Studies on the Adhesion of Polyimide Coatings on Copper Foil

K.-M. CHEN,[1,*] S.-M. HO,[1] T.-H. WANG,[1] J.-S. KING,[1] W.-C. CHANG,[1] R. P. CHENG,[2] and A. HUNG[3]

[1]Industrial Technology Research Institute, Materials Research Laboratories, Chutung, Hsinchu, Taiwan, R.O.C., [2]Department of Chemistry, National Taiwan University, Taipei, Taiwan, R.O.C., and [3]Department of Chemical Engineering, Ming-Hsin Engineering College, Hsin-Feng, Hsinchu, Taiwan, R.O.C.

SYNOPSIS

The peel strength and the color of the copper foil peeled at 90 degrees from five different polyimide films were studied. The interfacial surfaces of copper foil and polyimide were examined by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and energy dispersion analysis by X-ray (EDAX). There is a correlation between peel strength, and the color of the interfacial side copper caused by oxygen diffusion. Study of the imidization process carried out in vacuum indicates that the geometric arrangements of the atoms of polyimide also play a very important role in peel strength.

INTRODUCTION

The increase in package density and processing speeds associated with high speed integrated circuits (IC) demands new technologies to interconnect and package these microelectronic devices.[1,2,3,4] As a result thin film copper–polyimide multilayer packaging technology has been developed. This new technology requires a low dielectric constant material as the interlayer in order to maintain a tightly spaced conductive interconnect pattern, and to reduce parasitic capacitance which causes delay on signal propagation, unwanted crosstalk, and noise. Other requirements of the interlayer dielectric are:

1. Low moisture absorption
2. Strong adhesion to the metal layers
3. Chemical innertness
4. Mechanical properties
5. Thermal stability
6. Easy film application and good planarizing surface features
7. Practicable pattern generation
8. Reliability.

Among the organic polymers, condensation type polyimides meet most of the above requirements and are a good dielectric material for multilayer multichip packaging applications.

The exact nature of the polyimide–copper bond is still a matter of controversy. Two main theories have been reported: mechanical bonding and chemical bonding. Initial work in this field emphasized mechanical bonding, and most efforts were dedicated to the physical roughening of the substrate by different methods, as well as chemical treatments, in order to improve metal to polyimide adhesion.[5,6,7,8,9] It was reported that the kinetics of copper–polyimide interdiffusion is determined by the atomic diffusion of copper, while chemical interactions do not appear to play any important role.[10]

Recently, interfacial reactions at copper surfaces coated with polyimide films have been reported.[11,12] Cross-sectional TEM observations showed that fine particles, which were identified as Cu_2O, were precipitated in the polyimide side near the interface.[13,14] An interfacial reaction was also observed during initial contact of polyamic acid precursor with the copper substrate and leads to the postulation of the formation of copper carboxylate at the acid site of the polyamic acid precursor.[15,16] It was also reported that when polyamic acid was imidized while contacting with copper under inert atmosphere, a very small amount of oxidation occurred during the imidization process itself.[17,18]

In order to have a better understanding of the polyimide–copper bonding, four different polyamic acids were coated on shining copper foil and thermally imidized. The 90-degree peel strength test was conducted to study their adhesion strengths. The interfacial surfaces of the copper foil and polyimide film were examined by SEM to study their morphologies. They were also examined with energy dispersion analysis by X-ray (EDAX). The interaction of copper with polyimide was detected by XPS. In order to understand the effect of moisture absorption samples were immersed in boiling water for 24 h before measuring adhesion strength.

EXPERIMENTAL

Copper foils (thickness 25 μm) were degreased and cleaned in 5% NaOH for one minute at room temperature before coating. The polymeric coatings applied to such surfaces were:

1. PMDA/BTDA/PDA/ODA/siloxane (block copolyimide)
2. PMDA/BTDA/PDA/ODA/siloxane (random copolyimide)
3. BPDA/PDA/ODA (solvent : NMP)
4. BPDA/BTDA/PDA/ODA
5. BPDA/PDA/ODA (solvent : NMP/xylene = 4/1).

Except for coatings 3 and 5, the solvent is a four to one volume ratio of NMP to THF. The solid content is 15% for all coatings. Nominal structures of diamine and dianhydride are shown in Figure 1. Following the coating, all samples were prebaked at 100°C for half an hour. The subsequent immidization steps include heating the sample from room temperature to 350°C over a period of 0.5 h, 1 h, or 1.5 h, and then maintaining the temperature at 350°C for 1 h in air or vacuum (Table I). The thickness of the polyimide film was around 60 μm.

The copper foil was etched into $\frac{1}{8}$ in. wide strips. The adhesion strength between copper foil and polyimide film was studied by a 90-degree peel test. The polymeric side of polyimide–copper specimen was mounted onto a free-wheeling rotary drum with adhesive tape. The testing machine is model AG-5000A from Shimadzu. The peeling speed was kept constant at 25 mm/min. The interfacial surfaces of copper and polyimide were investigated by SEM (Cambridge Instruments Model 360 stereoscan). They were also analyzed with a VG Microlab Mark III XPS and a Kevex Microanalyst 8000 EDAX.

RESULTS

Adhesion Strength Study

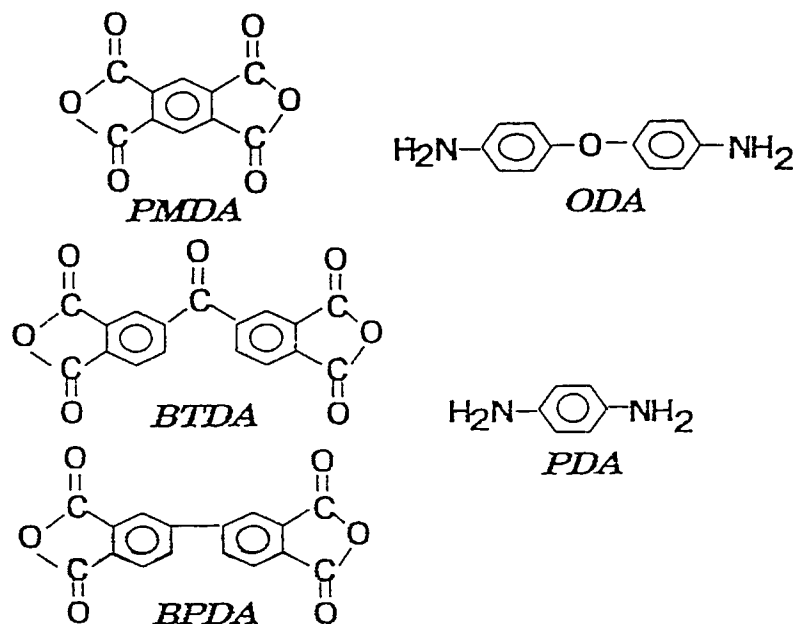The peel strength of the copper foil peeled at 90 degrees from the polyimide film and the colors of

Figure 1   Dianhydrides and Diamines

Table I **Key to Symbols for Specimen Composition and Imidization**

		Imidization Conditions		
Polyimide	A[a]	B[b]	C[c]	D[d]
1. PMDA/BTDA/PDA/ODA/siloxane (block copolyimide)	A1	B1	C1	D1
2. PMDA/BTDA/PDA/ODA/siloxane (random copolyimide)	A2	B2	C2	D2
3. BPDA/PDA/ODA (solvent : NMP)	A3	B3	C3	D3
4. BPDA/BTDA/PDA/ODA	A4	B4	C4	D4
5. BPDA/PDA/ODA (solvent : NMP/xylene = 4/1)	A5	B5	C5	D5

[a] A: in air, heated from room temperature to 350°C over 0.5 h, then maintained at 350°C for 1 h.
[b] B: in air, heated from room temperature to 350°C in 1 h, then maintained heated at 350°C for 1 h.
[c] C: in air, heated from room temperature to 350°C in 1.5 h, then maintained at 350°C for 1 h.
[d] D: in vacuum, heated from room temperature to 350°C in 1.5 h, then maintained at 350°C for 1 h.

the interfacial surface of copper foil are shown in Table II. When the composites of polyamic acids and copper foil were thermally imidized in air, the colors of the interfacial surface of the copper foils vary from gold, blue-violet, red-violet, yellow-brown, brown-violet to dark brown. There are correlations between the color and the peel strength. In general, the peel strength is strongest when the color is gold (> 7 lb/in.), followed by blue-violet color (5–7 lb/in.). Next comes red-violet or yellow-brown (2–3 lb/in.), with the dark brown color being the weakest (< 2 lb/in.). Among the polyimides studied only number 3 polyimide showed high peel strength (7–8 lb/in.).

When thermal imidization of polyamic acid was carried out in a vacuum, gold color of the interfacial surface of copper was observed for all samples. Three kinds of polyimides, number 3, number 4 and number 5, showed higher peel strength values (> 8 lb/in.) under these conditions than when they were imidized in air.

These results indicate that the extent of oxidation at the interfacial surface of copper is a determinant factor for peel strength, and it is influence by the oxygen content in the imidization environment.

The adhesion strength of polyimide–copper interfaces after immersion in boiling water for 24 h are shown in Table III. All the peel strengths are somewhat lower than those without boiling water treatment. However, the adhesion loss is not very large. That means the bonding between polyimide and copper is not severely affected by moisture.

Interface Studies

In general, the morphology of the interfacial sides of copper foil and polyimide film studied by SEM are rather smooth disregarding the peel strength (Fig. 2). When the polyamic acid film was thermally imidized in air, many small pits are found on the interfacial surface of the copper foil peeled from number 5, as well as number 4, polyimide film, both

Table II **Peel Strengths (lb/in) and Colors of Interfacial Surfaces of Copper[a]**

	Imidization Conditions			
Polyimide	A	B	C	D
1	3.4(A1) Violet-Brown	2.4(B1) Violet-Brown	1.3(C1) Dark-Brown	1.8(D1) Gold
2	3.4(A2) Yellow-Brown	2.6(B2) Yellow-Brown	2.2(C2) Violet-Brown	0.35(D2) Gold
3	7.8(A3) Light Blue-Violet Gold	8.0(B3) Light Blue-Violet	7.0(C3) Light Blue-Violet Gold	11.2(D3) Gold
4	2.1(A4) Brown-Red	1.5(B4) Brown-Red	2.5(C4) Brown-Red	8.2(D4) Gold
5	2.0(A5) Red-Violet	1.1(B5) Red-Violet	3.9(C5) Violet-Brown	14.4(D5) Gold

[a] See Table I for designations of symbols.

Table III   Peel Strengths (lb/in.) and Colors of Interfacial Surfaces of Copper after Immersion in Boiling Water for 24 h[a]

| Polyimide | Imidization Conditions | | | |
	A	B	C	D
1	1.4(A1)	0.9(B1)	0.9(C1)	1.7(D1)
	Dark-Orange	Dark-Yellow	Yellow-Brown	Gold
2	2.4(A2)	1.4(B2)	1.7(C2)	0.1(D2)
	Orange-Brown	Brown	Violet-Brown	Gold
3	6.8(A3)	4.2(B3)	5.0(C3)	9.2(D3)
	Light Blue-Violet Brown	Light Green-Yellow	Yellow-Brown	Gold
4	1.6(A4)	1.2(B4)	1.4(C4)	6.8(D4)
	Yellow-Brown	Yellow-Brown	Yellow-Brown	Gold
5	1.1(A5)	1.1(B5)	0.4(C5)	9.8(D5)
	Dark Orange-Red	Red-Brown	Yellow-Brown	Gold

[a] See Table I for designations of symbols.

of which were imidized by heating from room temperature to 350°C over a period of 1.5 h (Fig. 3). The color of all the interfacial surfaces of copper foil with small pits is red-violet. These small pits result from the interaction of copper with polyimide and oxygen to form some kind of copper complex, as copper is detected by EDAX at the interfacial surface of these polyimide films (Fig. 4). This also indicates that when the copper–polyimide coating was peeled, some of the copper complex stayed with the polyimide film. However, no obvious anchoring effect is produced by these small pits since the peel strength is not enhanced. For example, the peel strength of number 4 polyimide with small pits on the copper foil is as low as those without pits.

In the case of number 1 and number 2 polyimides, polyimide is detected on the interfaceside copper after the copper-polyimide coating was peeled, as shown by XPS studies (Fig. 5). This indicates that the mechanical strength of these polyimide films is very weak, resulting in cohesive failure of the polyimide film during peeling. This leads us to postulate that such low mechanical strength is the result of oxidative degradation of polymer catalyzed by interface copper.

DISCUSSION

There are many factors which can influence the extent of oxidation of interface copper and the interaction of polyimide and copper. These include:

1. The nature of polyamic acid
2. The coating thickness and solid content of polyamic acid

3. The oxygen content in the imidization ambient
4. The solvent effect.

Since the coating thickness and solid content of polyamic acid are the same in the present experiment, the extent of reactions is dependent on the chemical nature of polyamic acid, the flexibility of the polyimide and the transport or diffusion coefficient of oxygen through the polyimide film.

When imidization is carried out in vacuum, the effect of oxygen is negligible. Hence, the main effect on peel strength is the interaction of polyimide and copper. It has been reported that the interaction site between polyimide and copper is the carbonyl group of polyimide.[15,17] From our experimental results we found that the BPDA-based polyimides (number 3, number 4, and number 5) have higher peel strength ($\geq$ 8 lb/in.), while PMDA-based polyimides (number 1 and number 2) have lower peel strength (< 2 lb/in.). These results indicate that because of the presence of inter-phenyl-ring C — C single bonds the geometric arrangements of the atoms of BPDA-based polyimides is such that it facilitates the interaction of the carbonyl group with copper.

When imidization is carried out in air, oxygen can diffuse through the polyimide film into the polyimide-copper interface during the imidization process and convert the copper atoms into copper oxide (CuO). Since the bonding between copper and copper oxide is weak, this may be a possible explanation for the poor adhesion at the polyimide–copper interface when the interface copper is oxidized to a large extent.[11] As a result, the diffusion coefficient of oxygen through the polyimide film becomes a de-
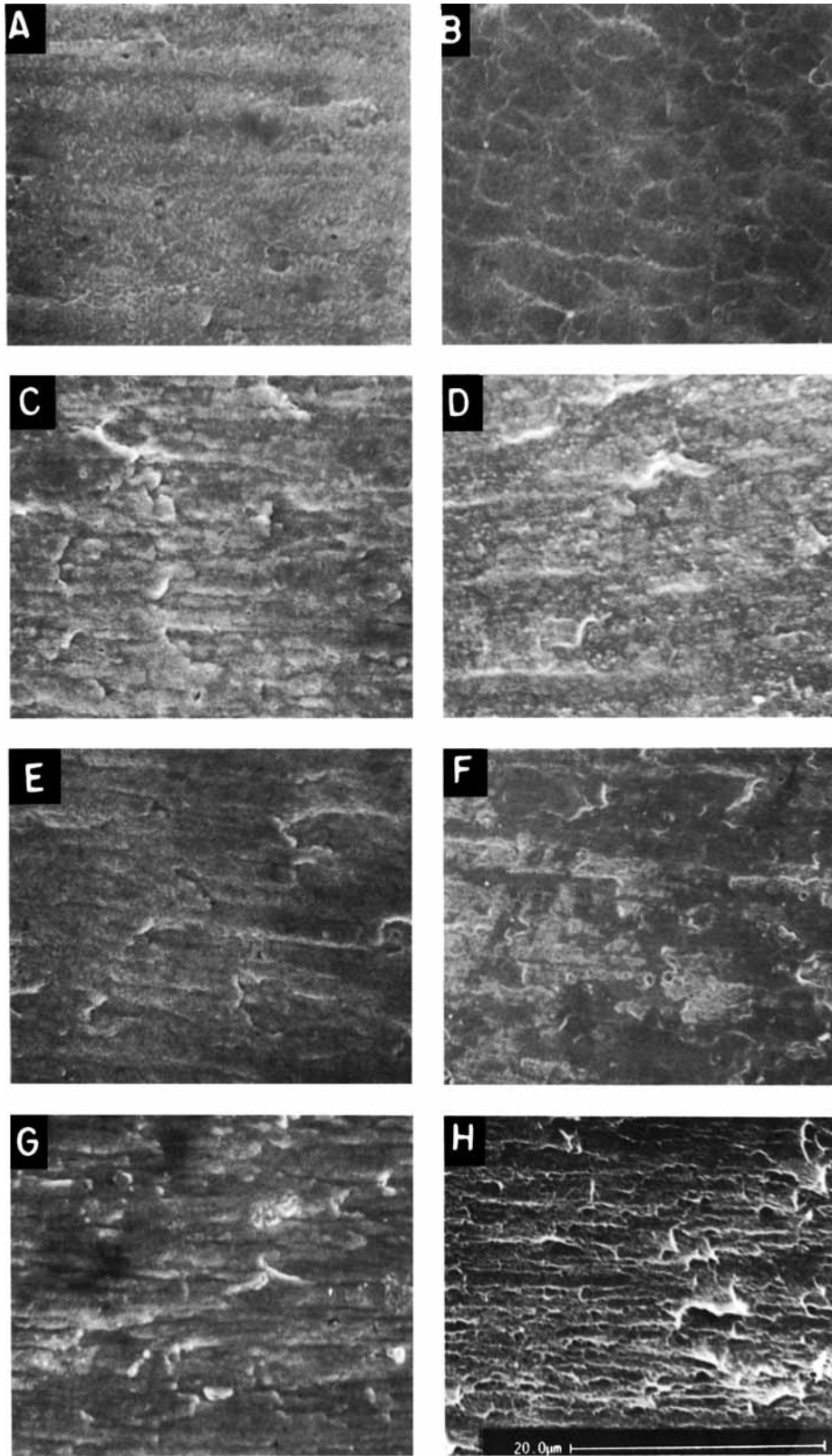
Figure 2 Morphology of the Interfacial Surfaces of Copper Foil and Polyimide Film: (a) A4 copper foil, (b) A4 polyimide film, (c) B3 copper foil, (d) B3 polyimide film, (e) D1 copper foil, (f) D1 polyimide film, (g) D5 copper foil, (h) D5 polyimide film. (For sample designations see Table I.)
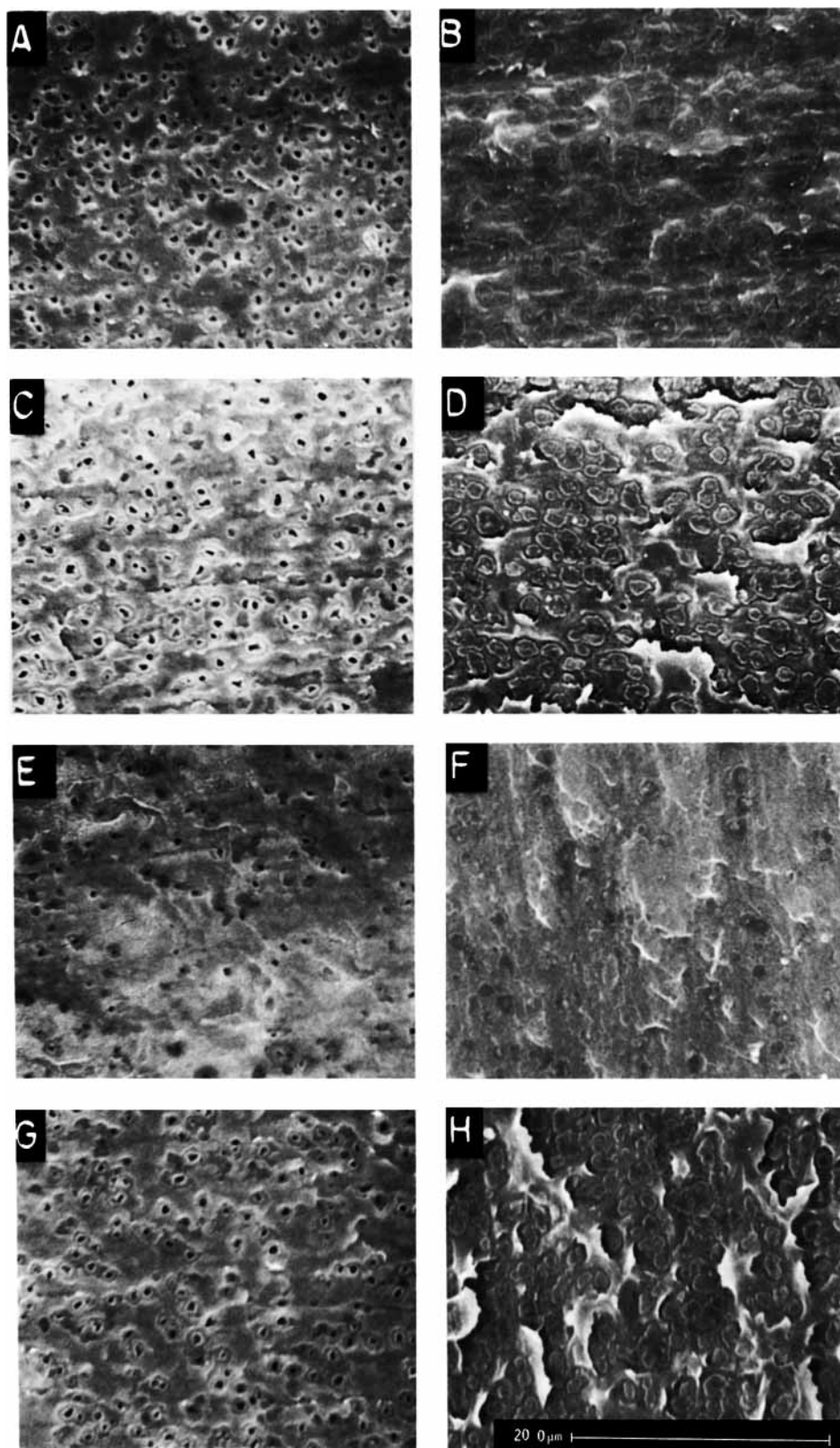
Figure 3 Morphology of the Interfacial Surfaces of Copper Foil and Polyimide Film: (a) A5 copper foil, (b) A5 polyimide film, (c) B5 copper foil, (d) B5 polyimide film, (e) C4 copper foil, (f) C4 polyimide film, (g) C5 copper foil, (h) C5 polyimide film. (For sample designations see Table I.)
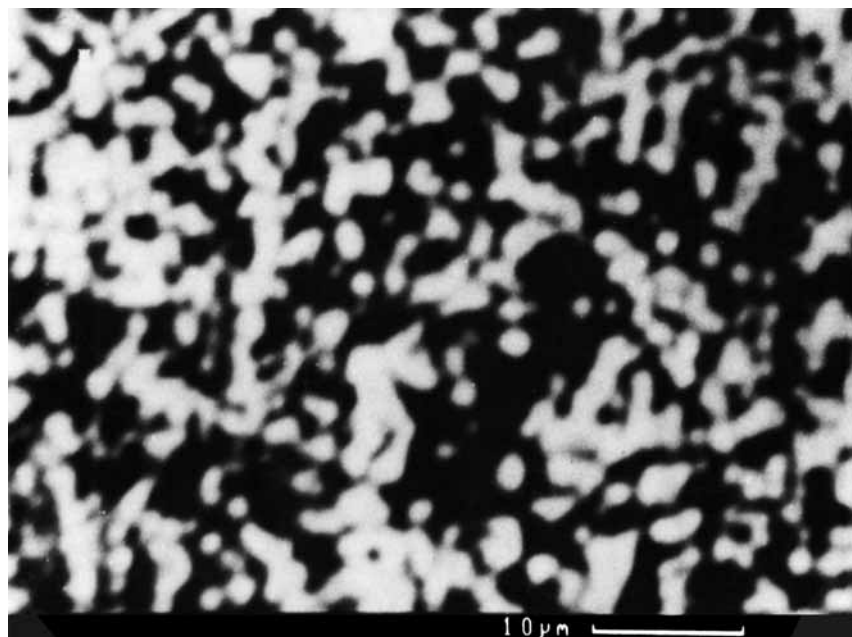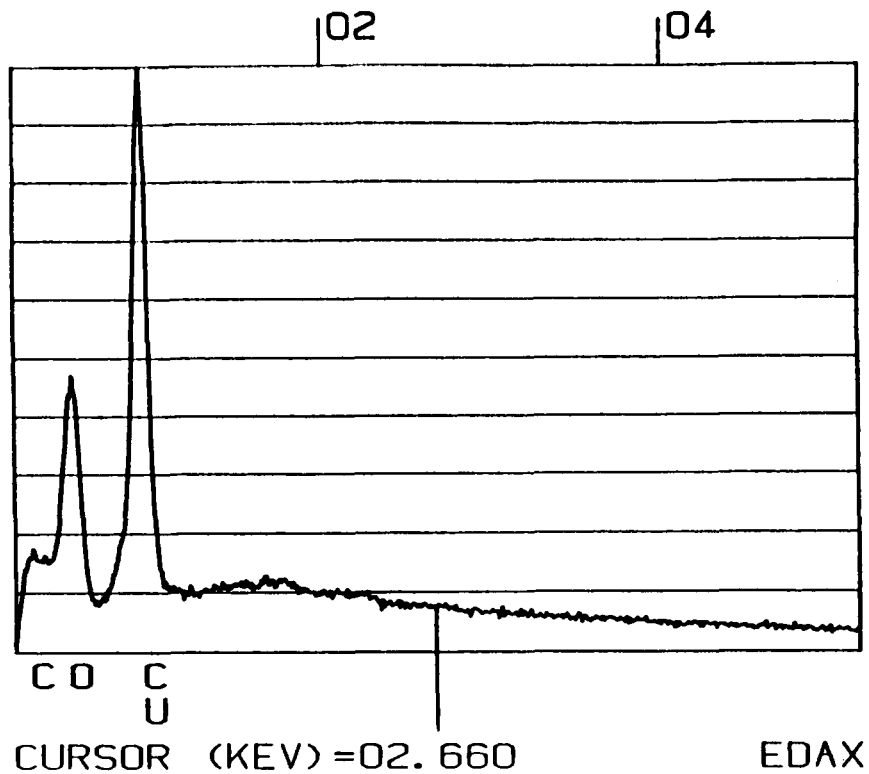
Figure 4 Distribution of Copper on Interfacial Surface of Polyimide Film.

termining factor in the peel strength. Some recent reports show that the crystallinity of the polyimide can influence the permeability of oxygen through polyimide film.[19,20,21] Generally, a crystalline region is stiffer than an amorphous one and it is more dif-ficult for oxygen to diffuse through the former. Oka-moto et al. found that BPDA/ODA could aggregate to form a crystalline region by annealing at 300°C.[20,21] In this experiment, number 3 polyimide, composed of the dianhydride reported by Okamoto,
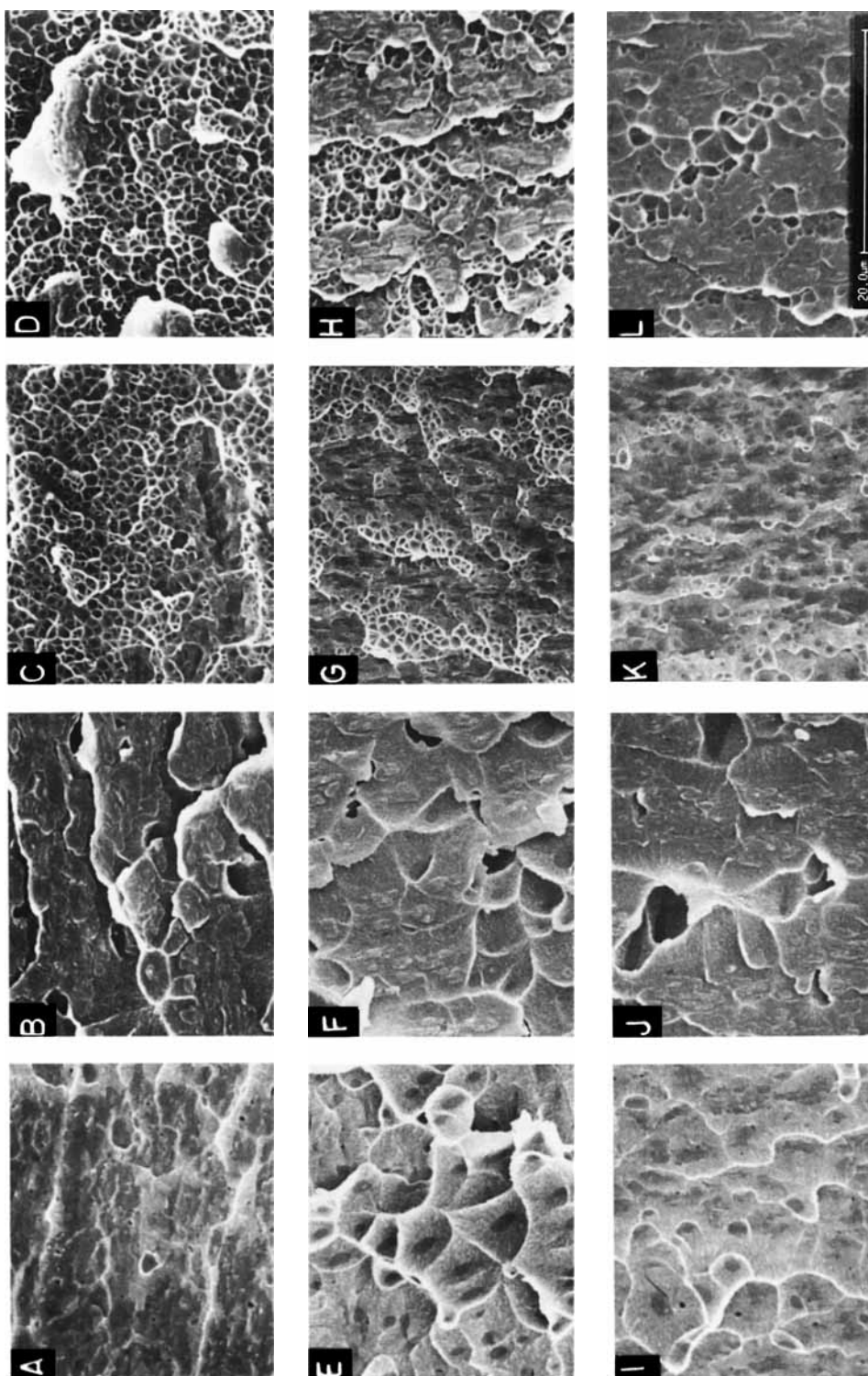
Figure 5 Morphology of the Interfacial Surfaces of Copper Foil and Polyimide Film: (a) A1 copper foil, (b) A1 polyimide film, (c) A2 copper foil, (d) A2 polyimide film, (e) B1 copper foil, (f) B1 polyimide film, (g) B2 copper foil, (h) B2 polyimide film, (i) C1 copper foil, (j) C1 polyimide film, (k) C2 copper foil, (l) C2 polyimide film. (For sample designations see Table I.)

was imidized at 350°C. Consequently, number 3 polyimide may contain a large crystalline region which could impede the diffusion of oxygen. The color of the interfacial surface of copper peeled from this polyimide is shiny light brown to red-gold. It suggests that little oxygen diffuses through this polyimide film. However, polyimide and copper do interact with each other, because by using XPS we can detect the existence of copper on the interfacial surface of polyimide and vice versa. In the present experiment, number 3 polyimide with an appropriate geometric arrangements of atoms and a low oxygen diffusion coefficient, is the only sample having high peel strength when it was imidized in air.

A high peel strength is expected for number 1 and number 2 polyimide containing siloxane, because the addition of siloxane will make the polyimide chain more flexible. However, it has also been reported that addition of siloxane can enhance oxygen permeability,[22,23] which may decrease the peel strength. In our experiment, the color of the interfacial surface of copper peeled from number 1 and number 2 polyimide which had been imidized in air was observed to be violet or brown indicating that copper has been oxidized. Furthermore, the interfacial surface morphologies of these polyimide films as detected by SEM (Fig. 5) are fragile, due to oxidative degradation. These results indicate that diffusion of oxygen is the dominant factor in affecting the interface bonding between polyimide and copper in these cases.

The structure of number 4 polyimide containing 40% BTDA is more flexible and is more permeable to oxygen diffusion. The color of its interfacial surface copper is an interdispersed pattern of red and brown, indicating that oxygen does diffuse through this polyimide film and oxidizes the interface copper to some extent. Therefore, the peel strength of this copper–polyimide coating is low when it was imidized in air. When it was imidized in vacuum, the peel strength is much higher ($\sim$ 8 lb/in.). This is another example of how oxygen content in the imidization environment can greatly influence the peel strength of the coating.

The composition of number 5 polyimide is the same as number 3 except 20% xylene is used as cosolvent. Therefore, the film properties of these polyimides are different. The color of the interfacial surface of copper peeled from number 5 polyimide is red-violet, indicating that some oxygen had diffused through this polyimide film and that the interface copper is moderately oxidized. Hence, it is speculated that xylene as cosolvent may loosen the infrastructure of the polyimide film and enhance

its permeability to oxygen causing a lowering of peel strength for this polyimide film when imidized in air.

CONCLUSION

From the peel strength studies in this experiment, we found that there is a correlation between peel strength and the color of the interfacial surface of copper. The peel strength is strongest when the color is gold (> 7 lb/in.). When the color is blue-violet the peel strength is around 5–7 lb/in. The peel strength is weaker than 4 lb/in. when the color is red-violet, yellow-brown, brown, or dark brown. Therefore, the color of the interfacial surface of copper can be used as a reference to estimate qualitatively the relative oxygen diffusion coefficient of the polyimide.

Besides a low oxygen diffusion coefficient, in order to obtain a high peel strength, the polyimide must have an appropriate geometric arrangement of atoms to facilitate the carbonyl group's interaction with the interface copper. Among the five polyimides studied, number 3 polyimide (composition BPDA/ODA/PDA) is the only one which fulfils this requirement.

REFERENCES

1. R. D. Rossi, *Hybrid Circuit Technology*, **Sept.**, 35 (1989).
2. M. J. Bowden and S. R. Turner, eds., *Polymers for High Technology*, ACS Symposium Series 346, American Chemical Society, Washington, DC, 1987.
3. A. M. Wilson, *Thin Solid Films*, **83**, 145 (1981).
4. A. W. Lin, *IEEE Transactions on Components, Hybrids, and Manufacturing Technology*, **13**, 207 (1990).
5. W. B. Lindsey, U.S. Patent 3,361,589 (1986).
6. H. Knorre and E. Meyer-Simon, U.S. Patent 3,702,285 (1972).
7. J. Hermer, U.S. Patent 3,770,528 (1973).
8. M. A. DeAngelo, U.S. Patent 3,791,848 (1974).
9. C. B. Yates and A. M. Wolski, U.S. Patent 3,857,681 (1974).
10. R. M. Tromp, F. Legoues, and P. S. Ho, *J. Vac. Sci. Technol.*, **A3**, 782 (1985).
11. S. A. Chambers and K. K. Chakravorty, *J. Vac. Sci. Technol.*, **A6**, 3008 (1988).
12. M. C. Burrell, J. Fontana, and J. J. Chera, *J. Vac. Sci. Technol.*, **A6**, 2893 (1988).
13. Y. H. Kim, G. F. Walker, J. Kim, and J. Park, *J. Adhesion Sci. -Tech.*, **1**, 331 (1987).

14. Y. H. Kim, J. Kim, G. F. Walker, C. Feger, and S. P. Kowalczyk, *J. Adhesion Sci. Technol.*, **2**, 95 (1988).

15. M. C. Burrell, P. J. Codella, J. A. Fontana, J. J. Cbera, and M. D. McConnell, *J. Vac. Sci. Technol.*, **A7**, 55 (1989).

16. M. C. Burrel, P. J. Codella, J. A. Fontana, and J. J. Chera, *J. Vac. Sci. Technol.*, **A7**, 1778 (1989).

17. D.-Y. Shih, J. Paraszczak, N. Klymko, R. Flitsch, S. Nunes, J. Lewis, C. Yang, J. Cataldo, R. MaGouey, W. Graham, R. Serino, and E. Galligan, *J. Vac. Sci. Technol.*, **A7**, 1402 (1989).

18. S. A. Chambers, V. A. Loebs, and K. K. Chakravorty, *J. Vac. Sci., Technol.*, **A8**, 875 (1990).

19. S. A. Stern, Y. Mi, and H. Yamamote, *J. Polym. Sci.*, **B27**, 1887 (1989).

20. K.-I. Okamoto, K. Tanaka, H. Kita, A. Nakamara, and Y. Kusuki, *J. Polym. Sci.*, **B 27**, 1221 (1989).

21. K.-I. Okamoto, K. Tanaka, H. Kita, A. Nakamura, and Y. Kusuki, *J. Polym. Sci.*, **B27**, 2621 (1989).

22. S. A. Stern, et al., *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 1263 (1987).

23. T. Nakagawa, et al., *Gas Separation and Purification*, **2**, 3 (1988).