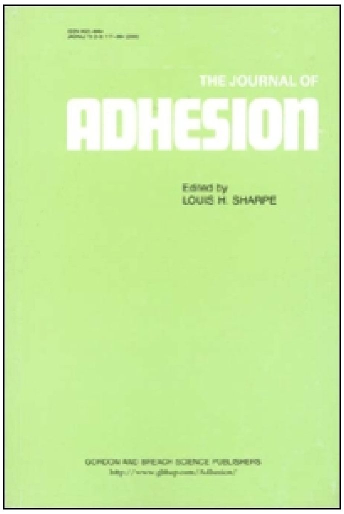

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

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To cite this Article Iwamori, Satoru , Miyashita, Takehiro , Fukuda, Shin , Nozaki, Shouhei , Fukuda, Nobuhiro and Sudoh, Kazufuyu(1997) 'Changes in the Peeled Surfaces of Copper Thin Films Deposited on Polyimide Substrates After Heat Treatment', The Journal of Adhesion, 63: 4, 309 — 321

To link to this Article: DOI: 10.1080/00218469708017225

URL: http://dx.doi.org/10.1080/00218469708017225

J. Adhesion, 1997, Vol. 63, pp. 309–321
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Changes in the Peeled Surfaces of Copper Thin Films Deposited on Polyimide Substrates After Heat Treatment

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(Received 15 October 1996; In final form 2 January 1997)

Peel strength between a copper (Cu) thin film and a polyimide (pyromellitic dianhydride-oxydianiline, or PMDA-ODA) substrate is reduced by heat treatment at 150°C in air. In this work, we investigated the peel strength, the morphology of the interface between Cu films and polyimide substrates using optical microscopy and electron microscopy, and chemical change of the interface using Auger electron spectroscopy (AES) and micro X-ray photoelectron spectroscopy (XPS). The analysis showed that CuO "lumps" were present on the peeled surface of PMDA-ODA after heat treatment at 150°C in air. The peeled surfaces of other polyimide substrates were also analyzed: biphenyl dianhydride-para phenylene diamine (BPDA-PDA) and biphenyl dianhydride-oxydianiline (BPDA-ODA). CuO lumps were present on the peeled surface of BPDA-ODA after the heat treatment, but not that of BPDA-PDA. Compared with the adhesion strength for the Cu thin film, the adhesion strength was high for the Cu/PMDA-ODA and Cu/BPDA-ODA laminates, but the adhesion strength was very low for the Cu/BPDA-PDA laminate. This low strength is the reason that CuO lumps were not detected on the peeled surface of the BPDA-PDA substrate. These CuO lumps were related to the adhesion degradation of the Cu/polyimide laminates after the heat treatment.

Keywords: Copper; polyimide; adhesion strength; copper particle; heat treatment; peeled surface

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INTRODUCTION

Polyimides (PI) have good thermal stability, chemical stability, and excellent mechanical properties such as a high modulus of elasticity. For these reasons, copper (Cu)-coated PI films are commonly used as printed circuit boards (PCBs). Without pre-treatment, such as plasma treatment, Cu/PI laminates do not have sufficient peel strength between Cu and PI. Inagaki *et al.* [1,2] reported that the peel strength between Cu and PI is improved by a plasma pre-treatment with either NO or N_2O gas [1,2].

Cu-coated PI films have a serious drawback, however, in that the peel strength between Cu and PI is reduced after heat treatment at 150°C in air. Chambers *et al.* [3] reported that Cu atoms in contact with a PI overlayer are completely oxidized to CuO after being exposed to air for several days. Shih *et al.* [4] reported that Cu catalyzes the oxidation of PI films after heat treatment at 350°C for 1 hr in air. Burrel *et al.* [5] also reported that Cu catalyzed the oxidation of PI films in air. Chambers *et al.* [6] reported that metal oxidation in Cu-coated PI films is accompanied by Cu diffusion into PI and PI decomposition after being exposed to high humidity (85% RH air at 85°C. Despite extensive research on Cu/PI films, there are few reports on the relationship between their peel strength and the morphology of the peeled surface. In this work, we therefore determined the effect of heat treatment on the adhesion degradation of Cu/PI laminates as well as on the morphology of the peeled surfaces and on the chemistry of the Cu/PI interface.

MATERIALS AND METHODS

The PI substrates used were Kapton-V (PMDA-ODA, TORAY-du Pont Chemical), Upilex-R (BPDA-ODA, Ubekousan), and Upilex-S (BPDA-PDA, Ubekousan). Figure 1 shows the structural formulas of these substrates. Figure 2 shows a schematic of the sputtering system (HSM-521, Shimazu Co. Ltd.) used to deposit Cu on the PI substrates. Table I lists the conditions for the pre-treatment by O_2 plasma and Cu sputtering. A 0.03-mm-thick layer of Cu was plated up on the Cu-sputtered thin film. This Cu layer was then patterned using a $FeCl_3$ solution and

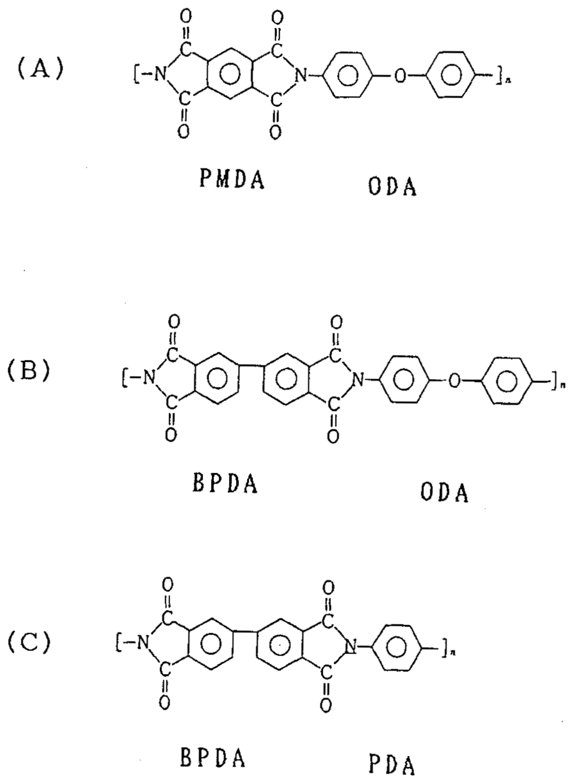


FIGURE 1 Structural formulas of the polyimides used as substrates in copper/polyimide laminates. (A) Kapton-V (PMDA-ODA), (B) Upilex-R (BPDA-ODA), and (C) Upilex-S (BPDA-PDA).

2-mm-wide IC tapes as resists. After the patterning, the Cu thin film was heat-treated at 150°C in air for either 24 hr, 48 hr, or 72 hr.

The peel strength of each laminate was measured by the 180°C peel test method [7] using a STROGRAPH M1 (Toyo-seiki, Inc.) with a crosshead speed of 50 mm/min. The peeled surfaces were analysed by Auger electron spectroscopy (AES), cross-sectional transmission electron microscopy (TEM), optical microscopy, and micro X-ray photoelectron spectroscopy (XPS). The micro XPS analysis was done using a Quantum 2000 (Physical Electronics, Inc.) with a spot size of 0.1 mm. The composition of the peeled surfaces of the Cu-side for each laminate was measured using AES in which an MH93-4001 Auger Spectrometer (Perkin-Elmer) was installed in the UHV chamber

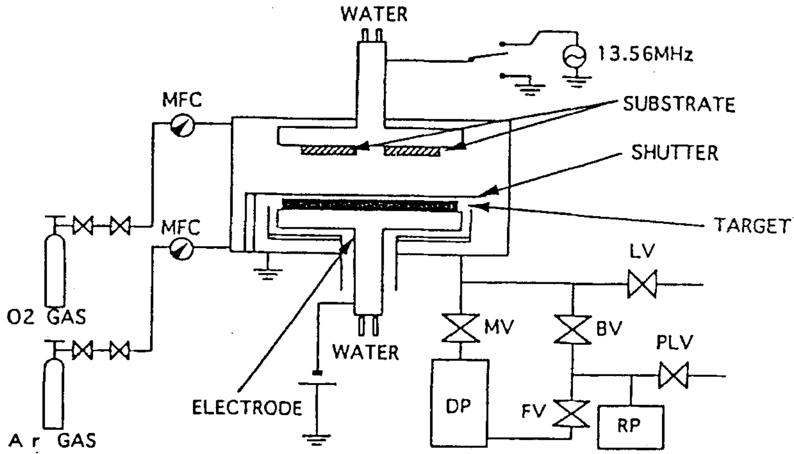


FIGURE 2 Schematic of sputtering apparatus used to deposit copper (Cu) on polyimide (PI) substrates.

TABLE I Experimental conditions of plasma treatment and copper deposition

	Plasma treatment	*Copper deposition*
Gas	O_2	Ar
Flow rate	10 sccm	10 sccm
Pressure	6.7 Pa	0.27 Pa
RF Power	400 W	160 W
Time	5 min	10 min

(2×10^{-8} Pa). The bright spots on the peeled PI surface were measured with an optical profilometer, WYKO HD-2000 (WYKO Co Ltd.), which is the standard for non-contact 3D magnetic head and disk testing.

RESULTS AND DISCUSSION

Table II shows the measured peel strengths for the three PI laminates with and without the O_2-plasma treatment. The results show that without this plasma treatment, the peel strength of all the laminates was less than 10 mN/m, but with this plasma treatment the peel strength increased to values of 20–100 mN/m. These results mean that

TABLE II Peel Strengths (mN/m) for three Cu/PI laminates with or without O_2 plasma treatment

Polyimides	*with plasma*	*without plasma*
PMDA-ODA	100 ± 20	10 ± 5
BPDA-DADE	80 ± 10	0
BPDA-PDA	20 ± 5	0

O_2-plasma treatment is effective in improving the peel strength. Table III shows the peel strength of unheated and 24-hr heat-treated (150°C in air) samples of the Cu/PI laminates. The results show that even if a PMDA-ODA substrate was treated with O_2 plasma, the peel strength was still reduced by the heat treatment.

Figure 3 shows a TEM micrograph of the interface for the PMDA-ODA substrate after heat treatment. A high concentration of small particles (10–100 nm) were dispersed in the PI. Electron beam diffraction patterns show these particles to be Cu_2O. Figure 4A shows an optical micrograph of the peeled surface at the Cu-side before heat treatment, and Figures 4B, 4C, and 4D show those after heat treatment at 150°C in air for 24 hr, 48 hr, and 72 hr, respectively. The heat-treated samples had many bright spots whose size increased with heat-treatment time and reached a diameter of 2000 to 25000 nm (Fig. 4D). Spots of the same diameter were also detected on the peeled PI surface (data not shown).

Figure 5 shows the distribution of carbon (C), nitrogen (N), oxygen (O), and Cu at the peeled Cu surface of the Cu/PMDA-ODA laminate as a function of heat-treatment time (150°C in air). C, N, and O, which all originated from the PI, were reduced by the heat treatment, whereas Cu increased. This result coincides with those in Figure 4, and indicates that area of the Cu attached to the peeled PI surface increased with heat-treatment time at 150°C in air.

TABLE III Peel Strengths (mN/m) of unheated and 24 hr heat treated samples of three Cu/PI laminates

Polyimides	*unheated*	*24 hr heat treated*
PMDA-ODA	100 ± 20	25 ± 10
BPDA-DADE	80 ± 10	30 ± 10
BPDA-PDA	20 ± 5	5 ± 5

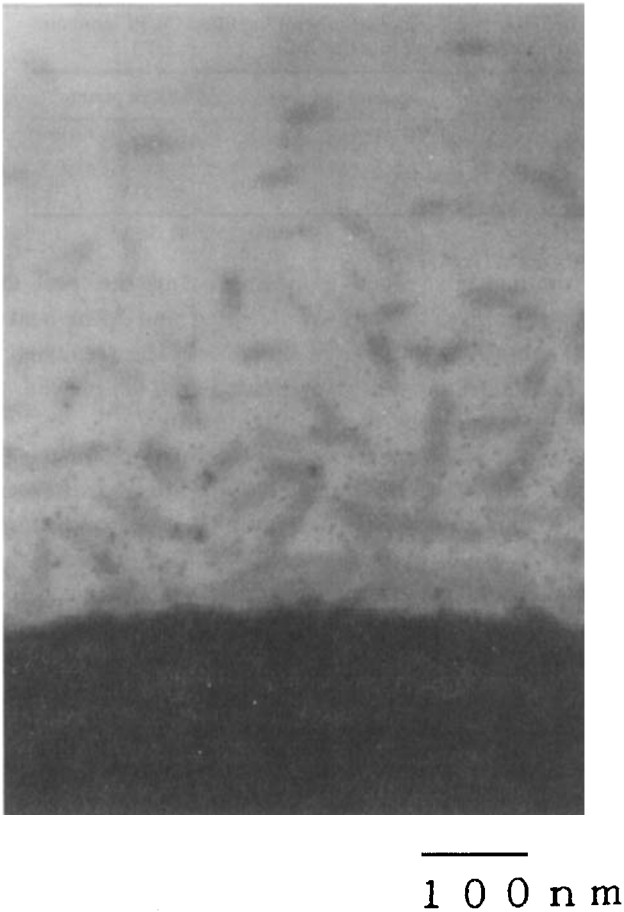


FIGURE 3 TEM micrograph of the interface of a Cu/PMDA-ODA laminate after heat treatment at 150°C in air.

We used micro XPS to determine the composition of the bright spots seen in Figures 4D and 4B. As a typical example, the bright spots on the peeled PI surface in Figure 4D were investigated (Fig 6A). The XPS result shows the spots to be metallic Cu because no chemical shifts of Cu can be recognized in the range from 930 to 950 eV (indicated with arrows). Figure 6B shows the spots on the peeled Cu surface in Figure 4B to be CuO or Cu_2O because chemical shifts were recognized in the range from 930 to 950 eV. These results indicate that

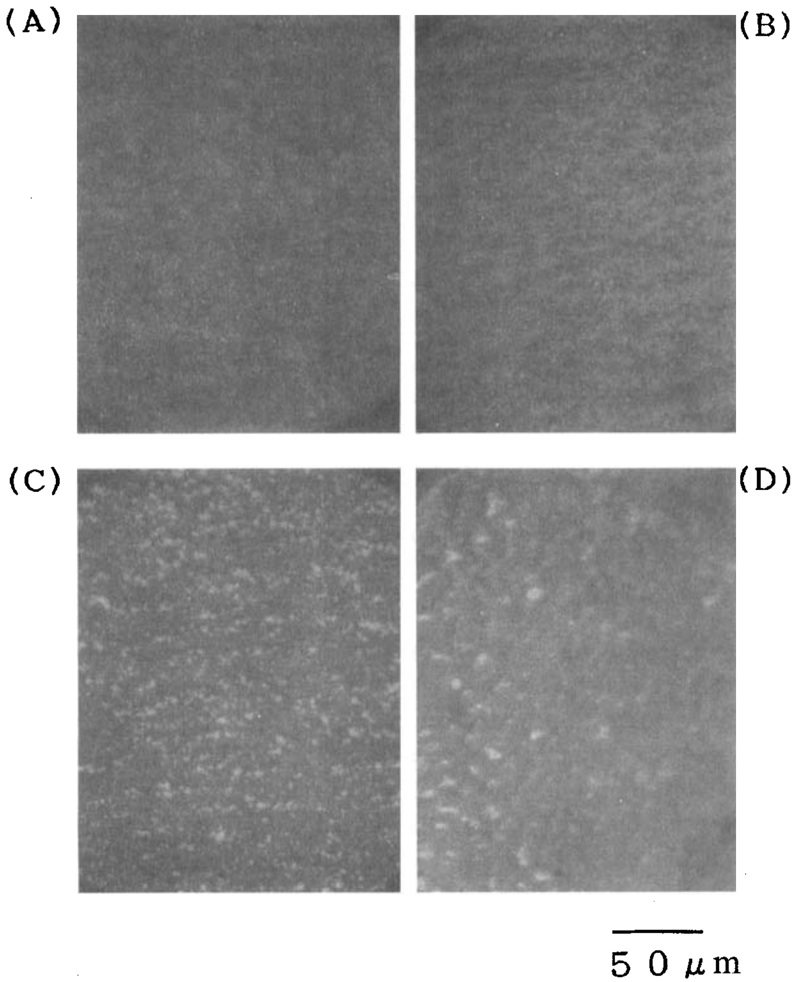


FIGURE 4 Optical micrograph of a peeled PI surface in a Cu/PMDA-ODA laminate: (A) before heat treatment, (B) after heat treatment at 150°C in air for 24 hr, (C) for 48 hr, and (D) for 72 hr.

the Cu oxidation at the interface did not occur after the peel experiment due to exposure to ambient oxygen.

Figures 7A and 7B show the peeled PI surfaces of the Cu/BPDA-ODA laminate before and after heat treatment (at 150°C in air), respectively. No bright spots were detected on the unheated sample (Fig. 7A), whereas, similar to the Cu/PMDA-ODA laminates (Figs. 4B,

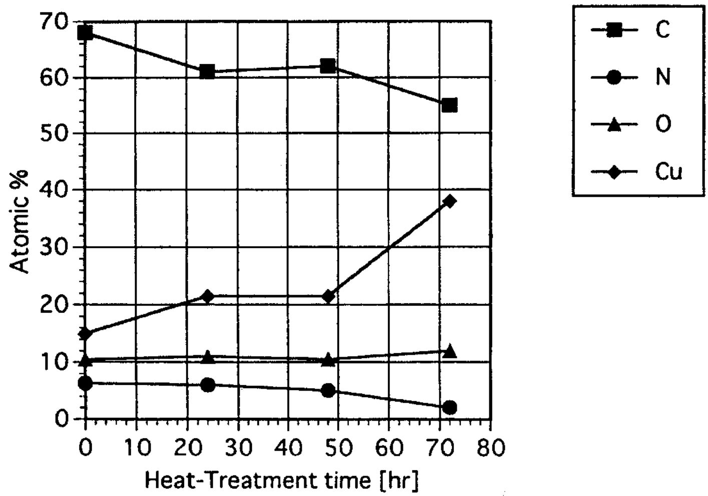
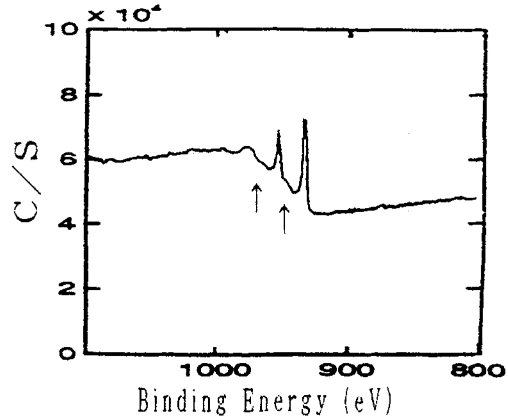


FIGURE 5 AES analysis of carbon (C), nitrogen (N), oxygen (O), and copper (Cu) on the peeled Cu surface of a Cu/PMDA-ODA laminate.

4C and 4D) many spots were detected on the heat-treated sample. Figures 8A and 8B show the peeled PI surfaces of the Cu/BPDA-PDA laminates before and after heat treatment (at 150°C in air), respectively. No bright spots were detected in either laminate. This phenomenon is presumed to be due to the low peel strength (poor adhesion) between the Cu and BPDA-PDA substrate.

The attachment mechanism of the Cu "lumps" on these peeled PI surfaces (bright spots in Figs. 4B, 4C, and 4D) may be Cu_2O particles diffusing into the PI layer. A metallic Cu atom in the Cu layer diffuses into the PI layer as Cu_2O, or a metallic Cu atom in the Cu layer is oxidized as Cu_2O and diffuses into the PI layer. For one of the possibilities, this diffusion may cause areas of both low density in which many vacancies are generated in the Cu layer, and high density in which few vacancies are generated in the Cu layer. These areas of low and high density explain the variations in uniformity of the Cu layer at the interface. The high-density areas generate the Cu bright spots on the peeled surface. This phenomenon is similar to the Kirkendall effect, where voids are produced by a high concentration of atoms moving to fill vacancies [8]. To confirm this, the bright spots were investigated with the WYKO profilometer. Figures 9A and 9B

(A)



(B)

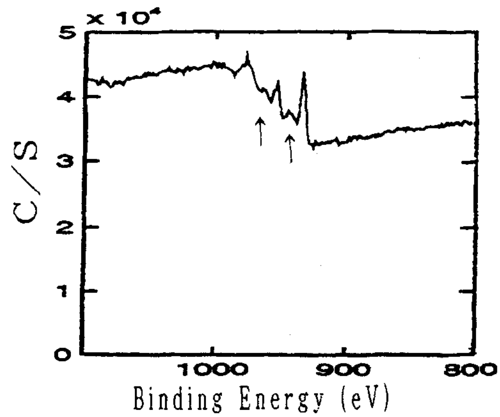


FIGURE 6 Micro XPS analysis of Cu/PMDA-ODA laminate (A) after heat treatment for 72 hr, and (B) after heat treatment for 24 hr.

show 2-D and 3-D topographies of the peeled PI surface treated at 150°C in air for 3 days. The bright spots in these figures correspond to the bright spots in the optical microscope observation (Figs. 4B, 4C and 4D). The arrows indicate one of the spots, whose height was estimated. Figures 9C and 9D show the sectional plans for X-axis and Y-axis, respectively. Taking into consideration that the roughness of O_2-plasma-treated PI surface is 4 nm, the bright spot indicated with arrow was a hillock with a height of about 70 nm.

Compared with the electrical potential of water and Cu and 150°C in air, both O and water can act as oxidizers for Cu. Furman *et al.* [9]

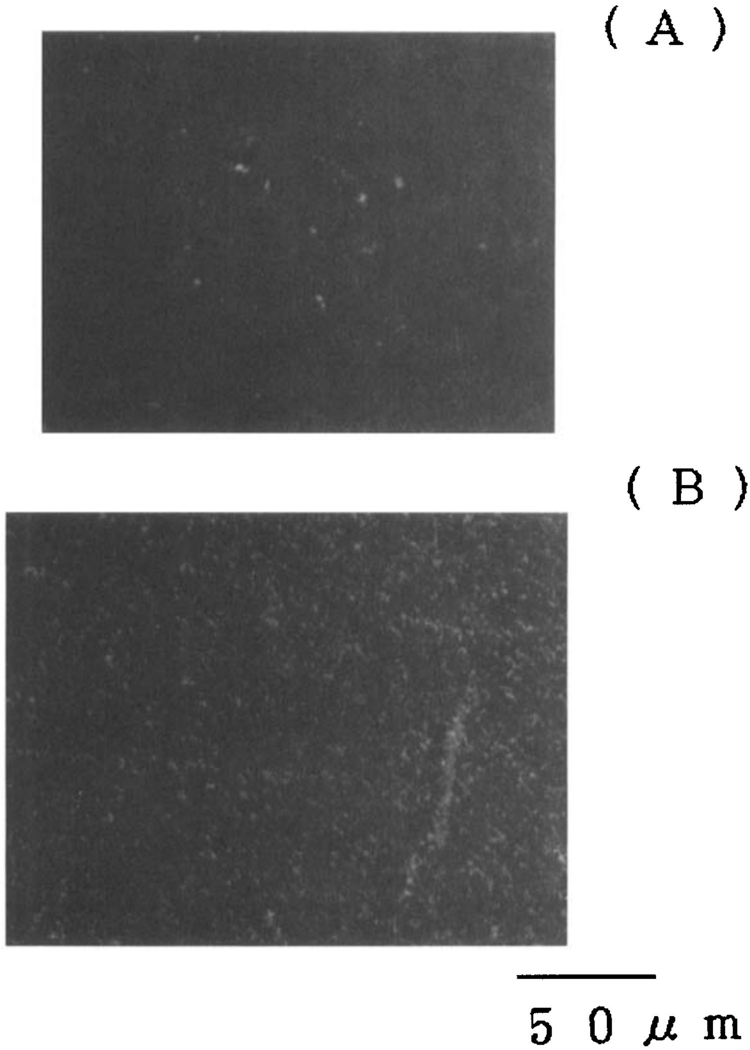


FIGURE 7 Optical micrograph of a peeled PI surface of a Cu/BPDA-ODA laminate: (A) before heat treatment and (B) after heat treatment at 150°C in air for 24 hr.

reported that the slight adhesion degradation of a Cu/Cr/PI laminate is possibly due to water reaction and hydrothermal weakening of the polyimide surface during a thermal cycle at 350–400°C. Though our system is different from theirs, our results are similar, in that not only O but also water may participate in the oxidation of Cu.

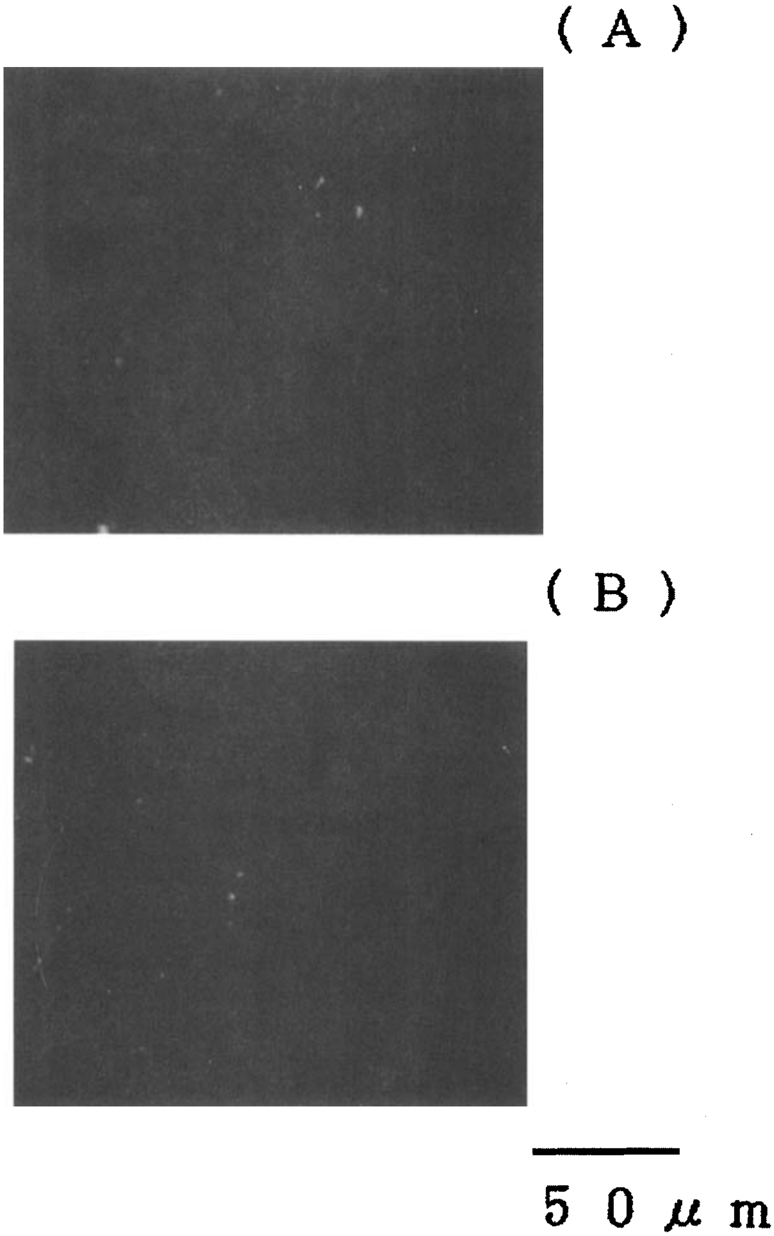


FIGURE 8 Optical micrograph of a peeled PI surface of a Cu/BPDA-PDA laminate: (A) before heat treatment and (B) after heat treatment at 150°C in air for 24 hr.

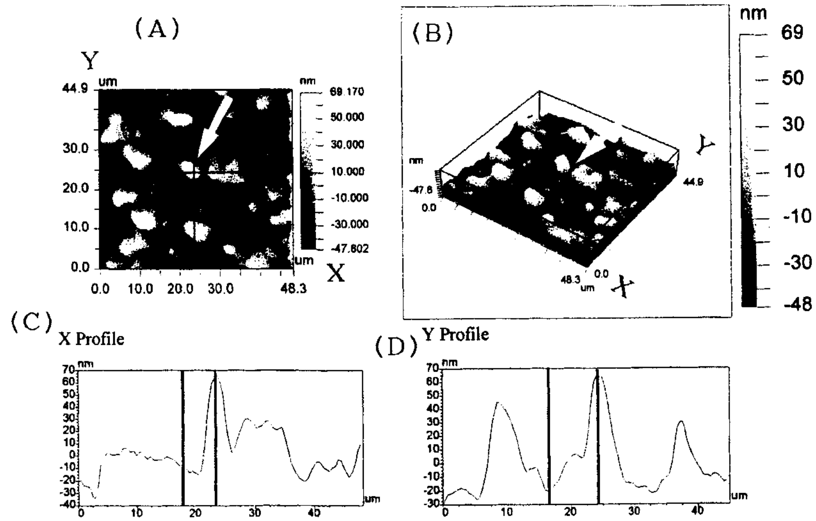


FIGURE 9 The topographies of the Cu bright spots on the peeled PI surface treated at 150 °C in air for 3 days. (A) and (B) show 2-D and 3-D topographies of these surfaces. (C) and (D) show the sectional plans for X-axis and Y-axis, respectively.

CONCLUSIONS

In a Cu thin film sputtered on a PI substrate (PMDA-ODA or BPDA-ODA), Cu "lumps" were found on the peeled surface after the laminate was heat-treated at 150°C in air. The concentration of these lumps increased with heat-treatment time.

In contrast, no Cu lumps were found on the peeled surface of a Cu/BPDA-PDA laminate even when it was heat-treated at 150°C in air. This is due to the low adhesion between Cu and this PI substrate.

These Cu lumps are somehow related to the adhesion degradation of the Cu/PI laminates after heat treatment.

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