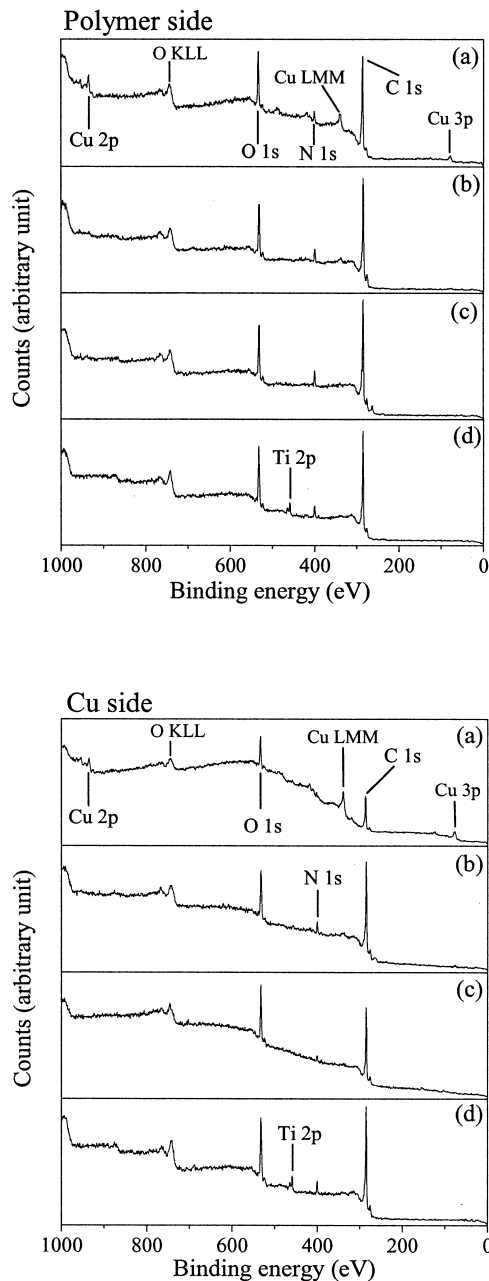


Fig. 5. XPS spectra of both polymer side and Cu side with Ar/N<sub>2</sub> plasma treatment. (a) Pure PI, (b) PI/TiO<sub>2</sub>-1 wt%, (c) PI/TiO<sub>2</sub>-3 wt% and (d) PI/TiO<sub>2</sub>-9 wt%.

mobility of polymer chain is diminished and hybrid film with high TiO<sub>2</sub> content is embrittled. For this reason, the hybrid films with high TiO<sub>2</sub> content were too brittle to afford larger load without fracture during the peel test.

According to Fig. 3, another involved factor in adhesion strength is plasma treatment which can affect the adhesion strength in two ways. First, the plasma treatment may change the surface morphology to provide mechanical interlocking between PI/TiO<sub>2</sub> hybrid film and Cu. Second, the plasma treatment may chemically modify the PI/TiO<sub>2</sub> hybrid film surface to form functional groups which ensure either chemical or physical bonds between the hybrid film



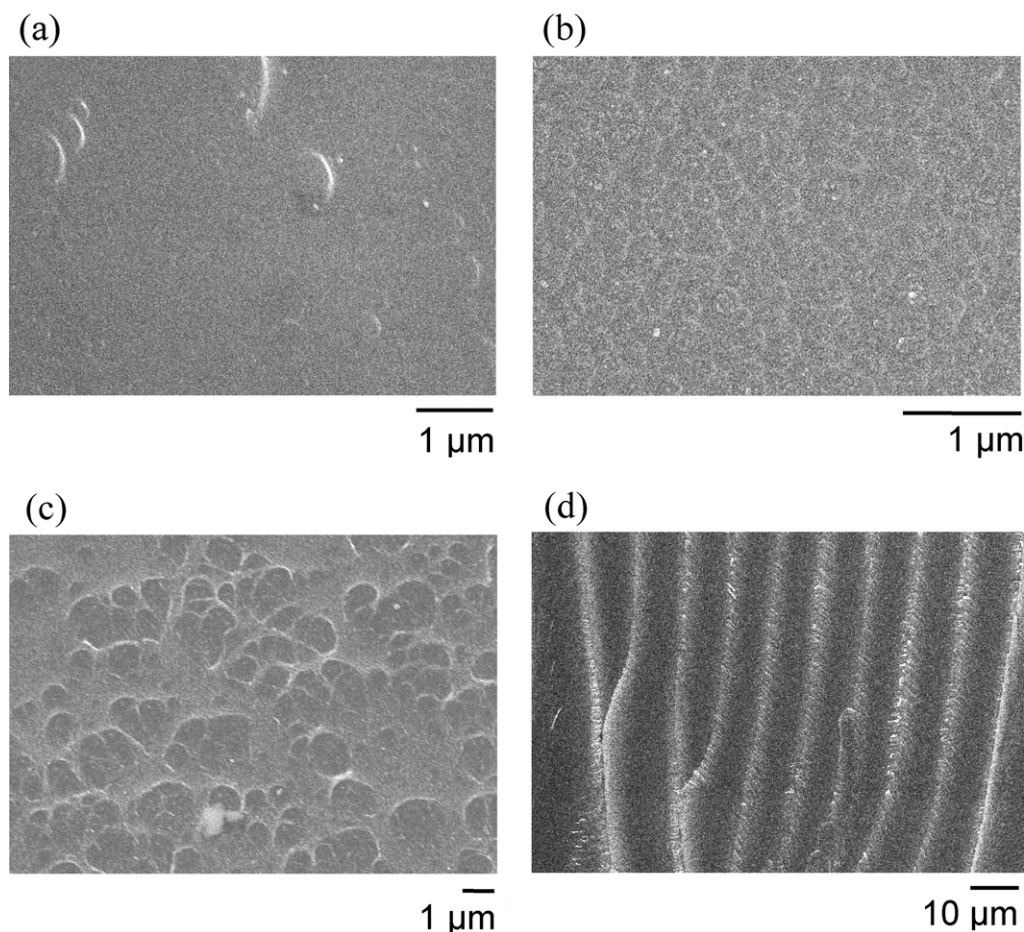


Fig. 6. SEM images of peeled-off surface of hybrid film with Ar/N<sub>2</sub> plasma treatment. (a) Pure PI, (b) PI/TiO<sub>2</sub>-1 wt%, (c) PI/TiO<sub>2</sub>-3 wt% and (d) PI/TiO<sub>2</sub>-9 wt%.

and Cu. It has been reported that active gases plasma (O<sub>2</sub> and N<sub>2</sub>) are used to increase the number of N- or O-containing functional groups such as C–O, C–N, C=O and OH at the PI surface [7,20,21]. Since metal atoms preferentially react with C–O, C–N or C=O, the interaction of such groups with Cu and/or Ti atoms is thought to have occurred at the interface. However, when an inert Ar gas is used for the surface treatment, the formation of N- or O-containing groups does not occur easily. This implies that the chemical interaction at the hybrid film and Cu interface becomes weak. That is why the lower adhesion strength is observed for Ar plasma treatment as compared with Ar/N<sub>2</sub> and Ar/O<sub>2</sub> plasma treatment.

The XPS analyses of PI/TiO<sub>2</sub> hybrid film (see Table 2) are consistent with that mentioned above. The plasma treatment leads to a large increase in the [O]/[C] atomic ratio but a smaller increase in the [N]/[C] atomic ratio. The [O]/[C] atomic ratio increases from 0.222 for the untreated hybrid film to 0.5–0.622 for the plasma-treated hybrid film. On the other hand, the [N]/[C] atomic ratio is 0.04 for the untreated hybrid film and 0.041–0.054 for the plasma-treated hybrid film. The correlation between the increase in [O]/[C] and [N]/[C] ratios and increase in adhesion strength

is observed. The Ar/O<sub>2</sub> plasma treatment shows similar atomic ratios with Ar/N<sub>2</sub> plasma treatment, but poor adhesion. It is suggested that the degradation (bond scission of imide rings) of hybrid film in the Ar/O<sub>2</sub> plasma may be more intense than Ar and Ar/N<sub>2</sub> plasma. As a result, the Ar/O<sub>2</sub> plasma-treated hybrid film surface easily contains a weak boundary which hampers adhesion [10]. We believed that the improvement in adhesion could be attributed to a combination of the lower surface resistivity resulted by TiO<sub>2</sub> incorporated and the plasma treatment.

To investigate the interfacial state, XPS spectra of PI/TiO<sub>2</sub> hybrid film surfaces modified by various plasma treatments after peel test are shown in Fig. 4. For PI/TiO<sub>2</sub>-9 wt% hybrid film, the apparent Cu peaks are only observed in Fig. 4(d) when hybrid film was activated by Ar/O<sub>2</sub> plasma treatment. There is no Cu signal detected for the other three plasma treatments. In order to understand this point, two represented plasma treatments (Ar/N<sub>2</sub> and Ar/O<sub>2</sub>) were chosen and both the hybrid film peeled from the Cu and Cu surface were analyzed by XPS and SEM. The peeled-off failure mode of hybrid film and Cu system was also investigated. In this study, the failed surface obtained after peel test were named as polymer side (the surface which

corresponds to the hybrid film) and Cu side (the surface adhered to hybrid film). Fig. 5 shows XPS spectra of both polymer side and Cu side modified by Ar/N<sub>2</sub> plasma treatment. The Cu 2p<sub>3/2</sub> (933 eV) peaks can be seen in the spectrum of polymer side as well as on the Cu side for pure PI (without TiO<sub>2</sub> additive). This result suggests that some PI is transferred to Cu side and some Cu diffuse to the PI surface during the peel test. In contrast, with TiO<sub>2</sub> additive, XPS analyses of peeled-off PI/TiO<sub>2</sub> hybrid film show no Cu signal. Therefore, it can be inferred that the peeled-off failure mode of pure PI–Cu system is different from that of PI/TiO<sub>2</sub> hybrid film–Cu system. When PI surface was activated by Ar/N<sub>2</sub> plasma treatment, the failure locus of pure PI–Cu system is at the interfacial layer. However, for the PI/TiO<sub>2</sub> hybrid film–Cu system the locus of failure occurred in the inner layer of hybrid film. Fig. 6 is the SEM image showing the morphology of peeled-off polymer side modified by Ar/N<sub>2</sub> plasma treatment. Except for pure PI, where smooth surface is presented, distinct lumpy surface is seen for PI/TiO<sub>2</sub> hybrid film. Especially, the images of PI/TiO<sub>2</sub>–1 wt% (Ar/N<sub>2</sub>) and PI/TiO<sub>2</sub>–3 wt% (Ar/N<sub>2</sub>), which the strongest peel strength were obtained, show significantly peeled-off deformation structure (Fig. 6(b) and (c)). However, PI/TiO<sub>2</sub>–9 wt% (Ar/N<sub>2</sub>) shows other type of surface failure (Fig. 6(d)). The long periodic deformation on surface could be due to its relative rigidity. High rigidity leads the hybrid film not easily to undergo plastic deformation during the peel test. Instead, it accumulates the energy until the critical value and the failure occurs. Fig. 6(d) shows a very regular period of failure. It is believed that some kind of correlation between the content of TiO<sub>2</sub> and the interface adhesion mechanism results in the distinct difference of peeled-off morphology.

The effect of Ar/O<sub>2</sub> plasma treatment on interfacial state was also examined by XPS and SEM. Fig. 7 shows the XPS spectra of polymer and Cu sides for the PI/TiO<sub>2</sub> hybrid film being subjected to Ar/O<sub>2</sub> plasma treatment. In Fig. 7, a distinct peak at the binding energy of 935 eV, attributable to the CuO species, is discernible in the spectra of polymer side (Fig. 7(c) and (d)) and Cu side (Fig. 7(a) and (b)). The existence of CuO could be due to the fact that the copper oxide was formed at the interface region during Cu sputtering. It is also suggested that the interface consisted of copper oxide is a weak boundary. When peel test was carried out, the interface of plasma treated region easily failed. Therefore, the Ar/O<sub>2</sub> plasma treatment showed poorer adhesion strength than Ar/N<sub>2</sub> plasma treatment. Based on Fig. 7, no Cu signal is detected on polymer side (Fig. 7(a) and (b)) for pure PI (Ar/O<sub>2</sub>) and PI/TiO<sub>2</sub>–1 wt% (Ar/O<sub>2</sub>), even TiO<sub>2</sub> is incorporated in the latter. Taking the AFM results into account, the more content of TiO<sub>2</sub> is incorporated; the rougher of the PI/TiO<sub>2</sub> hybrid film surface is observed after plasma treatment. The roughness provides an easy way for Cu to diffuse into polymer side. Hence, pure PI and PI/TiO<sub>2</sub>–1 wt% with slight surface roughness restrict the motion of Cu into polymer layer. That is why Cu peak is

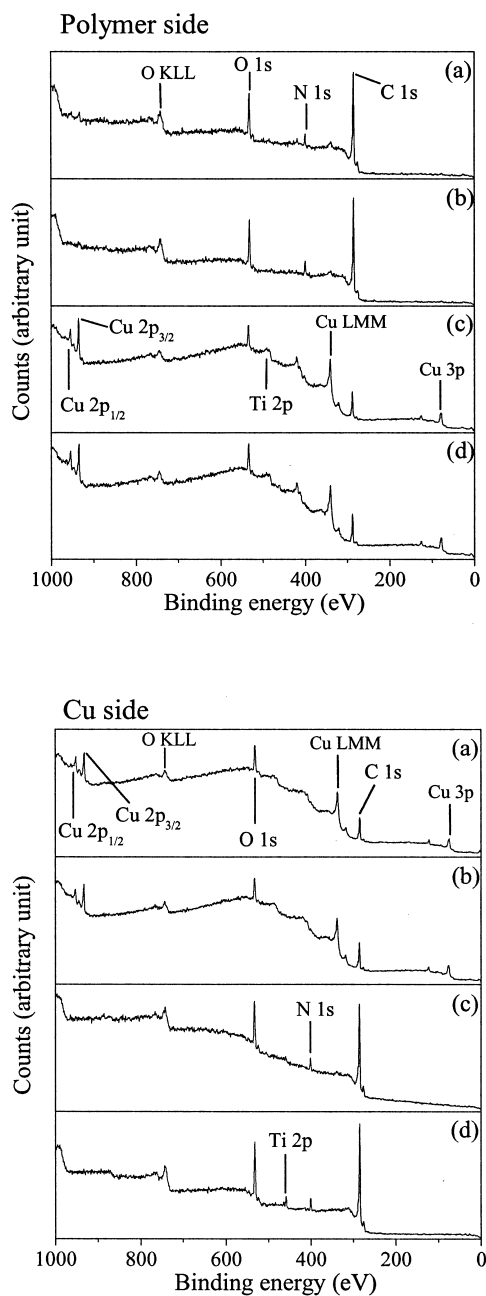


Fig. 7. XPS spectra of both polymer side and Cu side with Ar/O<sub>2</sub> plasma treatment. (a) Pure PI, (b) PI/TiO<sub>2</sub>–1 wt%, (c) PI/TiO<sub>2</sub>–3 wt% and (d) PI/TiO<sub>2</sub>–9 wt%.

only found from Cu side for pure PI (Ar/O<sub>2</sub>) and PI/TiO<sub>2</sub>–1 wt% (Ar/O<sub>2</sub>). On the other hand, for PI/TiO<sub>2</sub>–3 wt% (Ar/O<sub>2</sub>) and PI/TiO<sub>2</sub>–9 wt% (Ar/O<sub>2</sub>), the more rugged surface facilitates the diffusion of Cu into hybrid film and Cu signal is detected from the polymer side. The peeled-off failure mode of pure PI (Ar/O<sub>2</sub>) and PI/TiO<sub>2</sub>–1 wt% (Ar/O<sub>2</sub>) is at the interlayer of hybrid film and Cu because Cu signal is only found in Cu side. However, for PI/TiO<sub>2</sub>–3 wt% (Ar/O<sub>2</sub>) and PI/TiO<sub>2</sub>–9 wt% (Ar/O<sub>2</sub>), no Cu signal is detected on Cu side, suggests that the failure locus had shifted to

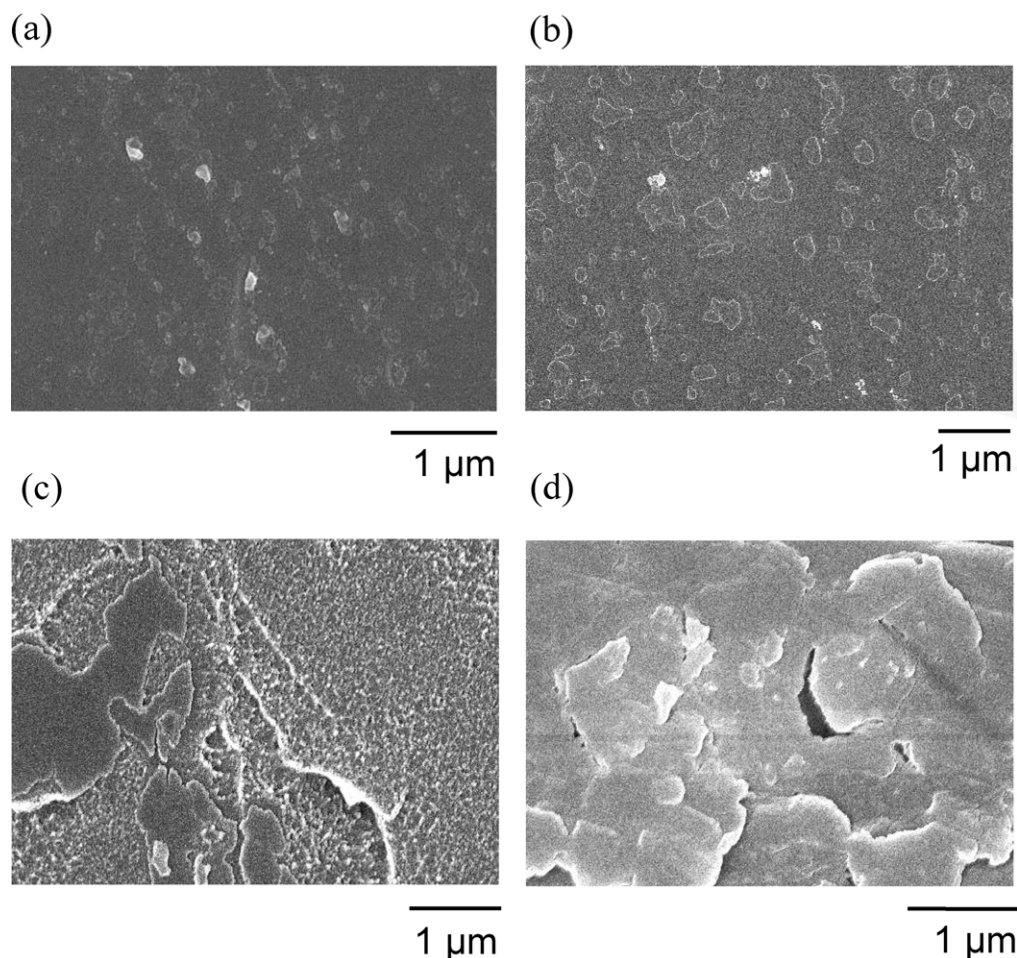


Fig. 8. SEM images of peeled-off surface of hybrid film with Ar/O<sub>2</sub> plasma treatment. (a) Pure PI, (b) PI/TiO<sub>2</sub>-1 wt%, (c) PI/TiO<sub>2</sub>-3 wt% and (d) PI/TiO<sub>2</sub>-9 wt%.

below the interlayer of PI/TiO<sub>2</sub> hybrid film and Cu. The SEM images of peeled-off polymer side modified by Ar/O<sub>2</sub> plasma treatment are shown in Fig. 8. The morphology of pure PI (Ar/O<sub>2</sub>) and PI/TiO<sub>2</sub>-1 wt% (Ar/O<sub>2</sub>) shows that there are some random islands which existed on the surface. With increasing the TiO<sub>2</sub> content, the structure of multi-level is observed. These results further suggest that adhesion strength as well as interfacial state between hybrid film and Cu will be affected by plasma treatment, the failure mode between hybrid film and Cu is also related. Further more work needs to be carried out of how the additive of TiO<sub>2</sub> affects adhesion strength and interface adhesion mechanism between PI/TiO<sub>2</sub> hybrid film and Cu.

#### 4. Conclusion

PI containing small amount of nanosized TiO<sub>2</sub> has significantly enhanced the adhesion strength with Cu. The improvement of adhesion strength could be attributed to the higher conductivity resulted by the existence of TiO<sub>2</sub> on the hybrid film surface. However, further addition of TiO<sub>2</sub>

caused a failure or crack in the polymer substrate instead of interfacial failure during the peel test. Owing to the increase in rigidity, the hybrid film is too brittle to afford larger load without fracture. It is also indicates that the adhesion strength is higher than the mechanical strength of the PI/TiO<sub>2</sub> hybrid film substrate. Another involved factor in adhesion improvement is the plasma treatment which led to enhance adhesion between the PI/TiO<sub>2</sub> hybrid film and Cu. The Ar/N<sub>2</sub> plasma treatment was more effective than Ar and Ar/O<sub>2</sub> plasma treatments. The PI/TiO<sub>2</sub>-1 wt% hybrid film treated with Ar/N<sub>2</sub> plasma exhibited the maximum adhesion strength of 9.53 N/cm. A correlation between the enhancement of adhesion strength and the values of [O]/[C] and [N]/[C] ratios is observed. A weak boundary layer of CuO found at the interface may be the reason why the Ar/O<sub>2</sub> plasma-treated hybrid film showed a poorer adhesion than Ar/N<sub>2</sub> plasma-treated one. In addition, the peeled-off failure mode is also deeply related to the content of TiO<sub>2</sub> and what kind of plasma treatment is used. The locus of failure is shifted from the inner layer of PI/TiO<sub>2</sub> hybrid film to the interlayer of hybrid film and Cu by Ar/N<sub>2</sub> and Ar/O<sub>2</sub> plasma treatment, respectively.



## Acknowledgements

Financial support from Taimide Technology Company is gratefully acknowledged. Authors thank PhD Shyi-Liang Jwo (Chung-Shan Institute of science and Technology, Taiwan) for kindly providing the instruments of sputtering copper.

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