Temperature Effect on PI/Cu Interface

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SYNOPSIS

The interfacial reaction and peel strength of polyimide with copper foil at various cure schedules have been investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and peel test to determine the temperature effect on polyimide/copper interface diffusion and adhesion. SEM studies indicate that the polyimide/copper interfaces are fairly smooth for all samples studied in this experiment. The TEM microstructure reveals the existence of a copper–polyimide interaction zone at the interface when it is cured at a temperature higher than 250°C, which also results in a high peel strength. XPS spectra revealed higher copper and carbonyl carbon contents at the polyimide interface when it is cured at a high-temperature schedule (350°C). From the results of these interface studies, it is concluded that chemical bonding resulting from the interaction of copper oxide and polyimide carbonyl group provides the binding force for polyimide and copper foil. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides are a class of high-temperature polymers with good thermal stability, low dielectric constant, ease of processing, and inertness to chemical attack.[1,2] All these properties enable polyimide to find widespread applications in microelectronic industries,[3-6] especially in high-density microelectronic devices. As metal/polymer interfaces can affect the adhesion of polyimide to the metal foil, they have been extensively studied.[7-10] The polymer-on-metal type interfaces, created by spin coating of a polyamic acid varnish onto a metal film followed by curing to form the polyimide, involve the interaction of metal (oxide) surface with the polyamic acid.[11-16] Two reactions were reported to occur at the interface boundary during the curing cycle: the interaction of Cu with polyamic acid and copper oxidation.[17] It was found that the rates of both reactions are controlled by the supply of oxygen to the interface and the curing temperature. Thus, the nature and thickness of the polyimide coating, the oxygen level in the curing ambient, and the curing temperature are the rate-determining factors.

The results of our previous study showed that oxygen diffusion rate is low in BPDA-based polyimide cured at 350°C with high packing density.[18] In the present experiment, BPDA-based polyimide was again employed. The thickness of the films was fixed to 25 μm. The curing ambient was air. The effects of curing temperature were studied by investigating the polyimide/copper interfaces formed by various cure schedules. The morphology of the polyimide/copper interface has been observed by scanning electron microscopy (SEM) after 90° peel test. The microstructure near the interfaces has been examined by transmission electron microscopy (TEM). The chemical reaction at the interface has been analyzed by X-ray photoelectron spectroscopy (XPS). The correlation of interface chemistry to the corresponding adhesion strength of the interface has also been investigated.

EXPERIMENTAL

The polyamic acid used in this experiment was BPDA/ODA/PDA random copolymer in *N*-methylpyrolidone (NMP). The mol ratio of BPDA : ODA : PDA was 0.98 : 0.70 : 0.30. The solid content was 13.4%. The viscosity was 5400 cps.

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The BPDA/ODA/PDA polyamic acid in NMP was spin coated on degreased 35 μm copper foil. Then, the samples were cured in air under various cure schedules as shown in Table I.

The copper foil was etched into $\frac{1}{8}$-in w strips. The adhesion strength between the copper foil and polyimide film was measured by a 90° peel test with tensile testing machine model AG 5000 A from Shimadzu. The copper foil was peeled from the polyimide at a constant peeling speed of 25 mm/min. The interfaces of copper and polyimide were investigated by SEM from Cambridge Instruments Model 360 stereoscan. They were also analyzed with VG Microlab Mark III XPS to study the chemical bonding at the interface sides.

The polyimide/copper interface structure was examined with a JEOL-2000EX and JEOL-2000FX TEM. To prepare a cross-sectional specimen for TEM observation, the Si substrate with the contact layers on top of it was cleaved in two pieces of 2 × 3-mm specimen. The polyimide/copper samples were cut to the same size. They were then bonded in alternating layers of polyimide and copper by epoxy. When the epoxy was cured, this composite specimen was mechanically grounded by 800-mesh alumina abrasive and then polished by 4000-mesh alumina abrasive from both sides until the thickness was reduced to about 20 μm. This slice was then glued to a Cu supporting ring and thinned again from both sides by a 5-KeV Ar ion milling process.

RESULTS

Experimental results indicate that various curing schedules can affect the peel strength, interface color, and interface composition of the polyimide/copper interface as delineated below.

Table I Imidization Conditions of Polyimide in Air

Symbols	Cure Schedule
A	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h
A-1	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h → RT $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h
B	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/3 h
B-1	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/3 h → RT $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h
C	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1.5\ h}$ 250°C/2.5 h
C-1	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1.5\ h}$ 250°C/2.5 h → RT $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h
D	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h
D-1	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h → RT $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h
D-2	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h → RT $\xrightarrow[\Delta]{0\ min}$ 300°C/0.5 h
D-3	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h→ RT $\xrightarrow[\Delta]{0\ min}$ 300°C/1 h
E	RT $\xrightarrow[\Delta]{1\ h}$ 100°C/1 h $\xrightarrow[\Delta]{1\ h}$ 200°C/1 h $\xrightarrow[\Delta]{1\ h}$ 300°C/1 h $\xrightarrow[\Delta]{0.5\ h}$ 350°C/1 h
E-1	RT $\xrightarrow[\Delta]{0.5\ h}$ 350°C/1 h
E-2	RT $\xrightarrow[\Delta]{1.5\ h}$ 350°C/1 h
E-3	RT $\xrightarrow[\Delta]{3\ h}$ 350°C/1 h

RT, room temperature; Δ, heating; Polyamic acid varnish, BPDA/ODA/PDA (solvent: NMP).

Peel Strength

The peel strengths of the copper foil substrate peeled from the polyimide films are shown in Table II. In general, the higher the cured temperature is, the higher the peel strength. When the curing temperature is lower than 300°C, higher peel strength is obtained with longer curing time, e.g., D-1 > D-3 > D, B > A, etc. However, when the curing temperature is at 350°C the peel strength is highest at E-1, which has a short cure time.

The peel strengths of the copper foil/polyimide imidized under various curing schedules have also been measured after boiling in water for 24 h and the results are shown in Table II. All peel strengths are lower than those without thermo heat treatment. It has been reported that polyimide can be hydrolyzed to polyamic acid if exposed to a T/H environment for a long period of time.[19] In the present experiment, the lowering of peel strength may be an indication of the occurrence of some hydrolysis.

Interface Color Changes

The color of the copper interface is brass for samples cured at a temperature lower than 300°C. However, when the curing temperature reached 350°C the color of the copper interface varies from orange or violet to light brown depending upon the cure schedule (Table II). These results indicate that when the curing temperature is lower than 300°C the copper at the interface is not oxidized. When the curing temperature is higher than 350°C, the copper at the interface is oxidized and the extent of oxidation will depend upon the cure schedule.

The color of the polyimide interface is yellow-brown when the curing temperature is lower than 250°C, becomes brown when the curing temperature reaches 300°C, and turns to dark brown when the curing temperature is at 350°C. The color change may be due to the amount of retained solvent and the packing density of polyimide chain. The higher the density is, the deeper the color becomes.

The color change of polyimide and copper at the interface at high temperature may also be associated with the catalytic oxidative degradation of polyimide by copper.

Interface Studies

SEM studies show that the surfaces of both the copper and polyimide interface are fairly smooth for all samples imidized under various cure schedules [Figs. 1(a) and 1(b)]. This indicates that the binding force between polyimide and copper is chemical bonding instead of mechanical interlocking.

The cross-sectional TEMs of polyimide/copper interfaces cured at for different schedules are shown in Figure 2. When the curing temperature is low,

Table II Peel Strengths of Copper/Polyimide and Color of Interface Side of Copper and Polyimide

	Peel Strength (lb/in)			
	Immersion in Boiling Water 24 hr		Cu	PI Film
Symbols	Before	After	Color	Color
A	2.3	0.2	Brass	Yellow-brown
A-1	5.5	2.8	Brass	Brown
B	3.9	0.2	Brass	Yellow-brown
B-1	4.9	2.7	Brass	Brown
C	4.1	0.4	Brass	Brown
C-1	4.5	2.7	Brass	Brown
D	6.5	3.3	Brass	Brown
D-1	8.1	3.8	Brass	Brown
D-2	6.7	4.8	Brass	Brown
D-3	6.1	4.1	Brass	Brown
E	7.7	4.6	Yellow-violet	Dark-brown
E-1	10.6	6.8	Yellw-orange	Dark-brown
E-2	7.8	6.6	Yellow-violet	Dark-brown
E-3	5.0	3.7	Light-brown	Dark-brown

Polyimide: BPDA/ODA/PDA.

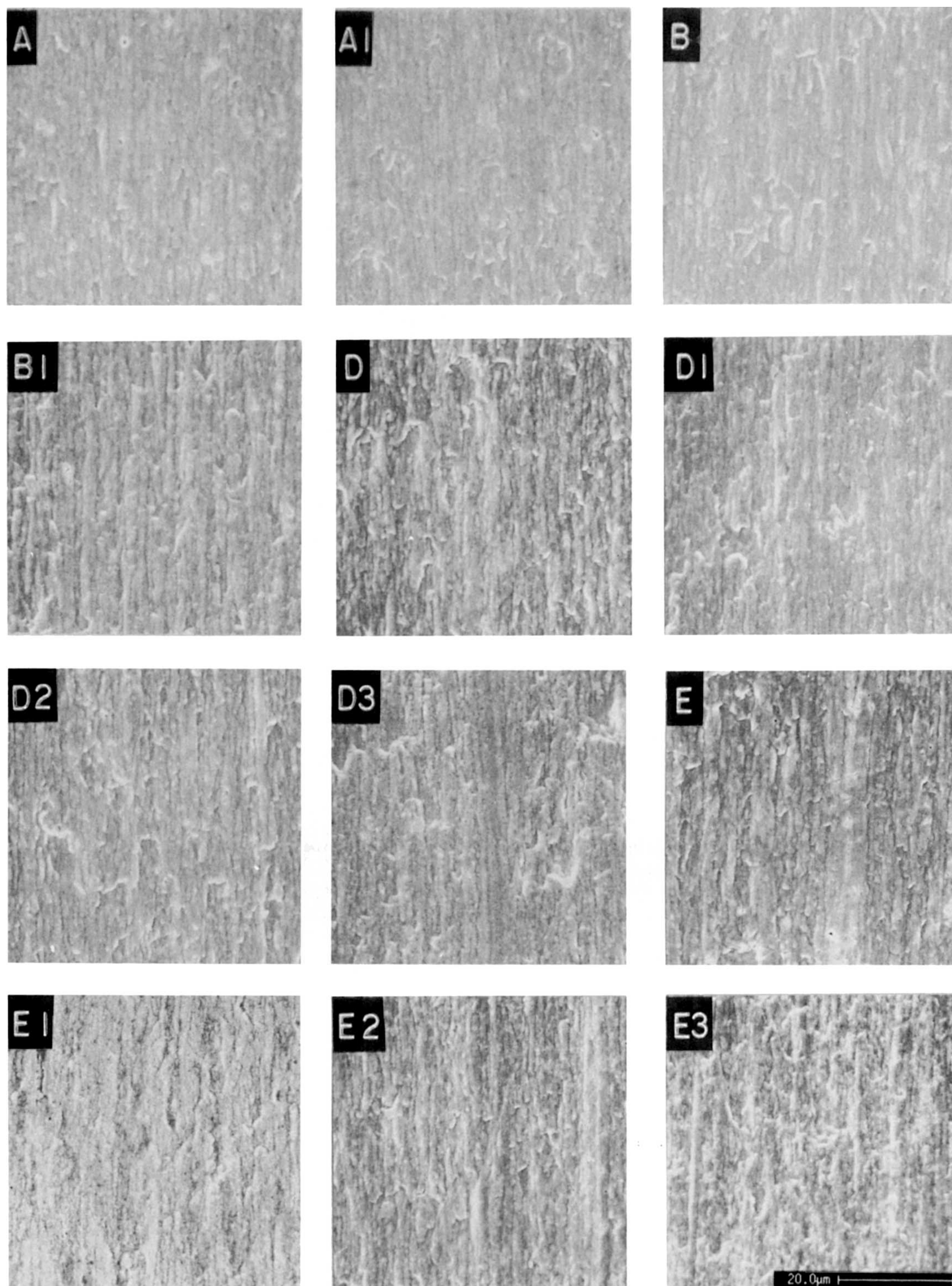

Figure 1(a) The morphologies of the interfaceside of copper foil after peel test (see Table I).

there are many small precipitated copper oxide particles distributed evenly near the interface and the edge of the interface is clear cut. As the curing temperature increases, the precipitated copper oxide particles become large and fewer in number. When the curing temperature is 300 or 350°C, a gap exists between the interface and the copper oxide precipitating area. Also at a 350°C cure schedule, a copper–

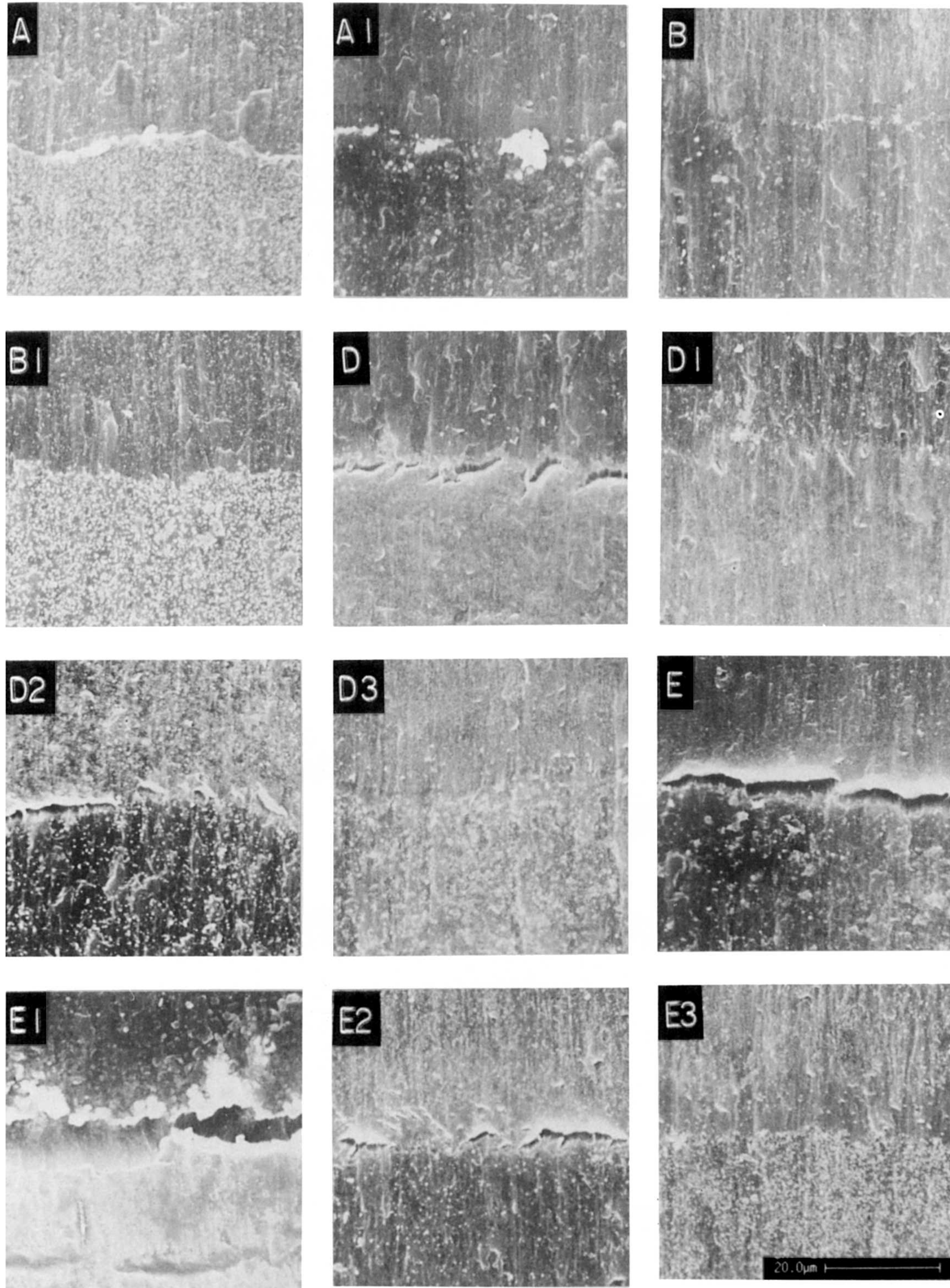

Figure 1(b) The morphologies of the interfaceside of polyimide film from various cure schedules (see Table I).

polyimide interaction zone occurred at the interface. The copper oxide is identified as Cu_2O by scanning transmission electron microscopy (STEM).

XPS spectra of polyimide interface are shown in Figures 3 and 4. The copper content increases from 1.48% when cured at 200°C to 21.9% when cured at

350°C. From the analysis of the structure of polyimide used in this experiment, we found that the peak at 293 eV is due to carbonyl carbon which is complexed with copper. This peak increases as the curing temperature increases from 200 to 350°C.

DISCUSSION

The aforementioned difference in peel strength, colors, and interface composition of polyimide/copper foil interface during various cure schedules can be attributed to the interaction of the polyamic acid, solvent NMP, and oxygen from the air with the copper (oxide) surface. When the polyamic acid varnish is spin coated onto copper foil, the polyamic acid, solvent NMP, and oxygen from the air can interact with the copper (oxide) surface. It has been reported that polyamic acid reacts with copper (oxide) to form a polyamic–copper complex and this polyamic–copper salt can diffuse into the polyamic acid if there is a liquid medium around. Once diffused into the polyamic acid, the complex will precipitate out as copper oxide particles in the polyimide upon curing of polyamic acid.[11,12]

As the evaporation of NMP is slow when the curing temperature is lower than 250°C, there is ample time for the NMP solvent to interact with the interface copper. Once the copper at the interface is oxidized to copper oxide, it will dissolve in NMP and diffuse into the polyimide film. And, these reactions take place to a great extent when the curing temperature is low (200, 250°C), and almost all of

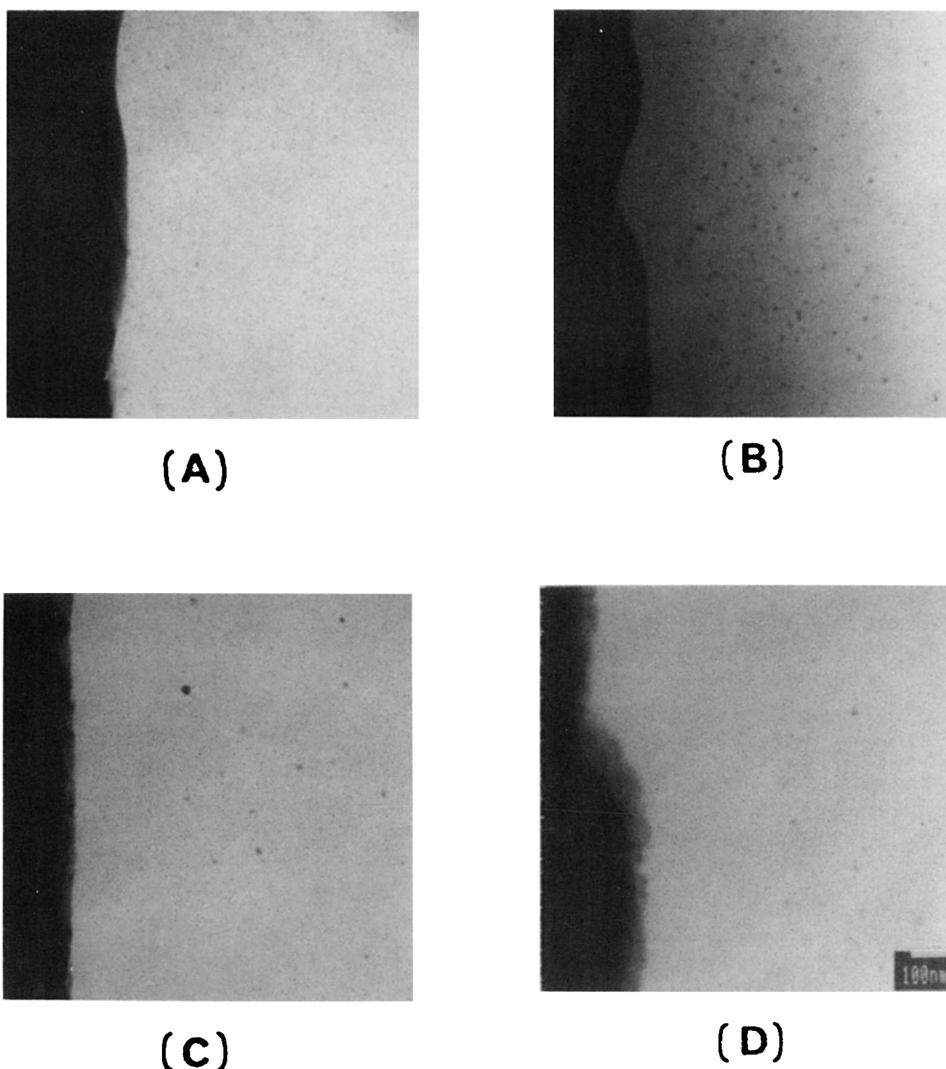

Figure 2 Cross-sectional TEM showing the PI–Cu interface and Cu oxide particles. Curing temperature: (A) 200°C; (B) 250°C; (C) 300°C; (D) 350°C.

Figure 3 ESCA spectra of Cu_{2p1} and C_{1s} peaks obtained from cured polyamic acid films after peel test. The cured temperature: (a) 200°C; (b) 300°C; (c) 350°C.

the copper oxide can be carried away by the NMP solvent. When the solvent NMP is finally completely evaporated, the copper oxide will precipitate out and stay on the spot. Therefore, the distribution of copper oxide is even, the particle of copper oxide is small, and there is no gap between the polyimide/copper interface and the distribution area of copper oxide particles. Thus, the copper interface is brass. Also, the copper content at the polyimide interface is low, and the peak of carbonyl carbon is small because there is less need for conformational orientation of the carbonyl group to complex with copper oxide.

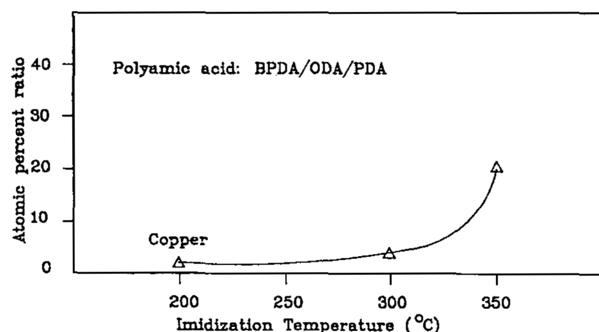

Figure 4 Atomic percent ratio of copper on polyimide surface after peel test obtained from ESCA spectra analysis.

The rate of NMP evaporation is faster when the curing temperature is higher (300 or 350°C) and there is a shorter period of time for the NMP solvent to interact with the interface copper (oxide). Hence, there is comparatively smaller amount of copper (oxide) dissolved in NMP and diffused into the polyimide film. Because NMP is quickly evaporated, there is no more copper oxide diffused into the polyimide film when there is no NMP at the interface. As NMP is evaporating, the copper oxide dissolved in NMP keeps on diffusing toward the inside of the polyimide film and finally precipitated out. Therefore, there is a gap between the polyimide/copper interface and copper oxide particle distribution area.

After the NMP solvent is completely evaporated, the copper complex formed at the interface cannot be carried away. It stays at the interface. Therefore, the copper interface resulting from high curing temperature shows various colors depending upon the cure schedule. Also, the copper content at the polyimide interface is high, and a copper–polyimide interaction zone is developed at the interface. The peak of carbonyl carbon is also larger at the polyimide interface due to more polyimide carbonyl group oriented toward the interface to complex with the copper oxide.

The results of the above studies indicated that the binding force between polyimide and copper is a chemical bonding resulting from the interaction of copper oxide and the polyimide carbonyl group.

The appearance of higher peel strength at a high-temperature cure schedule of short curing time (E-1, Table I) can be explained as follows.

When the curing temperature is low, the rate of NMP evaporation is slow too, so most of the copper oxide formed at the interface is carried away by NMP. This reduces the bonding sites between copper and the polyimide carbonyl group, so the binding force between polyimide and copper is low. When the curing temperature is high, the NMP solvent evaporates very quickly and the copper oxide formed after complete removal of NMP from the interface will stay and interact with the polyimide carbonyl group, forming an interaction zone. This increase in the binding between copper and the polyimide carbonyl group results in a higher binding force at a high curing temperature. However, care should be taken to prevent overoxidation of the copper surface, which may result in poor adhesion between copper and copper oxide and in turn lead to decrease in peel strength.[14] The catalytic oxidative degradation of polyimide at the PI/Cu interface at a high temperature may also lead to decrease in peel strength. Therefore, among the high-temperature cure schedules the peel strength is highest for the short cure time.

CONCLUSION

The binding force between polyimide and copper of polymer-on-metal type interface is a chemical bonding resulting from the interaction of copper oxide and the polyimide carbonyl group. Among the four cure schedules studied, the high-temperature (350°C) schedule can result in a higher peel strength owing to the formation of a chemical bond between the interface copper oxide and the polyimide carbonyl group. In the low-temperature cure schedules, the formed copper oxide is carried away by NMP; thus, the chemical bonding sites with the polyimide carbonyl group are reduced and a lowering of peel strength occurs.

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