

# Metallization of Polyimide Film by Wet Process

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## SYNOPSIS

The interfacial adhesion strength of metallized polyimide (BPDA/ODA/PDA) has been studied with respect to polyimide surface molecular structure, reactions during electroless nickel deposition, baking, copper electroplating, and thickness of polyimide film. Each factor is discussed in terms of its influence on the peel strength. For practical application, operation at optimized conditions for each step of the metallization process is essential for sustaining the mechanical integrity of the copper/polyimide laminate. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polyimide (PI) is widely used in the fabrication of electronic circuitry, because of its low dielectric constant, high thermal stability, low moisture absorption, low thermal expansion, good mechanical properties, high chemical resistance, and ease of processing. For successful applications, good adhesion between polyimide and metals, particularly copper, is necessary. Thus, numerous techniques have been utilized to achieve this goal. These fabrication technologies include evaporation or sputtering of metal onto a cured polyimide surface in an ultrahigh vacuum system.<sup>1-5</sup> Other efforts to improve adhesion of metal to polyimide include the roughening of the polyimide substrate surface by cathodic sputtering,<sup>6</sup> chemical treatment,<sup>7,8</sup> and reactive ion etching.<sup>9</sup>

An additive method for circuit preparation on a polyimide substrate, as disclosed in some U.S. patents,<sup>10-12</sup> has low metal to polyimide adhesion strength, which limits its application to the printed circuit industry. Krause and Rider<sup>13</sup> have reported a novel process to metallize Kapton polyimide, based on the redox properties of polyimide in aqueous media, but adhesion values fall to less than 1 lb/in. after the solder float test at 280°C. Modification of

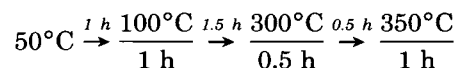
Krause's process, by incorporating a heat treatment step, resulted in a high adhesion value after the solder float test, as has been reported for surface texturing of the Kapton polyimide.<sup>14,15</sup>

This article reports optimized processing conditions for the metallization of a BPDA/ODA/PDA polyimide by a wet process.

## EXPERIMENTAL

The polyamic acid (PAA) solution was prepared by mixing 3,3',4,4'-bisphenyl tetracarboxylic dianhydride (BPDA) at room temperature with *p*-phenylene diamine (PDA) and 4,4'-oxydianiline (ODA) in *N*-methyl-2-pyrrolidone (NMP)/acetone solvent with a 3 : 2 volume ratio of NMP to acetone. The resulting polyamic acid solution had 15% solid content and viscosity of 2200 cps. The flow chart of the metallization process is shown in Figure 1.

The PAA was imidized in air by heating for a certain period of time at each of the following successive temperatures:



The microetching solution contains 37.4 wt % KOH, 10 wt % methanol, and 7 wt % ethylenediamine. The activation solution used was Electro-Brite catalyst C-473 from Electrochemicals Co.,

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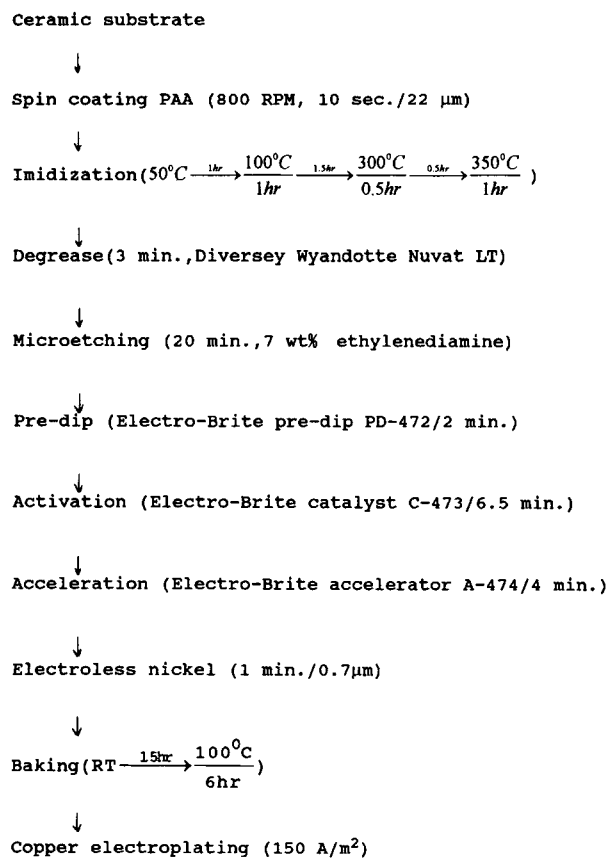


Figure 1 Flow chart of metallization process.

Ohio. The acceleration solution used was Electro-Brite accelerator A-474, from Electrochemicals Co. Ohio. The electroless nickel solution contained 11.25 g sodium citrate, 6 g sodium hypophosphite, 5.25 g nickel chloride, and 7.5 g ammonium chloride in 250 mL aqueous solution. The pH was kept at 8–9, and the plating temperature was 30–40°C. The copper electroplating solution contained 82.5 g copper pyrophosphate, 338 g potassium pyrophosphate, 4 mL ammonia, 22.5 g potassium oxalate, and 12 g potassium nitrate in 1000 mL of aqueous solution. The pH was kept at 8.2–8.8, the plating temperature was 52–58°C, and the current density was 100–200 A/m<sup>2</sup>. Unless specified, the general process parameters are as described in Table I.

After copper had been electroplated to a certain thickness, it was etched into  $\frac{1}{8}$  inch-wide strips. The adhesion strength between the metal part and polyimide was studied with a 90° peel test machine from Shimadzu, model AG-5000A, at a constant peeling speed of 25 mm/min.

## RESULTS AND DISCUSSION

The chemical nature of the metal-polymer interface has generally been accepted to have a significant effect on the adhesion of metal to polymers.<sup>16–20</sup> For metallizing polymers, the interface can be influenced

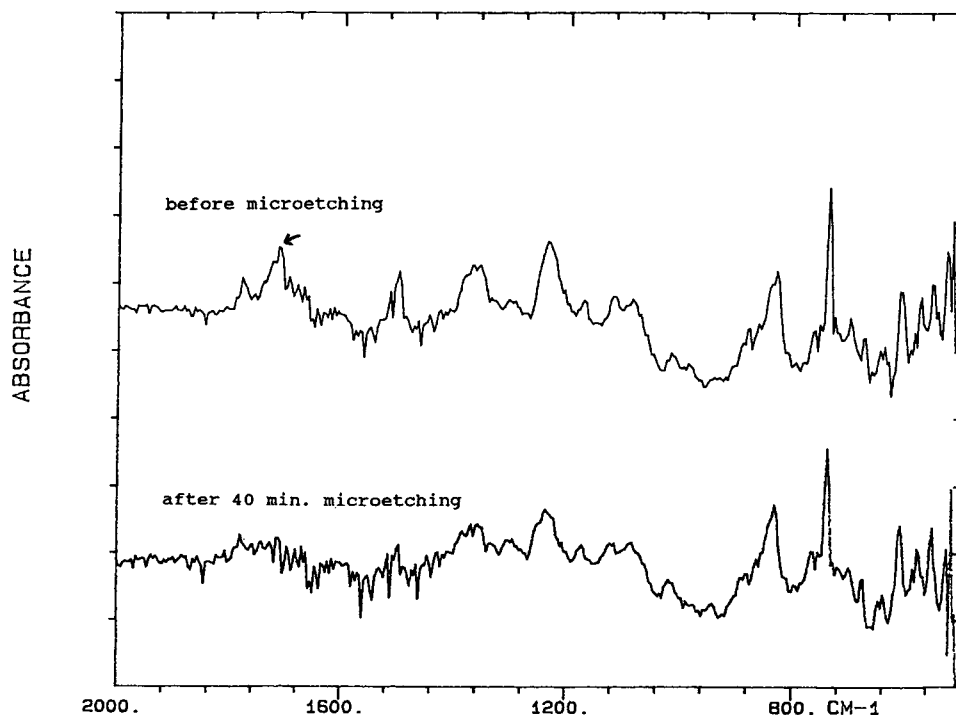
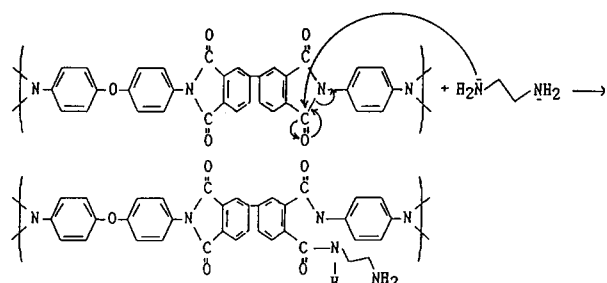


Fig. 2 ATRIR spectra of PI film

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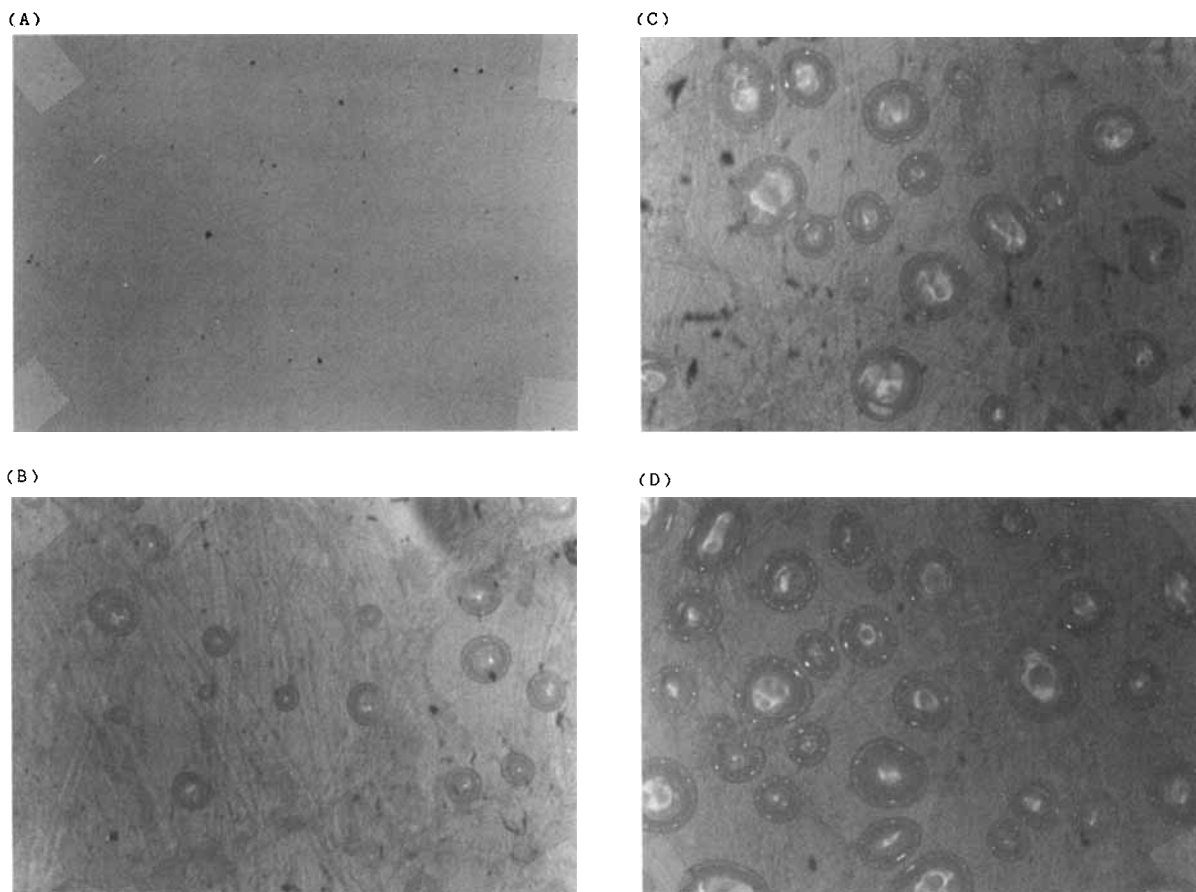
**Figure 3** The reaction of primary amine of caustic solution with imide group on PI surface.

by the polymer surface molecular structure and the metallization process, as shown by some U.S. patents,<sup>21-23</sup> and by the present study.

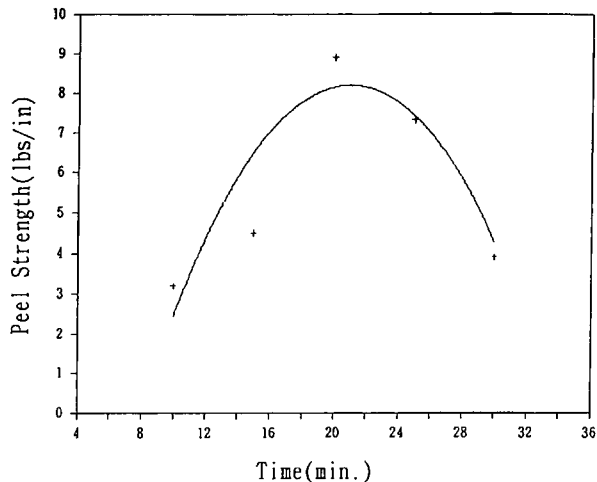
#### The Effect of Polyimide Surface Modification on Adhesion

The polyimide surface was microetched by a caustic solution (37.4% KOH), containing 7% ethylenedi-

amine. Comparing the attenuated total reflective IR spectra of films, before and after microetching, we found that the intensity of the  $\phi$ -N absorption band near  $1720\text{ cm}^{-1}$  obviously decreased after 40 min of microetching (Fig. 2). This phenomenon may be explained in term of an amidization reaction between the primary amines in the etching solution and the imide groups on the polyimide surface (Fig. 3). This partially amidized polyimide is more hydrophilic and more permeable towards the activation solution.<sup>24</sup> The surface topography of the polyimide, microetched in the caustic solution, is shown in Figure 4. The water droplets absorbed on the surface of the polyimide films increased with microetching time. However, the best adhesion to metal, without the loss of its bulk physical properties, occurred only at a critical microetching time. Excessive microetching treatment may degrade the physical properties of the surface, causing the solvent to diffuse into the bulk, leading to poor adhesion. With the present experimental condition, a 20-min microetching provided the best surface for subsequent



**Figure 4** Surface topography of PI films (A) before microetching, (B) after 10 min microetching, (C) after 20 min microetching, and (D) after 30 min microetching.



**Figure 5** Adhesion strength variation with time of microetching.

processing steps and resulted in high metal-polyimide adhesion, as shown in Figure 5 by the plot of peel strength vs. microetching time.

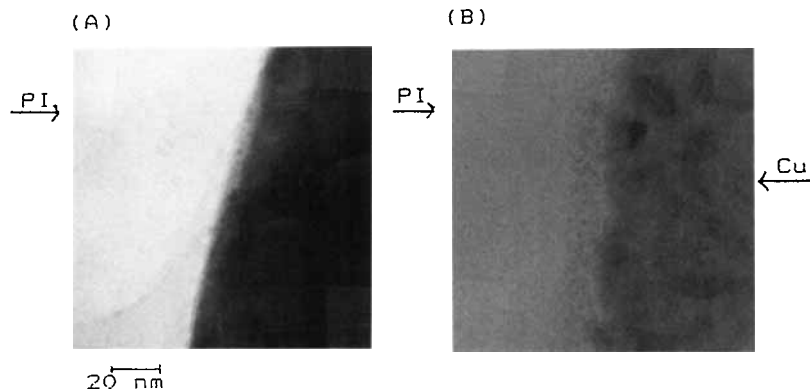
#### The Effect of Electroless Nickel Deposition

It has been reported that copper migrates into polyimide at an elevated temperature, causing degradation of polyimide around the vicinity of a copper cluster.<sup>25-27</sup> Our experimental results confirmed such a finding. Direct metallization of copper onto the polyimide surface results in low peel strength of < 1 lb/in., due to copper migration, which was observed by transmission electron microscopy and is shown in Figure 6.

This copper migration can be inhibited with chromium deposition at the copper-polyimide in-

**Table I** Process Parameters

Process	Condition
Ceramic Substrate	96% Alumina (5 cm × 5 cm)
Spin Coating	400 RPM/5 sec → 400 RPM/10 sec; thickness of polyimide film after imidization = 22 μm
Imidization	50°C $\xrightarrow{1\text{ h}}$ 100°C/1 h $\xrightarrow{0.5\text{ h}}$ 300°C/0.5 h $\xrightarrow{1.5\text{ h}}$ 350°C/1 h (in air)
Degrease	Nuvat LT 17.5 g Volume 250 mL Immersion Time 3 min
Microetching	KoH 37.4 wt % Methanol 10 wt % Ethylenediamine 7 wt % Immersion Time 20 min
Predip	PD-472 60 g Conc. HCl 8.75 mL Volume 250 mL Immersion Time 2 min
Activation	C-473 10 mL PD-472 60 g Conc. HCl 8.75 mL Volume 250 mL Immersion Time 6.5 min
Acceleration	A-474 17.5 mL Volume 250 mL Immersion time 4 min
Electroless Nickel Baking	Caustic Electroless Nickel Solution RT $\xrightarrow{1.5\text{ h}}$ 100°C/6 h
Copper Electroplating	Current Density 150 A/m <sup>2</sup> Plating Time 140 min Thickness of Cu 35 μm



**Figure 6** Cross-sectional TEM analyses of (A) PI/Ni interface and (B) PI/Cu interface.

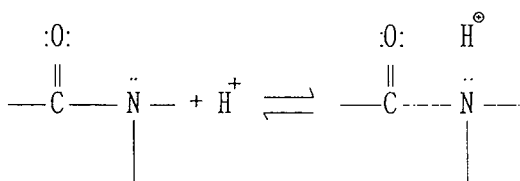


Figure 7 Polyimide surface in acidic solution.

terface and resulted in a laminate with better metal/polyimide adhesion.<sup>28</sup> At the same temperature, diffusion of nickel in polyimide was less rapid than copper,<sup>26</sup> so the presence of the nickel layer can also act as a barrier to inhibit copper migration and to enhance adhesion strength.<sup>29</sup>

The efficiency of nickel as an adhesion promotor depended on how nickel was metallized onto the polyimide film. The peel strength of the metal-polyimide laminate was much stronger when using a caustic electroless nickel solution ( $\sim 8.5$  lb/in.) instead of an acidic electroless nickel solution ( $< 1$  lb/in.) (solution composition is shown in Table II). The difference in adhesion strength might be due to generalized acid-base complex formation between

the polyimide surface and electroless deposition during metallization. As metallic nickel and copper are both weak acids,<sup>30</sup> they could interact with the  $\pi$ -system of aromatic ring or the nitrogen of the imide group on a polyimide surface during the metallization process in a caustic solution, resulting in a composite with high peel strength. However, when the metallization took place in an acidic solution, the presence of protons (Fig. 7) inhibited the interaction of metal with the polyimide surface and resulted in a composite with low peel strength. In the case of metallization by electroless copper, because copper migration after baking can cause degradation of the copper-polyimide bond, the peel strength is low.

The thickness of the electroless nickel deposition from the caustic solution has an effect on peel strength, as shown in Figure 8. If the electroless nickel deposit is too thick, it is difficult for the water, absorbed by polyimide during the wet process, to evaporate and delamination of the metal-polyimide composite will result. The optimal nickel thickness for the present experiment is  $0.7 \mu\text{m}$  at 60 sec deposition time.

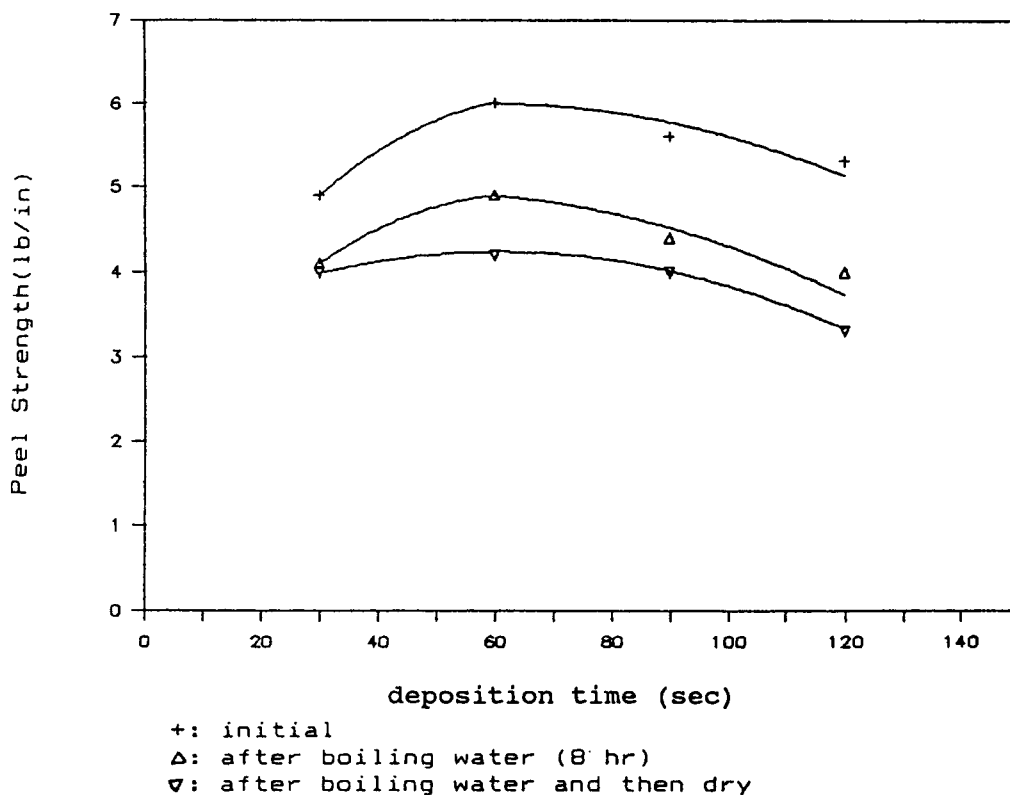
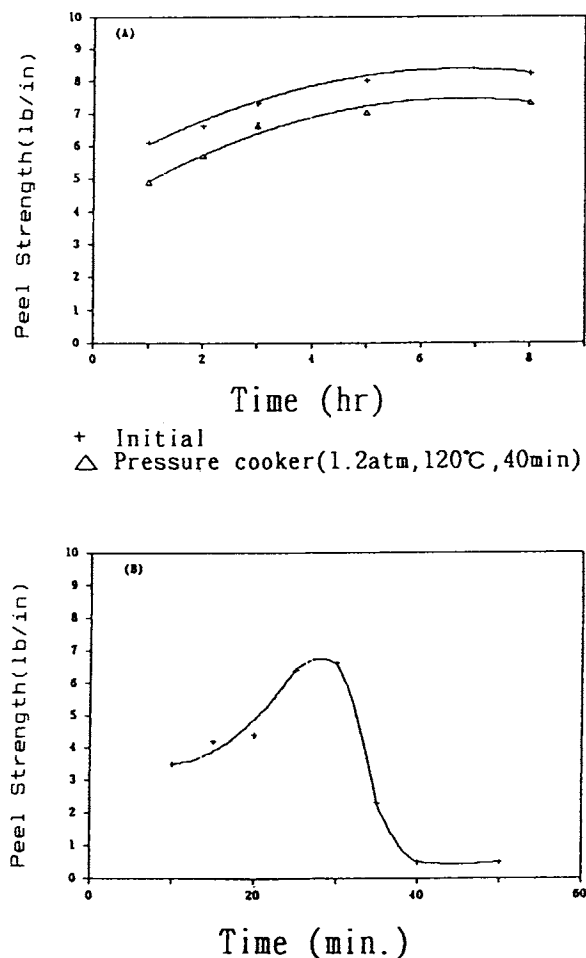


Figure 8 Adhesion strength variation with time of electroless nickel deposition (deposition time 60 sec  $\sim 0.7 \mu\text{m}$  thickness, thickness of copper  $12 \mu\text{m}$ ).



**Figure 9** Adhesion strength variation with time of baking (A) at 100°C and (B) at 200°C.

### Baking

The effect of baking on peel strength is shown in Figure 9. The adhesion of the nickel/polyimide laminate was poor without baking, due to fact that the water, absorbed by polyimide during wet processes, was difficult to evaporate. Heat treatment might facilitate the water evaporation, might release stress, and might improve adhesion. Nevertheless, baking in air at high temperature (200°C) resulted in a decreased adhesion value of the laminate. This might be due to the oxidation of nickel at the interface. The optimal condition in the present case is baking at 100°C for 6 h.

### The Effect of Current Density on Adhesion Strength

If the electroplating of copper was carried out at a current density of 150 A/m, polycrystalline copper,

with slightly compressive stress, was deposited.<sup>31</sup> When it was plated to the same thickness at 200 A/m<sup>2</sup>, the adhesion strength of the laminate was lower, because of a positive tensile stress of the deposit (Fig. 10).

### The Effect of Thickness of Polyimide Film and Copper on Adhesion Strength

The plot of peel strength vs. thickness of polyimide film is shown in Figure 11 and indicates that the peel strength was higher with thinner polyimide film; however, during peeling, deformation of the film may occur with too thin a film. The optimal thickness for practical application is 25 μm. The effect of the thickness of electroplating copper on peel strength is shown in Figure 12. The peel strength was higher with a thicker copper layer. In this study, the copper thickness was kept at 35 μm, the practical thickness for the fabrication of tape automated bonding (TAB) during studies made on other parameters.

### Thermo-Moisture Effect

The peel strength of each experimental condition was lower after thermal-moisture treatment (Figs.

**Table II** Solution Composition

Caustic Electroless Nickel Solution	
Sodium Citrate	11.25 g
Sodium Hypophosphite	6 g
NiCl <sub>2</sub> × 2 H <sub>2</sub> O	5.25 g
Ammonium Chloride	7.5 g
Volume	250 mL
pH	8~9
Temperature (°C)	30~40
Acidic Electroless Nickel Solution	
NiSO <sub>4</sub> × 6 H <sub>2</sub> O	5 g
Sodium Hypophosphite	6 g
Succinic Acid	4.5 g
Maleic Acid	4 g
Volume	250 mL
pH	5.2
Temperature (°C)	95
Pb (CH <sub>3</sub> COO) <sub>2</sub>	1 mg
Caustic Electroless Copper Solution	
Electro-Brite 2000 A <sup>a</sup>	2.25% by Volume
Electro-Brite 2000 B <sup>a</sup>	15.0% by Volume
Electro-Brite 2000 C <sup>a</sup>	1.75% by Volume
Deionized water	Balance
Temperature	49~55°C

<sup>a</sup> Electrochemicals Co., Ohio.

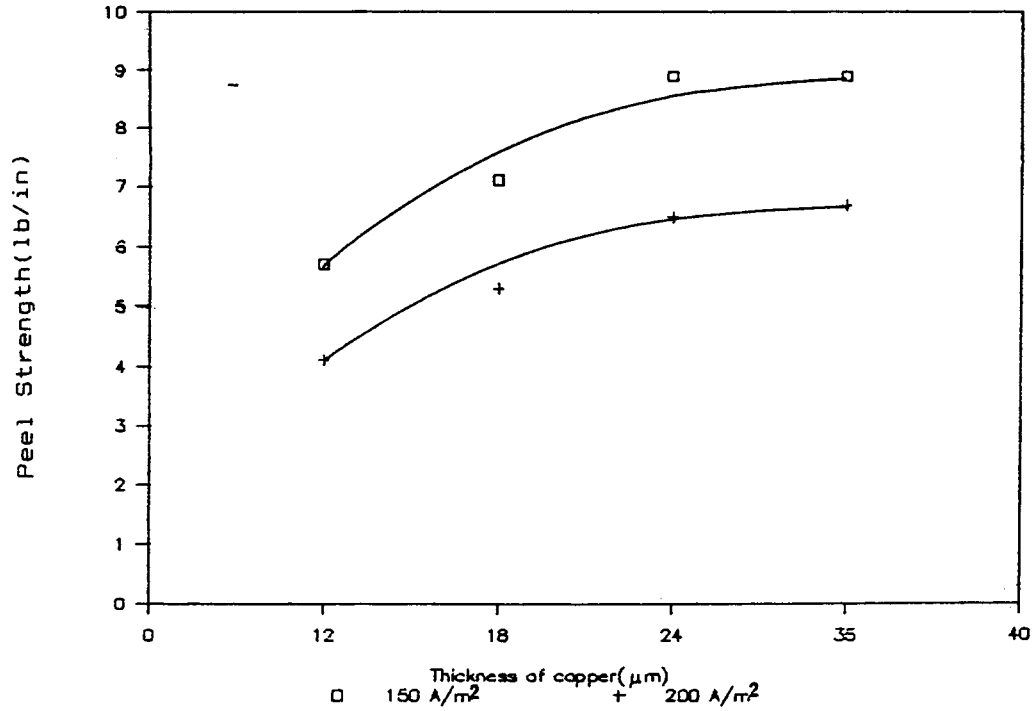


Figure 10 Effect of current density on peel strength.

8, 9, and 12), indicating that some reactions had taken place, leading to the failure of interfacial adhesion.

**CONCLUSION**

As a metal-polyimide laminate must withstand a hostile environment during fabrication of a multi-layer microelectronic device, strong interfacial

adhesion must be maintained in order to sustain mechanical integrity. This article presents a means for the fabrication of well-adhered, electroless, nickel/electroplating copper layers on a BPDA/ODA/PDA polyimide substrate, with an adhesion strength of ~8.5 lb/in., through polyimide surface

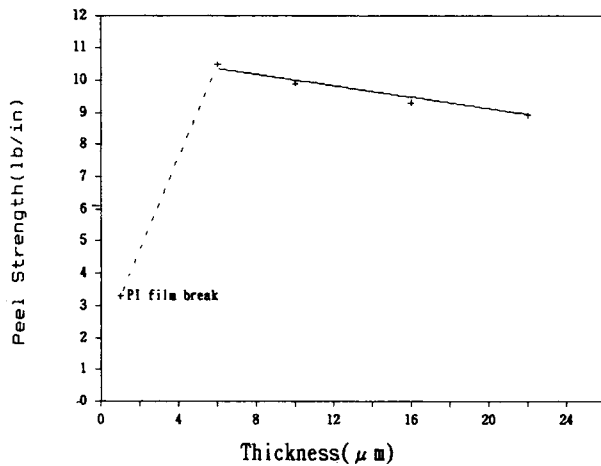


Figure 11 Effect of the thickness of polyimide film on peel strength.

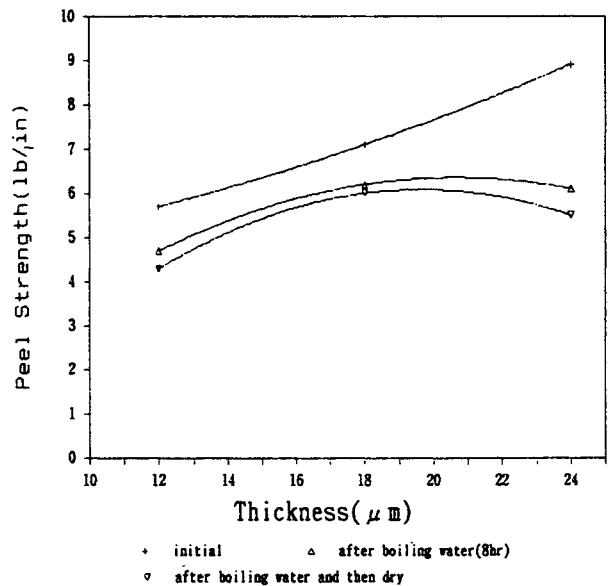


Figure 12 Effect of the thickness of copper on peel strength.

structure modification by caustic solution containing 7% ethylenediamine for 20 min at room temperature, and through optimizing the different steps of the metallization process, such as maintaining the thickness of electroless nickel at 0.7  $\mu\text{m}$  under caustic solution, baking in air for 6 h at 100°C to evaporate the water absorbed in polyimide, and electroplating copper at 150 A/m<sup>2</sup> current density to a thickness of 35  $\mu\text{m}$ . It is speculated that the formation of the acid-base complex between metal atoms (weak acid), with the  $\pi$ -system of aromatic ring (weak base) or nitrogen of the imide group (moderate base), is the mechanism leading to good adhesion of metal—polyimide laminate.

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