Interfacial Behavior of Polyimide/Primer/Copper System by Preoxidation of the Primer

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ABSTRACT: The copolymers of vinyl imidazole (VI) and vinyl trimethoxy silane (VTS) were applied as the corrosion inhibitors and the adhesion promoters for the polyimide/copper system at elevated temperatures. The mol ratios of VI to VTS were 100 : 0, 70 : 30, 30 : 70, and 0 : 100. Preoxidation of the primer was performed to improve the reactivity of the primer on poly(amic acid). A peel test was performed to evaluate the adhesion strength of the polyimide/primer/copper system after heat treatment at 400°C in a nitrogen atmosphere. The effect of the preoxidation of the primer on corrosion protection and adhesion promotion were investigated by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The adhesion strength of the polyimide/primer/copper system depended on not only the chemical interaction between polyimide and the preoxidized primer, but also the thermal stability of the primer. It showed the highest value when the mol ratio of VI to VTS was 30 : 70. The primer layer reduced or suppressed copper diffusion into the polyimide layer. The degree of corrosion protection by the primer was affected by its thermal stability and its reactivity on copper. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2518–2524, 2000

Key words: polyimide/copper system; adhesion promotion; corrosion protection

INTRODUCTION

Polyimides have been widely utilized for the microelectronic applications, due to their high thermal stability, good mechanical property, low moisture absorption, low dielectric constant, and good chemical resistance.[1,2] Good adhesion of polyimide to copper is essential for microelectronic applications. Polyimide/metal interface, which can be formed by spin coating poly(amic acid) solution onto a metal surface, is important for good adhesion. Accordingly, many studies has been intensively studied to control polyimide/metal with poly(amic acid).

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In multilevel thin-film packaging, poly(amic acid) is spin coated onto the metal substrate, and then cured at high temperature (~400°C). When poly(amic acid) is coated onto copper, its acid functionality was reported to react with a copper surface to form a carboxylate that decomposes upon curing.[3,4] Solvent plays a major role in the aggregation of copper-rich precipitates and their diffusion away from the interface. As a result, copper oxides are left in the cured polyimide layer, which deteriorates the dielectric property and the material property of polyimide. Transmission electron microscopy (TEM) confirmed the existence of very fine copper oxide particles in the polyimide layer.[5] Polyimide film with copper oxide particles had almost twice the dielectric constant in comparison with the pure materials.[4]

Therefore, the modification of the polyimide/copper system has been tried to provide polyimide with both an adhesive property to copper and an electrical property.[6,7] For the purpose of corrosion protection and adhesion promotion for the polyimide/copper system, therefore, silane-based imidazole copolymer with high thermal stability was synthesized in our previous study.[8] The copolymer of vinylimidazole (IV) and vinyltrimethoxy silane (VTS) was applied as an adhesion promoter as well as a corrosion inhibitor for the polyimide/copper system. The effect of the copolymer composition on adhesion promotion and corrosion protection for polyimide/copper was investigated by the measurement of peel strength and interfacial analyses. The adhesion strength of the polyimide/primer/copper system was dependent on the thermal stability of the primer and the chemical interaction between polyimide and the primer.

In this study, preoxidation of the primer has been carried out to improve the reactivity of the primer with polyimide. Adhesion strengths of polyimide/preoxidized primer/copper were evaluated by a peel test, and interfacial analyses were carried out to characterize the locus of failure. For effective interfacial analyses, the copper side and polymer side after the peel test were investigated with Fourier transform infrared reflection and absorption spectroscopy (FTIR-RAS), microattenuated total reflectance (micro-ATR), and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

VI and VTS were purchased from the Aldrich Chemical Co. (USA), and distilled *in vacuo* to yield pure and colorless liquids. Azobisisobutyronitrile (AIBN) from Wako Pure Chemical Industries, Ltd. (Japan), was dissolved in warm methanol (35°C), recrystallized in an ice bath, and then dried in a vacuum oven at room temperature for 2 days. *N*-Methyl-2-pyrrolidinone (NMP) was purchased from the Aldrich Chemical Co., dehydrated with phosphorous pentoxide, and distilled under reduced pressure. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) and oxydianiline (ODA) were purchased from the Aldrich Chemical Co., and recrystallized in acetic anhydride and ethanol, respectively.

VI and VTS were copolymerized in benzene at 68°C with stirring in argon atmosphere using AIBN as an initiator. The total monomer concentration was 2 *M*, and the initiator concentration was fixed at 2×10^{-3} *M*. The mol ratios of VI to VTS were 100 : 0, 70 : 30, 30 : 70, and 0 : 100. For the brief expression, four copolymers were named as Polyvinylimidazole (PVI), 7030, 3070, and Polyvinyltrimethoxysilane (PVTS), respectively. 7030 and 3070 denote the copolymer where the mol ratio of VI to VTS are 70 : 30 and 30 : 70, respectively. The copolymerization and hydrolysis scheme of VI and VTS is shown in Figure 1.

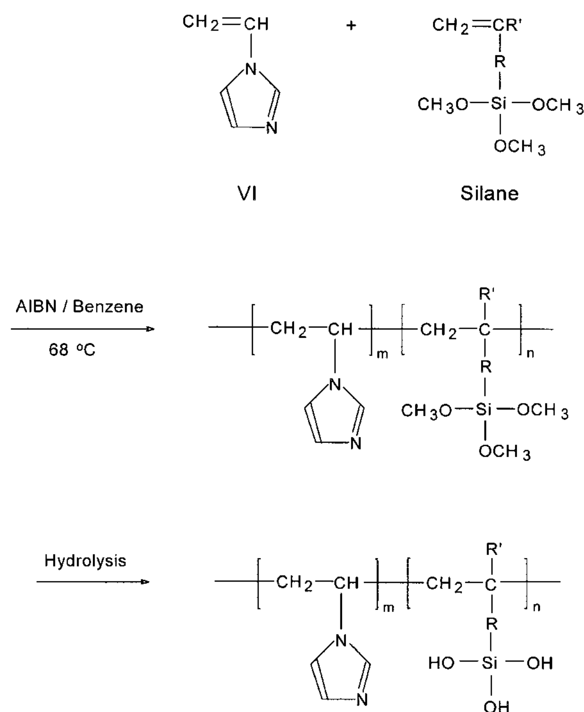

Figure 1 Schematic diagram of copolymerization and hydrolysis.

BTDA-ODA poly(amic acid) was prepared by reacting stoichiometric amounts of BTDA and ODA. ODA was dissolved in NMP, and BTDA was added into the ODA/NMP solution at room temperature. The total solid content was 15 wt %. The reactor was stirred in an ice-water bath for 12 h. Viscous poly(amic acid) (PAA) solution was obtained and refrigerated until use. Figure 2 shows the synthesis scheme for BTDA-ODA polyimide.

Copper plates (1.2 mm thick, Poongsan Co. in Korea) were mechanically polished with No. 5 chromic oxide, washed with *n*-hexane and acetone in an ultrasonic bath. They were rinsed with 1% HCl/distilled water solution, distilled water, and acetone, and then dried with a stream of nitrogen gas. Copolymer solution was cast onto copper plates with microsyringe as the primer, and the samples were dried at 60°C for 12 h to remove the

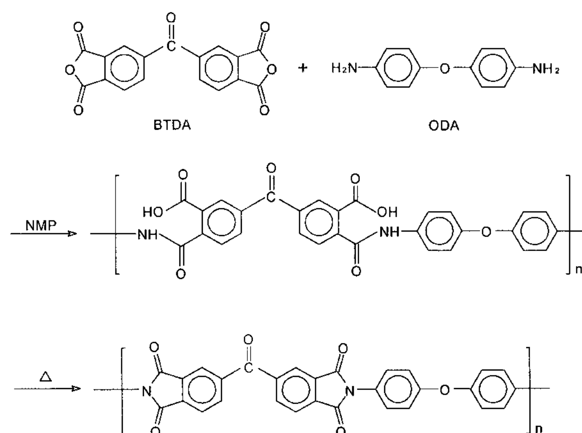

Figure 2 Synthesis scheme of BTDA-ODA poylimide.

residual solvent in the copolymer film. Film thickness was calculated based on the concentration of the copolymer solution, copolymer density, and the area of the copper surface. In this study 1 μm-thick films were used.

For the purpose of preoxidation of the primer, primer-coated copper plates were heated at 200°C for 30 min in air atmosphere, and then coated with diluted PAA solution (7 wt %). Imidization was performed at 100°C for 30 min, at 150°C for 30 min, and 250°C for 1 h. After imidization the coating thickness was ca. 15 μm.

The imidized samples were heat treated at 400°C in a furnace with a continuous flow of nitrogen. After heat treatment, the whole polymer layers (5 mm wide) were peeled from the copper substrates. The peel strengths were measured by the 90° peel test, using a Lloyd Universal Testing Machine. Figure 3 shows a shematic diagram of peel strength measurement. The peel rate was 1.5 mm/min, and at least three measurements were performed. Peel energy (Ga) was calculated by the following equation.

$$G_a = F/W \tag{1}$$

where F is the peel force and W is the width of the sample.

After peeling off the polymer layer from the copper substrate, both the copper side and the polymer side were analyzed with Fourier transform infrared reflection and absorption spectroscopy (FTIR-RAS), microattenuated total reflectance (micro-ATR), and X-ray photoelectron spectroscopy (XPS) to characterize the locus of failure.

XPS analysis was carried out with Escalab 220i-XL system from FISIONS instruments to characterized PI/primer/copper system after the peel test. Survey scan was performed, and AlKα radiation (1486.6 eV) was used as the X-ray source. The sample was positioned at a take-off angle of 45° with respect to the detector. The X-ray source was operated at a base pressure of $\sim 10^{-8}$ Torr.

FTIR-RAS was used to characterize copper surfaces after adhesion test. The spectrometer was continuously purged with dry nitrogen gas to remove water vapor and atmospheric CO_2. Absorbance spectra were obtained using Bomem MB-100 spectrometer at a resolution of 4 cm^{-1}, and 100 scans were collected. Graseby Specac P/N 19650 monolayer/grazing angle accessory was used. The angle of incidence was 78°, and a freshly polished copper coupon was used to obtain the reference spectrum.

Micro-ATR analysis was performed to characterize the polymer film peeled off the copper substrate. ATR attachment from the Harrick Co. was used. A germanium IRE with an end-face angle of 45° were utilized, and its dimension was 10 × 5 × 1 mm. The reflection number in the germanium IRE was 10, and 100 scans were collected.

Scanning electron microscopy (SEM) was used to observe the copper side after the peel test. The instrument used in this experimental was a JEOL JSM 840A microscope, and specimens were coated with a thin layer of gold to eliminate charging effects.

RESULTS AND DISCUSSION

Preoxidation of the primer was performed to improve the reactivity of the primer on poly(amic

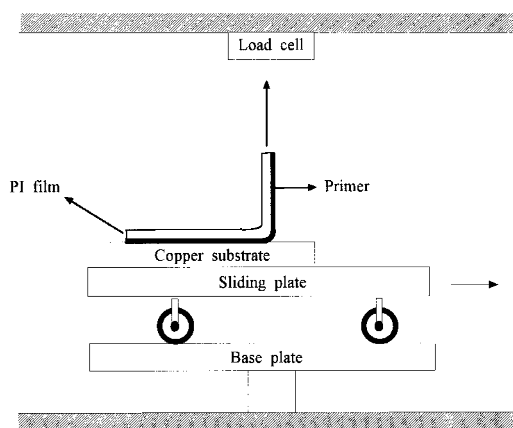

Figure 3 Schematic diagram of measurement of peel strength.

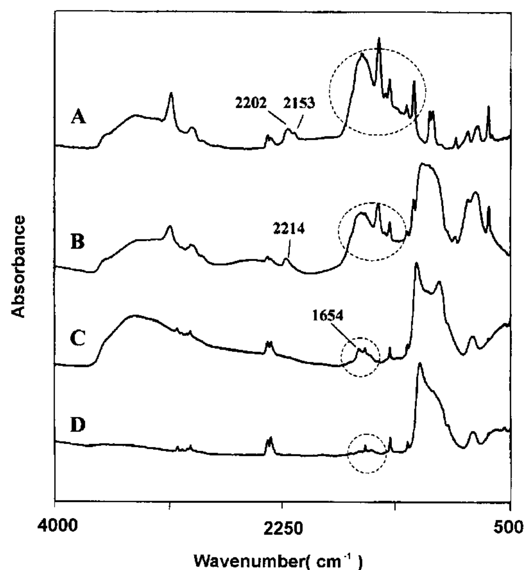

Figure 4 R-A spectra of the primers on copper plates after heat treatment at 200°C for 30 min in air: (A) PVI, (B) 7030, (C) 3070, and (D) PVTS.

acid) by dint of introduction of the polar groups into the primer. The primer-coated copper plates were heated at 200°C for 30 min in air atmosphere for preoxidation of the primer. It was reported that PVI coated on a copper plate did not suffer from severe thermal degradation of PVI and corrosion formation of copper at 200°C.[9–11] Figure 4 demonstrates R-A spectra of the primer coated on copper plates after heat treatment. No corrosion peak is observed in all spectra, but some spectra changes are observed as a result of thermal oxidation of the primers. In spectra A and B, the peak at 2214, 2202, and 2153 cm^{-1} are related to the nitrile group, and the broad band around 1654 cm^{-1} is designated to the C═O ketonic, unconjugated C═C, and conjugated C═N stretching modes.[14,15] These products from thermal oxidation originate from the oxidation of the copolymer backbone and the cleavage of the imidazole ring. In addition, some N—H groups result from the imidazole ring cleavage.[13,14] These polar groups are expected to improve the chemical reactivity of the primer on poly(amic acid). Especially, the N—H groups, which are newly formed by preoxidation of the primer, reacts on poly(amic acid) to induce chemical bonding in the interphase region. The reaction of aminosilane on the poly(amic acid) was reported in a previous article.[15] In addition, C≡N group improved the adhesion between copper and Kapton film.[16] In spectrum C, the nitrile peak at 2213 cm^{-1} is hardly shown, but some oxidative peaks appear in the 1800–1500 cm^{-1} region distinctly. In spectrum D, thermo-oxidative peaks are also distinguishable, but the peak from N—H group is not included in this region. From the result, it can be concluded that the introduction of the polar reactive functional group into the primer is attained by preoxidation of the primer. Its amount is increased with increasing the mol ratio of VI in the primer.

Figure 5 represents the peel strength of the polyimide/primer/copper systems with preoxidation of the primers. Peel strength of the preoxidized sample is the highest in the 3070 system. For the purpose of the explanation of this result, the interfacial phenomena in the PI/primer/copper systems were investigated. Both the copper surfaces were analyzed with FTIR, ESCA, and SEM.

Figure 6 shows IR spectra of the polyimide/PVI/copper and polyimide/7030/copper systems with the preoxidized primer layer. Copper oxide peak does not appear in two R-A spectra. Corrosion formation was suppressed during heat treatment at 400°C despite the preoxidation of the primer. In the polyimide/PVI/copper system, the ATR spectrum shows the broad band from oxidized PVI as well as the characteristic peaks of polyimide. The broad band in the 1700–1200 cm^{-1} suggests that the preoxidized PVI layer underwent a severe thermal oxidation. The R-A spectrum has a strong broad band 1645 cm^{-1},

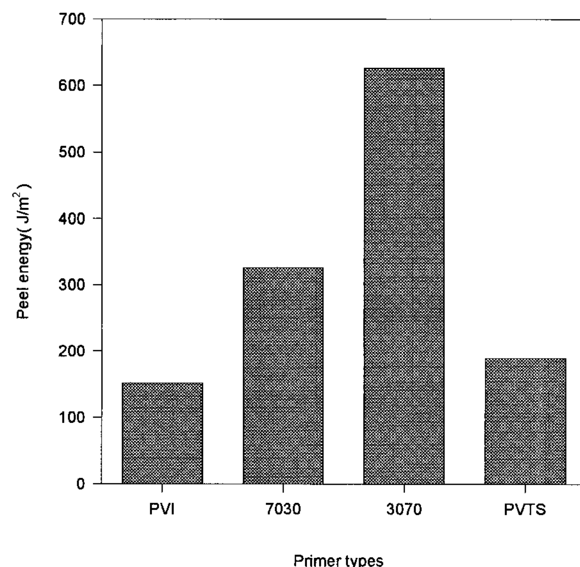

Figure 5 The peel energy of polyimide/preoxidized primer/copper systems.

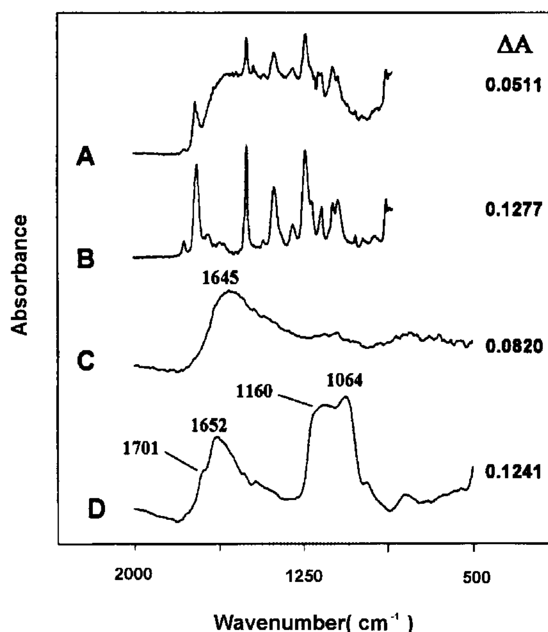

Figure 6 IR spectra of the PI/PVI/Cu system and PI/7030/Cu with preoxidation of the primer after the peel test. (A) ATR of the PVI system, (B) ATR of the 7030 system, (C) R-A of the PVI system, (D) R-A of the 7030 system.

which is associated with the products from thermal oxidation of PVI. This implies that failure during the peel test occurred in the bulk of the preoxidized PVI layer. For PVI, preoxidation deteriorates the mechanical property of the PVI layer. As a result, failure occurs in bulk of the preoxidized PVI layer rather than in the interphase region of PVI/copper.

In the case of the preoxidized 7030 copolymer, the ATR spectrum gave a feature similar to that of polyimide film. In R-A spectra, however, polyimide characteristic peaks in the 1800–1300 cm^{-1} region are not distinguishable. The peaks at 1160 and 1064 cm^{-1} are designed to the Si—O—Si linkage from silane unit of the primer. The peaks around 1652 cm^{-1} are designated to C═O, C═C, and C═N stretching modes from polar oxidation products, which contain C═O stretching of the amide group. This suggests that during polyimide film formation process poly(amic acid) in the interphase region is likely to interact with the preoxidized primer to form the amide bond and aliphatic imide, instead of formation of aromatic imide. This amide bond and aliphatic imide formation in the interphase region is considered to have the positive effect on the peel strength of the sample.

XPS study of the polyimide/PVI/copper and polyimide/7030/copper systems with the preoxidized primer was carried out to investigate failure phenomena in the interphase region. XPS spectra of the polymer sides after the peel test are demonstrated in Figure 7. Cu2p3 peak appeared in spectrum A. This indicates that copper diffusion is facilitated in the preoxidized PVI system. Preoxidation of PVI is considered to deteriorate the film property of PVI, and to induce a more defect formation during heat treatment. In spectrum B, copper peak is not distinct, and Si peaks are observed. Preoxidation of the 7030 copolymer did not cause the copper diffusion into the polyimide layer.

IR spectra of polyimide/3070/copper and polyimide/PVTS/copper systems with the preoxidized primer layer are demonstrated in Figure 8. ATR spectrum is completely different from a typical one of polyimide film because of the appearance of the copolymer peaks in the spectrum. The peaks from the siloxane network structure appear at 1031 cm^{-1}, which indicates that some failure proceeds in the bulk of the 3070 copolymer. In addition, the peak at 1646 cm^{-1} is assigned to C═O stretching in the amide group as a results of interfacial bond formation between poly(amic acid) and the primer during polyimide film formation. This amide peak is also observed at 1645 cm^{-1} in

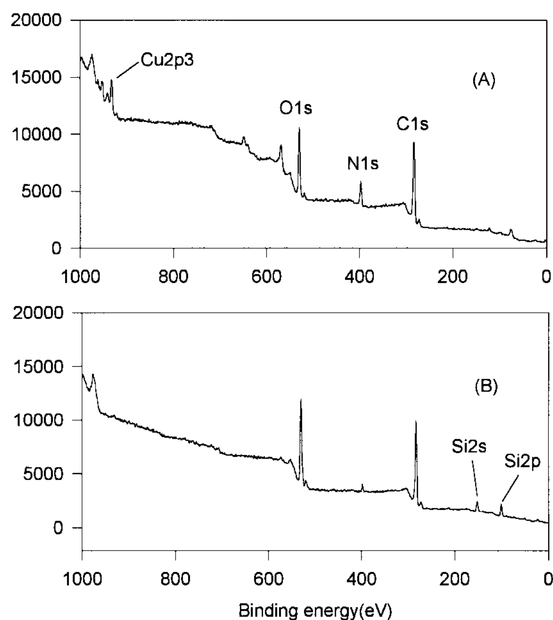

Figure 7 XPS spectra of polymer sides in the PI/PVI/Cu and PI/7030/Cu system with preoxidation of the primer after the peel test. (A) PVI, and (B) 7030.

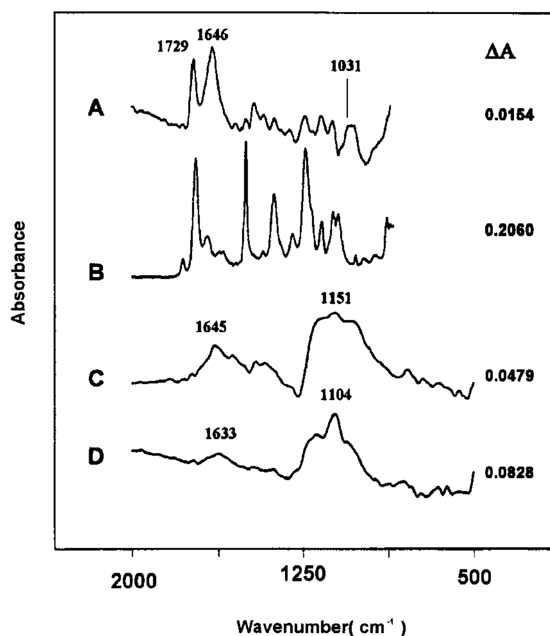

Figure 8 IR spectra of the PI/3070/Cu system and PI/PVTS/Cu with preoxidation of the primer after the peel test: (A) ATR of the 3070 system, (B) ATR of the PVTS system, (C) R-A of the 3070 system, and (D) R-A of the PVTS system.

R-A spectra. Distinguishable polyimide peaks do not appear in the R-A spectrum any longer, and most peaks originate from the infinitive siloxane network structure of the primer. From these spectra, it can be inferred that much chemical interaction between poly(amic acid) and the preoxidized primer exist in the interphase region, and that the locus of failure is in the interphase. Some cohesive failure mode in the primer layer indicates the enhanced interfacial strength between polyimide and the primer. This is attributed to not only the increased compatibility of the primer with poly(amic acid), but also the formation of a chemical amide bond between poly(amic acid) and the preoxidized primer.

In the polyimide/PVTS/copper system, the ATR spectrum is similar to that of polyimide film, and the R-A spectrum indicates the Si—O—Si network formation only. This suggests that interfacial failure occurred between the primer and polyimide.

Figure 9 shows XPS spectra of the polymer sides in the polyimide/3070/copper and polyimide/PVTS/copper systems with the preoxidized primer after the peel test. Copper peaks are not found in the polyimide/3070/copper system. Copper diffusion is completely suppressed by the 3070 copolymer at elevated temperature.

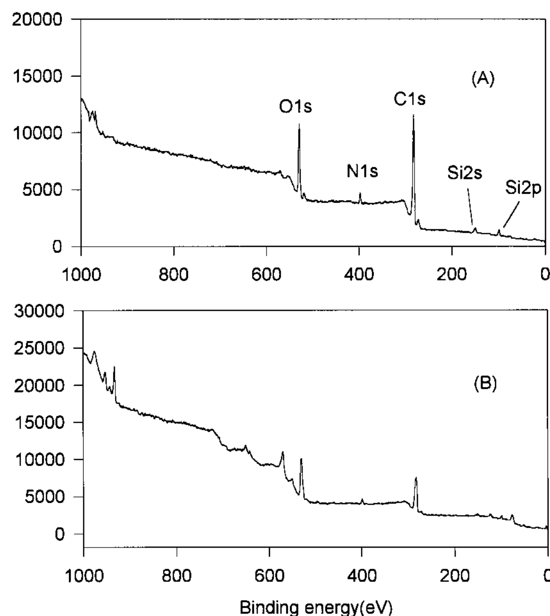

Figure 9 XPS spectra of polymer sides in the PI/3070/Cu and PI/PVTS/Cu systems with preoxidation of the primer after the peel test: (A) 3070, and (B) PVTS.

In the polyimide/PVTS/copper system, the copper peak is observed. Preoxidation of PVTS did not suppress copper diffusion into the polyimide layer. This may be attributed to the film defects formed during PVTS film formation.

To observe the locus of failure in the polyimide/3070/copper system, the peeled copper surface was investigated with SEM (Fig. 10). SEMs represents the complex feature. Locus of failure is mainly composed of the primer bulk and the polyimide-primer interphase.

Figure 10 Scanning electron micrograph of the copper side in the PI/3070/Cu sample with preoxidation of the primer after the peel test.

Table I Locus of Failure and Corrosion Formation in the PI/Primer/Cu System with Preoxidation of the Primer

Oxidized Primers	Locus of Failure	Corrosion Formation
PVI	PVI layer	some
7030	primer–PI interphase	no
3070	primer–PI interphase	no
PVTS	primer/PI interface	some

The locus of failure and corrosion formation in the polyimide/primer/copper system with preoxidation of the primer are summarized in Table I. These differences in the locus of failure are affected by the chemical bond formation and mechanical property of the interphase region between polyimide and the primer, and the thermal stability of the primer layer. For PVI, even if many polar reactive groups are introduced into the primer layer, its adhesion strength is weakened by preoxidation of PVI because the mechanical property of PVI is deteriorated by preoxidation. Failure occurs in the PVI layer acting as a weak boundary layer. In the case of the 7030 and 3070 copolymer, preoxidation of the primer induces the interfacial bond formation in the polyimide/copper interphase region. Accordingly, the interfacial adhesion strength is improved, and it is dependent on the mechanical strength of the polyimide–primer interphase region. Because the 3070 copolymer forms a stronger interphase region due to thermally stable structure, it has a higher adhesion strength. In the case of PVTS, even though it is preoxidized, it has little interfacial bond formation with polyimide in comparison with the other primers. Failure occurs in the polyimide/primer interface without a remarkable increase of adhesion strength.

CONCLUSIONS

Preoxidized primers, PVI, 7030 copolymer, 3070 copolymer, and PVTS, were applied as the primer of the polyimide/copper system. After heat treatment at 400°C in nitrogen atmosphere, the adhesion strengths of the polyimide/primer/copper systems were the highest in the 3070 system. From FTIR, XPS, and SEM analyses, the adhesion strengths of the systems depended on the thermal stability of the primer and the chemical interaction of the primer with polyimide. The increment of VI content in the primer increased the chemical interaction of the primer with polyimide, and decreased the mechanical and thermal property of the primer. On the other hand, the silane unit in the primer improved the mechanical property and thermal stability of the primer. The 3070 copolymer not only formed the thermally and mechanically stronger interphase, but also had some chemical interaction with polyimide through the amide and aliphatic imide bond formation. The silane unit played a role in the migration of copper oxide into the polyimide layer. The 7030 copolymer and 3070 copolymer suppressed copper diffusion into the polyimide layer, but PVTS could not, due to the film defect during heat treatment.

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REFERENCES

1. Ghosh, M. K.; Mittal, K. L., Eds. Polyimides: Fundamentals and Applications; Marcel Dekker, New York, 1996.
2. Feger, C.; Khojasteh, M. M.; McGrath, J. E. Polyimides: Materials, Chemistry and Characterization; Elsevier, New York, 1989.
3. Kowalczyk, S. P.; Kim, Y.-H.; Walker, G. F.; Kim, J. Appl Phys Lett 1988, 52, 375.
4. Kim, Y.-H.; Kim, J.; Walker, G. F.; Feger, C.; Kowalczyk, S. P. J Adhesion Sci Technol 1988, 2, 95.
5. Shih, D.-Y.; Paraszczak, J.; Klymko, N.; Flitsch, R.; Nunes, S.; Lewis, J.; Yang, C.; Cataldo, J.; McGouey, R.; Graham, W.; Serino, R.; Galligan, E. J Vac Sci Technol A 1989, 7, 1402.
6. Jang, J.; Jang, I.; Kim, H. J Adhesion Sci Technol 1998, 12, 323.
7. Jang, J.; Jang, I.; Kim, H. J Appl Polym Sci 1998, 68, 1343.
8. Kim, H.; Jang, H. Polymer 2000, 41, 6553.
9. Eng, F.; Ishida, H. J Electrochem Soc 1988, 135, 608.
10. Eng, F.; Ishida, H. J Appl Polym Sci 1986, 32, 5035.
11. Eng, F.; Ishida, H. J Mater Sci 1986, 21, 1561.
12. Bellamy, L.; The Infra-red Spectra of Complex Molecules; Wiley, New York, 1975.
13. Colthup, N.; Daly, L.; Wiberley, S. Introduction to Infrared and Raman Spectroscopy; Academic Press, New York, 1975.
14. Hansen, J.; Kumagai, M.; Ishida, H. Polymer 1994, 35, 4780.
15. Linde, G.; Gleason, R. T. J Polym Sci Chem Ed 1984, 22, 3043.
16. Inagaki, N.; Tasaka, S.; Ohmori, H.; Mibu, S. J Adhesion Sci Technol 1996, 10, 243.