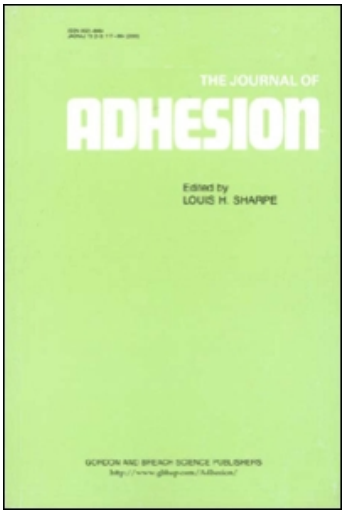

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A New Approach to the Copper/Epoxy Joint Using Atmospheric Pressure Glow Discharge

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A new approach for adhering copper to an epoxy resin was studied. In this new approach, the copper surface was first treated with hydrogen plasma generated by the atmospheric pressure glow (APG) discharge. Then a thin film of γ-aminopropyltriethoxysilane (γ-APS) was formed on the treated copper surface. The copper oxide formed by air on the copper surface deteriorated the adhesion by forming a weak boundary layer, part of which could separate from the surface. This oxide layer was reduced when an APG hydrogen plasma was applied for a couple of minutes at a frequency of 13.56 MHz and a power input of 200 W. The resulting peel strength at the copper/epoxy interface increased up to *ca.* 0.9 Kg/cm. Curing temperature of γ-APS was also an important factor in obtaining good adhesion at the copper/epoxy interface, with the highest value of peel strength occurring at a curing temperature of 120°C.

KEY WORDS adhesion; strength; copper; epoxy; hydrogen plasma; reduction; copper oxide; atmospheric pressure glow; γ-APS.

INTRODUCTION

Obtaining good adhesion between copper and a resin matrix has recently become a significant subject in manufacturing electronic components, such as microelectronic devices and printed circuit boards. Therefore, much work has been done to understand the mechanism of adhesion at the copper/resin interface. Burkstrand studied, by X-ray photoelectron spectroscopy (XPS), the metal/polymer interfaces formed by evaporated metals such as copper, nickel, and chromium and found that oxygen-containing polymers formed metal-oxygen chelate complexes at the interfaces, causing an increase in adhesion strength.[1] Kim *et al.* studied the interfacial structure between copper and polyimide prepared by spin-coating. By cross-sectional TEM observation, they revealed very fine Cu-rich particles distributed in the polyimide.[2] In addition, much work on improving adhesion between the copper surface and polymers has recently been reported. There have been many reports that the chemically-formed copper oxide on copper surfaces, the so-called black and red/bronze oxide, improved adhesion with epoxy resin, which is utilized as a practical method for manufacturing printed circuit

boards.[3-5] Nakamura *et al.* studied the treatment of copper surfaces by triazine thiols, and found that the treated copper foil improved adhesion with glass-reinforced epoxy prepregs.[6]

Since the standard Gibbs energy of formation for copper oxide is a large negative value, copper is easily oxidized in air to form a thin copper oxide layer. Chemically-formed copper oxide, such as black oxide, has a microfibrous topography and adheres well to a resin matrix. On the other hand, it is thought that the copper oxide formed in air is mechanically weak.[7] In this work, we investigated the influence of the oxide layer formed on copper foils upon adhesion to an epoxy resin, and found that increasing the thickness of this layer weakened the adhesion strength. Furthermore, we established a new method for creating a copper/epoxy joint by treating the copper surface with hydrogen plasma generated by an atmospheric pressure glow (APG) discharge, and then forming a thin film of a coupling agent on the treated surface.

The APG discharge method is a new and practical technology which generates a stable glow discharge at atmospheric pressure with three simple requirements: (i) use of a source frequency of over 1 kHz, (ii) insertion of a dielectric plate (or plates) between two metal electrodes, (iii) use of helium or argon as a diluent gas.[8] Thin film formation and surface modification by glow discharge at atmospheric pressure were easily attained using the APG discharge method.[9] Before this method was developed, these had only been possible in a high vacuum condition. In the APG discharge, reactive species are excited to radicals by helium or argon atoms at metastable energy states – the Penning effect. We found that hydrogen, which has a high dissociation energy, was dissociated by the APG discharge of helium, and the resulting hydrogen plasma effectively reduced the oxide layer on the copper surface, creating a strong adhesion with epoxy resin.

2 EXPERIMENTAL

2.1 Treatment of the Copper Foil Clad Sheets

The samples used for this study were commercial copper foil clad sheets for printed circuit boards (1.0 mm in thickness). These boards had copper foil of 35 μm in thickness on both sides of a glass-reinforced epoxy sheet. Prior to treatment, the surface of the copper foil was mechanically polished to clean up contamination and remove the corrosion inhibitor. The average peak-to-valley height (roughness) of the foil after polishing was 3.0 μm. To study the influence of the surface oxide layer, the sheets were preheated to various temperatures using an oven. They were then dipped, after cooling, into the coupling agent solution, γ-aminopropyltriethoxysilane (γ-APS), diluted with deionized water or isopropyl alcohol (IPA) of a guaranteed grade at a concentration of 2 wt%, for 1 minute and dried at normal laboratory conditions. The sheets were then re-heated in the oven to cure the coupling agent on the copper foil. To evaluate the adhesive properties of a sample, two sheets of partially-cured epoxy impregnated glass cloth (prepreg; 0.15 mm in thickness) and a copper foil (18 μm in thickness) were laminated on both sides of the treated sheet. Then, the lamination was compressed in two stages-1) at a pressure of 0.5 MPa and temperature of 120°C for 20 minutes to melt the epoxy resin of the prepreg; 2) at a pressure of 4 MPa and temperature of 170°C for

90 minutes to harden the resin. The laminated sample was cut into 10-mm wide peel strips using a blade saw. The hardened resin of each sample was then manually stripped with a knife to expose the surface-treated copper layer. The adhesion strength at the copper/epoxy interface was evaluated by a 90° peel test with a constant crosshead speed of 50 mm/min using a tensile tester.

2.2 Surface Treatment by The APG Discharge

The effect of hydrogen plasma treatment prior to the coupling agent treatment on the adhesion strength was investigated for the copper foil clad sheets preheated to various temperatures. A schematic of the experimental apparatus is shown in Figure 1. The purities of the helium and hydrogen gases were more than 99.9999 and 99.999%, respectively. The parallel plate electrodes had dielectric plates placed on their inner surfaces. The distance between the dielectric plates was 5 mm. A 7 × 7 cm copper foil clad sheet was placed on the lower dielectric plate. Prior to the experiment, the reactor pressure was lowered below 0.05 Torr by a rotary pump, then the mixture gas was introduced to atmospheric pressure. To introduce the mixed gas into the plasma zone, a U-shaped glass tube with both ends closed and holes of 1 mm diameter every 5 mm along the tube was used. The experimental conditions of the plasma treatment were as follows:

Frequency : 13.56 MHz
Power input : 200 W
Helium flow rate : 5000 cm^3/min
Hydrogen flow rate : 50 cm^3/min

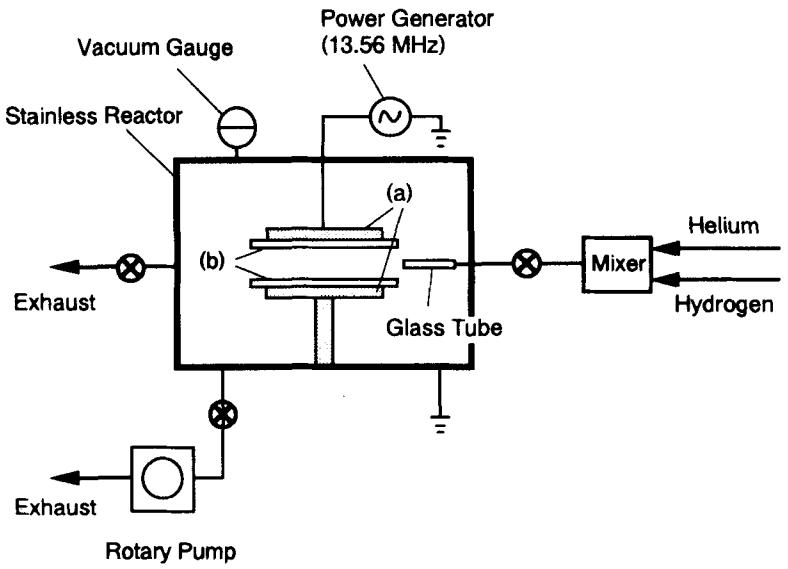

FIGURE 1 Diagram of the experimental apparatus. (a) Upper and Lower Electrodes, (Brass, 100 mm in diameter) (b) Dielectric Plates (Insulator) (Pyrex, 130 mm in diameter and 1 mm in thickness).

2.3 Surface Characterization

In order to investigate the reduction of the oxide layer and the composition of the fracture surface after peel tests, XPS and Auger electron spectroscopy (AES) were performed with an XPS analyzer (Fisons Instruments Surface Science, UK, ESCALAB 220i-XL). MgKα radiation ($E = 1242.6$ eV) was employed as the X-ray source. IR measurements for the γ-APS film on the copper foil clad sheets were performed with an FT-IR spectrophotometer (Nicolet Instrument Co., Ltd, USA, 160 SX). Quantitative concentration analysis of Cu ions in an aqueous solution of γ-APS was made by inductively-coupled plasma (ICP) atomic emission spectrum analysis with an ICP spectrometer (Nippon Jarrell-Ash Co., Ltd, Japan, ICAP575-Mark II). Phase analysis of thin Cu layers was performed with an X-ray diffractometer (Rigaku Denki Co., Ltd, Japan, RU-200) operated at 50 kV and 160 mA using CuKα radiation with an X-ray radiation angle of 1°.

3 RESULTS AND DISCUSSION

3.1 The Influence of the Oxide Layer on Adhesion

Figure 2 shows the relationship between the preheat temperature of the copper foil clad sheets and the peel strengths of the laminated samples. The thicknesses of the oxide

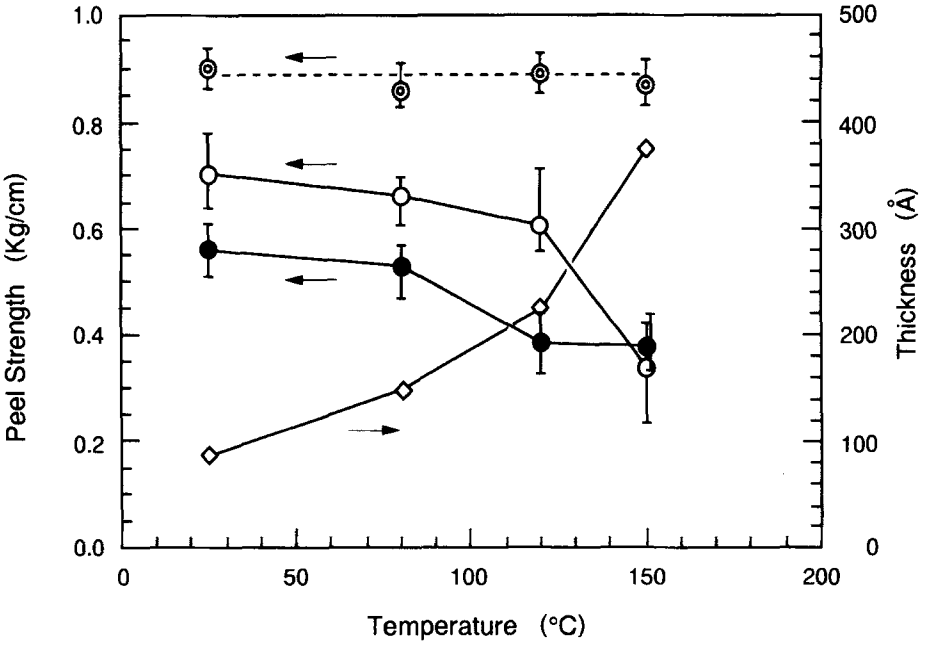

FIGURE 2 Peel strength and thickness of oxide layers expressed as a function of preheat temperature. (○): solvent of γ-APS was deionized water. (●): Solvent was IPA. (◎): Plasma treatment was performed for 5 minutes after preheating at each temperature. Solvent was deionized water. (◇): Thickness of oxide layers formed on the copper foil clad sheets.

layers formed on the copper foils, analyzed by XPS, are also shown in this figure. The thickness was determined by comparison with standard samples (sputtered Cu_2O film on a silicon wafer, 2000 Å in thickness). These results show that as the preheat temperature increased, the thickness of the surface oxide layer increased, lowering the peel strength. Notice that when using IPA as a solvent for γ-APS, the peel strength of the laminated samples was lower than that with the deionized water. This may be attributed to the difference in the degree of hydrolysis of γ-APS. Furthermore, the dotted line in this figure shows the peel strengths of the laminated samples in which the copper foil was treated with the APG hydrogen plasma for 5 minutes after preheating at each temperature. It is obvious that the peel strength of these laminated samples – which were made from copper foil clad sheets preheated at different temperatures – recovered to the same level, *ca.* 0.9 Kg/cm. This level is comparable with the peel strength obtained with the conventional black oxide treatment (0.9–1.2 Kg/cm).[5] The effect of the APG hydrogen plasma on the adhesion improvement will be discussed later on.

It is known that iron and aluminum oxide are dissolved into γ-APS solution due to the decomposition of the oxides by the amine.[10] Therefore, we investigated the dissolution of copper ions from the copper foil into the γ-APS solution. The copper foil clad sheets preheated at room temperature, 80, 120, and 150°C, were cut into 6 × 3 cm sections and each was immersed in 100 cc of 2 wt% γ-APS aqueous solution. The solution containing each sheet was then stirred for 60 minutes using a magnetic stirrer. The pH of the aqueous solution was 10.8 prior to the immersion, and was not changed after stirring. Table I shows the resulting concentrations of the copper ion. The results indicate that there was no significant difference in the dissolution of the copper ion among the copper foil clad sheets preheated even at different temperatures.

Table II shows the XPS analysis for both the copper and resin sides of the fracture surfaces after the peel tests of the laminated samples made from copper foil clad sheets which were either previously preheated to 150°C for 3 hours in the oven (peel strength was 0.33 Kg/cm) or treated by the APG hydrogen plasma (0.90 Kg/cm). The amount of copper detected on the copper side of the former sample was higher than the latter by more than a factor of 10, and the amount of silicon and nitrogen – constitutive elements of the coupling agent – were also high. However, the amount of carbon and bromine-constitutive elements of the prepreg – were small. From these results, it is estimated that the fracture of the laminated sample made from copper foil clad sheet preheated to

TABLE I
Copper concentration in 2 wt% γ-APS aqueous solutions

Heating conditions of copper foil clad sheets	Copper conc. (ppm)
Control solution	< 0.1
Room temp.	61
80°C for 3 hrs.	56
120°C for 3 hrs.	60
150°C for 3 hrs.	55

TABLE II
The results of the XPS analyses of both the copper and resin sides of the fracture surfaces after peel tests

Treatment of copper foils	Peel strength (Kg/cm)	Atomic concentration of elements (%)											
		Copper side						Resin side					
		C	N	O	Cu	Br	Si	C	N	O	Cu	Br	Si
Preheating to 150°C for 3 hrs.	0.33	52.33	6.18	15.89	22.96	0.82	1.82	48.82	7.07	14.88	21.11	4.22	3.91
Plasma treatment for 5 min.	0.90	92.98	0.78	2.81	1.47	1.17	0.80	85.46	2.09	7.91	1.42	1.95	1.17

150°C occurred near the copper/coupling agent interface. On the other hand, for the laminated sample made from copper foil clad sheet treated by the APG hydrogen plasma, less copper was detected on the copper side of the fracture surface. This shows that the fracture mainly occurred in the epoxy resin, which obscured the signal of copper in the XPS analysis. Therefore, it is thought that the plasma treatment increased the joint strength at the interface between the copper and the epoxy surface.

The XPS analysis on the resin side of the fracture surface showed a large amount of copper for the sample preheated to 150°C. Furthermore, the binding energy of the copper peak of this sample was 3 eV higher than that of copper metal, and the O(1s) spectrum was split into peaks at 532.0 and 530.4 eV. The latter oxygen peak is due to Cu_2O. These results indicate that the oxide layer formed a weak boundary, part of which remained on the resin side after the peel test.

3.2 FT-IR Analysis of γ-APS Films

The curing condition of γ-APS was also an important factor in obtaining high adhesion strength at the interface. Figure 3 shows the relationship between the curing temperature of the coupling agent and the peel strength. Each sample that had not been preheated was plasma-treated for 5 minutes before being dipped in the coupling agent. The highest peel strength was obtained at a curing temperature of 120°C. It is noteworthy that the variation of the data was minimal at this temperature. In this study, a curing temperature of 120°C was used.

An FT-IR analysis for γ-APS thin films on the copper foil clad sheets- which had been cured at several temperatures- was performed. The results are shown in Figure 4. As the curing temperature increased, the peak at 2930 cm^{-1} (C-H stretching) diminished, while those at 1130 and 1060 cm^{-1} (Si-O-Si stretching) broadened and split. These results show that the coupling agent was condensed and three-dimensionally crosslinked to have an inorganic characteristic. Furthermore, the peak at 1570 cm^{-1} (NH_3) diminished, and the one at 1660 cm^{-1} (C = N stretching) became pronounced. Culler *et al.* reported that these changes were assumed to be based on the following reaction: the bicarbonate salt ($RNH_3^+ HCO_3^-$) was formed by the reaction of the primary amine in γ-APS with the H_2O remaining in the film and the CO_2 from the air. Then, the bicarbonate salt was deformed and converted to an imine (RCH = NH) by

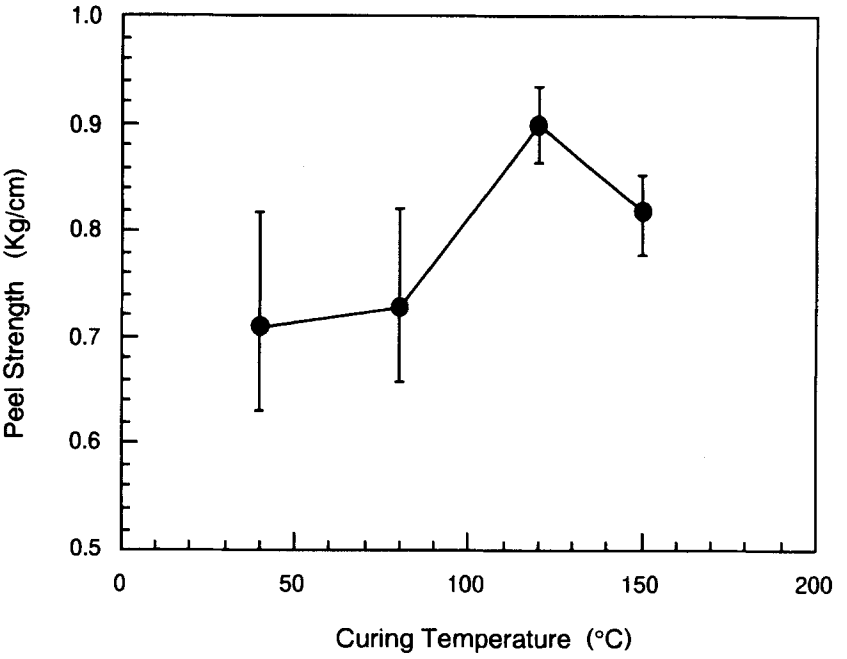

FIGURE 3 Peel strength expressed as a function of curing temperature of γ-APS. The samples were not preheated but plasma- treated for 5 minutes previously.

heating.[11] They also stated that the formation of the imine and high cross-linkage of γ-APS would decrease the reactivity of the coupling agent with epoxy resins. In this study, the peel strength of the laminated sample made from the copper foil clad sheet cured at 120°C was the highest, although the formation of imine was recognized and the coupling agent acquired an inorganic characteristic, which may be due to the strength of the coupling agent.

In this study, the γ-APS film was thick (approximately 500–800 Å). With the increase of the curing temperature, γ-APS was condensed and three-dimensionally crosslinked to have inorganic characteristics, increasing the strength of the layer and decreasing the probability of fracture within this layer. Further increase of the curing temperature, however, may result in the deterioration of peel strength because of the above-mentioned deformation of the coupling agent.

3.3 The Effect of the APG Treatment on the Copper/Epoxy Joint

In order to obtain strong adhesion at the copper/epoxy resin interface, the effect of the APG hydrogen plasma for reducing the surface oxide layer of the copper foil was investigated. In the APG discharge, a fraction of the helium atoms is excited by a high frequency power input to metastable helium radicals with an energy as high as 19.8 or 20.7 eV. The dissociation energy of hydrogen is 13.6 eV, and the energy of the

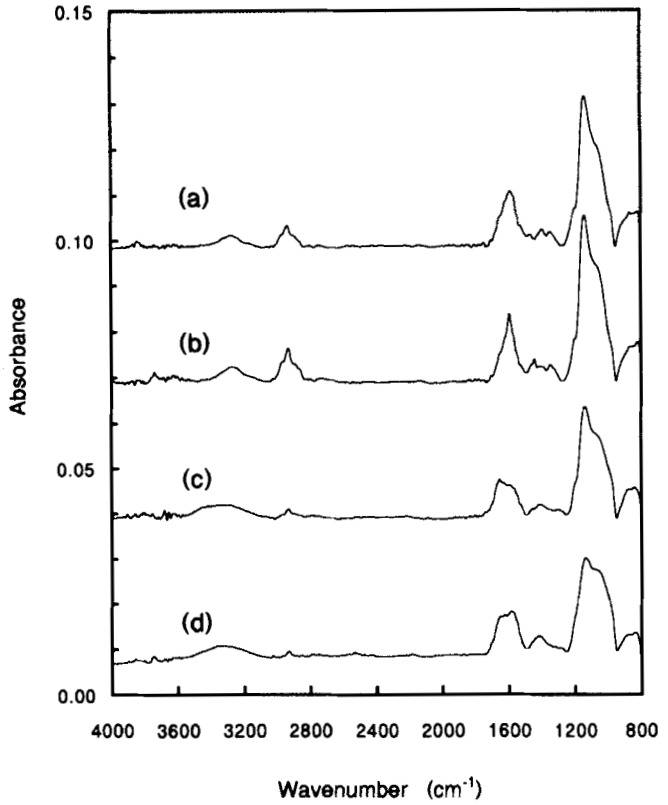

FIGURE 4 FT-IR spectra of the γ-APS films on the copper foil clad sheets. The samples were cured for 3 hours at temperatures of (a) 40°C , (b) 80°C, (c) 120°C and (d) 150°C.

metastable helium radicals is high enough to dissociate hydrogen. By analyzing the spectra of the APG discharge during an experiment, the emission at 656.3 nm based on the hydrogen radicals was observed as well as emissions based on the helium radicals. These radicals are thought to be produced by the above-mentioned Penning reaction between the hydrogen atoms and metastable helium radicals.

Figure 5 shows the peel strengths of the laminated samples made from copper foil clad sheets preheated to 150°C for 3 hours as a function of the time of the APG hydrogen plasma treatment. Notice that the peel strength increases with the plasma treatment time. The AES of the copper surface in Figure 6 shows that the copper oxide layer formed by the preheat to 150°C was Cu_2O and that the layer was reduced to copper metal by the APG hydrogen plasma treatment. Comparing Figure 5 with Figure 6 shows that the recovery of the peel strength coincided with the reduction of the surface oxide layer.

In order to investigate the details of the reduction behavior of the surface copper oxide layer, we prepared copper films by sputtering on silicon wafers at a base pressure of approximately 2×10^{-7} Torr. These samples were preheated to 150°C for 3 hours,

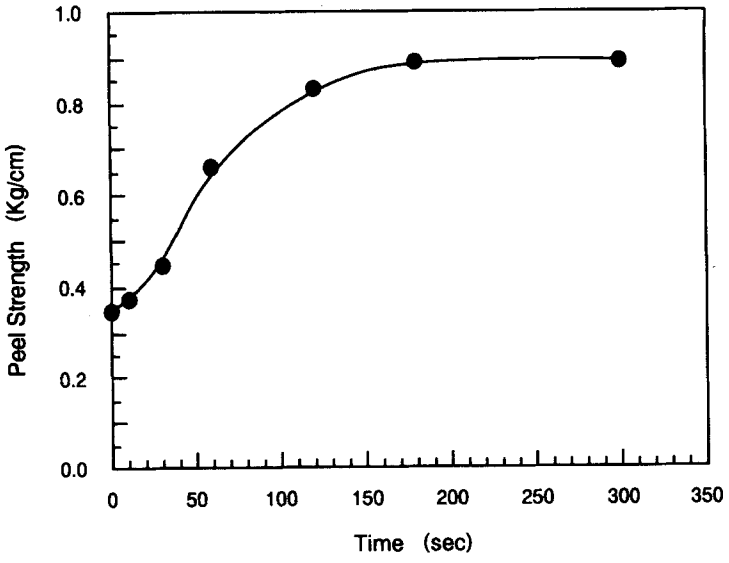

FIGURE 5 Peel strength expressed as a function of the plasma treatment time of the copper foil clad sheets. The samples were preheated to 150°C for 3 hours.

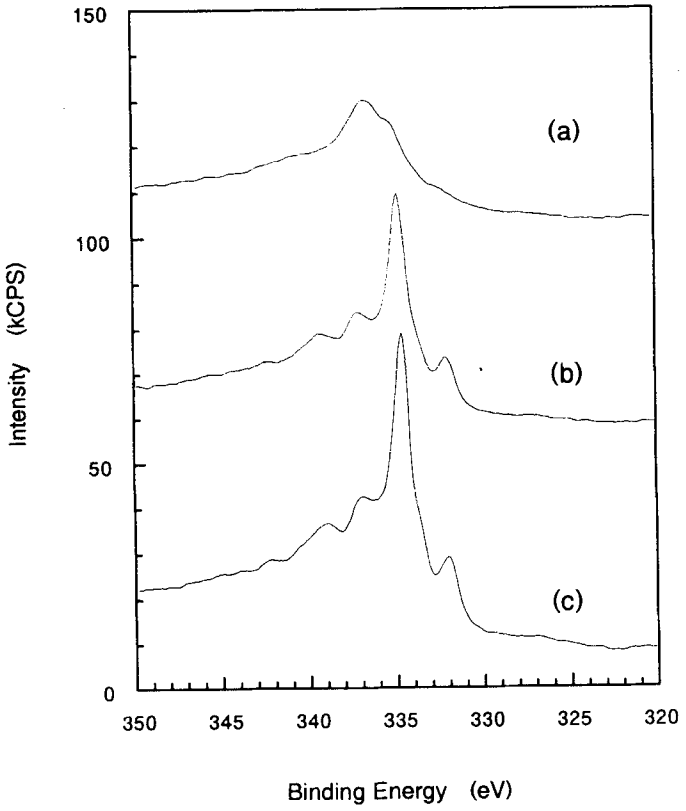

FIGURE 6 Cu (LMM) Auger electron spectra at the surfaces of the copper foils. The samples were preheated to 150°C for 3 hours and plasma-treated for (a) 0 min, (b) 0.5 min and (c) 2 min.

and XRD and XPS analyses of the surface layer within 1000 angstroms from the top surface were performed. The XRD analysis showed no crystalline material except copper in this layer. From the results of the XPS analysis, it was found that the oxide layer was several hundred angstroms in thickness, through which the level of oxygen present gradually decreased. The weak boundary layer formation may be caused by these oxygen atoms intruding into copper atoms and deforming the crystal structure. The XPS analysis also showed that the reduction occurred first on the surface, and then proceeded from the surface to the inner part of the oxide layer. Eventually, the whole layer recovered its original state of copper metal, and the peel strength was restored.

4 CONCLUSION

Peel strength at the copper/epoxy interface was improved up to *ca.* 0.9 Kg/cm by treating the copper oxide surface with the APG hydrogen plasma and by forming a thin film of γ-APS on the treated surface. It was found that the peel strength deteriorated when a copper oxide layer formed on the copper surface. This layer formed a weak boundary, part of which separated from the surface during the peel test. The layer was, however, readily reduced by the APG hydrogen plasma at a frequency of 13.56 MHz and a power input of 200 W within 5 minutes. In accordance with the reduction, the peel strength was recovered. The curing temperature also influenced the adhesion of the copper/epoxy joint with the highest value of peel strength being obtained at a curing temperature of 120°C.

References

1. J. M. Burkstrand, *J. Appl. Phys.* **52,** 4795 (1981).
2. Y. H. Kim, G. F. Walker, J. Kim and J. Park, *J. Adh. Sci. Tech.* **1,** 331 (1987).
3. C. W. Miller and P. C. Laberge, *J. Vac. Sci. Technol. A* **7,** 1818 (1989).
4. H. K. Yun, K. Cho, J. H. An and C. E. Park, *J. Mat. Sci.* **27,** 5811 (1992).
5. B. C. Jackson, *Trans. Institute of Metal Finishing* **65,** 8 (1987).
6. Y. Nakamura, K. Mori and K. Tamura, *J. Adh. Soc. Jap.* **17,** 308 (1981). [in Japanese]
7. A. J. Kinloch, *Adhesion and Adhesives* (Chapman & Hall, London, 1987), p. 144.
8. T. Yokoyama, M. Kogoma, T. Moriwaki and S. Okazaki *J. Phys. D: Appl. Phys.* **23,** 1125 (1990).
9. S. Okazaki, M. Kogoma, H. Uchiyama, M. Uehara, K. Naito, H. Kawano and Y. Sawada, *Proc. 9th Symp. Plasma Processing* (The Jap. Soc. Appl. Phys.), 257 (1992).
10. K. L. Mittal, Ed., *Adhesion Aspects of Polymeric Coatings* (Plenum Press, New York, 1983), p. 70.
11. S. R. Culler, H. Ishida and J. L. Koenig, *Polym. Composites* **7,** 231 (1986).
12. F. J. Boerio, J. W. Williams and J. M. Burkstrand, *J. Colloid and Interface Sci.* **91,** 485 (1983).