Curl-Free High-Adhesion Polyimide/Copper Laminate

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SYNOPSIS

6-Amino-2-(*p*-aminophenyl)benzimidazole (BIA) was synthesized and employed as a diamine component in the preparation of polyamic acid. The mechanical and thermal properties of polyimides made from BIA as a diamine component were investigated. A high-adhesion, curl-free polyimide/copper laminate has been obtained by using BIA as a diamine component. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides with their overall balance of thermal, mechanical, and electrical properties are frequently used as interlevel dielectrics in high-density multilevel interconnection technology.[1-5] The latter is often used in high-performance computers, work stations, telecommunications, and space applications because of its capability to provide high-density packing and fast operation speed. For the betterment of such applications, the formation of well-adhered polyimide/metal laminate is crucial. A considerable amount of effort has been directed to promote such an adhesion,[6-8] such as modification of the polyimide surface by wet processes or by plasma treatment[9,10] and to investigate the adhesion mechanisms and interfacial structures by various surface analysis techniques, such as X-ray photoelection spectroscopy, secondary ion mass spectroscopy, and transmission electron microscopy.[11-16]

The polyimide/metal laminate for tape automated bonding (TAB) is produced by applying a solution of polyamic acid onto a metallic foil and then imidizing thermally.[17] However, the imidized coating usually shrinks after cooling, resulting in the curling of the composite films. Currently, a process for producing a polyimide/metal laminate having a curvature radius of at least 25 cm has been reported.[18]

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The object of the present experiment was to produce a curl-free high-adhesion polyimide/copper laminate by using 6-amino-2-(*p*-aminophenyl)-benzimidazole (BIA) as a diamine component in the preparation of the polyimide precursor: polyamic acid.

EXPERIMENTAL

Oxydianiline (ODA), 1,4-phenylene diamine (PDA), 4-nitro-1,2-phenylene diamine, and 4-nitrobenzoyl chloride were obtained from Merck (Germany). Biphenyl tetracarboxylic dianhydride (BPDA) was from Ube (Japan). All chemicals were reagent grade and were used as received without further purification.

Preparation of 6-amino-2-(*p*-aminophenyl)benzimidazole (BIA)

A mixture of 30.6 g 4-nitro-1,2-phenylene diamine and 200 mL 1-methyl-2-pyrrolidinone (NMP) was stirred in a three-necked flask while a solution of 38.3 g 4-nitrobenzoyl chloride in 200 mL NMP was added slowly at room temperature over the period of 1 h. The reaction temperature was then raised to 150°C. After 3 h stirring at 150°C, the mixture was cooled and poured into water. The precipitate was filtered off, recrystallized from *N,N*-dimethylacetamide (DMAC), and dried in vacuum at 80°C to give 27.7 g (62% yield) of pale green needle crystal that was determined to be 5(6)-nitro-2-(*p*-nitro-

phenyl)benzimidazole by elemental analysis (C, 51.57%; H, 3.35%; N, 18.33%; $C_{13}H_{10}N_4O_5$). Its melting temperature was 358°C.

Five grams of the above-synthesized compound, 200 mL of methanol, and 0.5 g of 5% palladium-on-carbon was hydrogenated in a shaking flask at 55 psi at room temperature for 4 h. The resulting solution was filtered. The filtrate was evaporated to dryness under vacuum, giving yield to a red solid (52% yield) 6-amino-2-(*p*-aminophenyl)benzimidazole (BIA) as determined by elemental analysis (C, 69.61%; H, 5.40%; N, 25.0%; $C_{13}H_{12}N_4$). The melting temperature was between 247 and 249°C.

Preparation of Polyamic Acid

The diamines were dissolved in sufficient NMP, and the solution was stirred at room temperature with solid dianhydride added in portions at the mole ratio of dianhydride to diamine of 0.99. The solid content was controlled to 15 wt %. The reaction proceeded for 6 h with stirring under a nitrogen atmosphere to give a viscous clear polyamic acid solution. The inherent viscosity of polyamic acid was obtained by dissolving 0.5% of polyamic acid in NMP at 30°C, then the time of flow of the solution by a Kusana Ubbelohde viscosimeter was measured and the following equation calculated:

$$\eta_{inh} = \frac{\ln(t/t_0)}{0.5\ g/dL} = 2\ln(t/t_0)dL/g$$

Properties of Polyimide Films

Polyamic acid resins were cast on a 35 μm-thick electrolytical copper foil using a doctor blade to obtain a cured film at a thickness of approximately 25 μm. They were then imidized by heating in nitrogen atmosphere for 1 h at each of the following successive temperatures: 150, 250, and 350°C.

The laminate was cut into 5 mm-wide and 50 mm-long strips to measure the degree of curling. Figure 1 shows a side view of a polyimide/copper laminate that is provided to explain the degree of curling.

The copper foil of the laminate was then etched into $\frac{1}{8}$ in.-wide copper strips. The adhesion strength between polyimide and copper was studied by a 90° peel test machine from Schimadzu, Model AG-5000A. The peeling speed was kept constant at 10 mm/min.

The thermal and mechanical properties of the polyimide film were measured from films with all the copper being etched away. The tensile strength and elongation of polyimide films were measured with a Schimadzu AG-5000A Autograph tensile test machine at a test speed of 10.0 mm/min and the load cell was 10 kg. The thermal expansion coefficient (C.T.E.) between 50 and 250°C and glass transition temperature of the polyimide films were obtained from DuPont TMA Model 2940 at a 10°C/min heating rate. Thermogravimetric diagrams of polyimide films were obtained from DuPont TGA Model 951 at a 20°C/min heating rate in N_2.

RESULTS AND DISCUSSION

It is a well-known fact that the physical properties of the polymeric compounds are highly affected by their chemical structures. Thus, theoretically, curl-free polyimide/copper laminate can be obtained by modifying the polyimide chemical structure such that its physical properties, especially its thermal expansion coefficient, is in close agreement to that of the pure copper. Based on this postulation, polyamic acids of different molecular structures were synthesized. The physical properties of the polyimide films derived from these polyamic acids were studied and the results are shown below.

The Effect of Diamine Structure on PI Morphology

Polyamic acids with different molecular structures were synthesized by varying the structures of diamine or diamine mixtures in the imidization process with BPDA dianhydride. The molecular structures of diamines and BPDA dianhydride used in this study are as shown in Figure 2. PDA is a con-

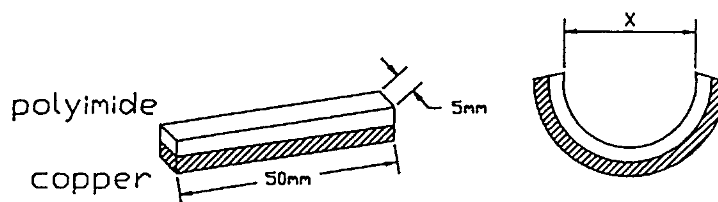

Figure 1 The degree of curling for polyimide/copper laminate.

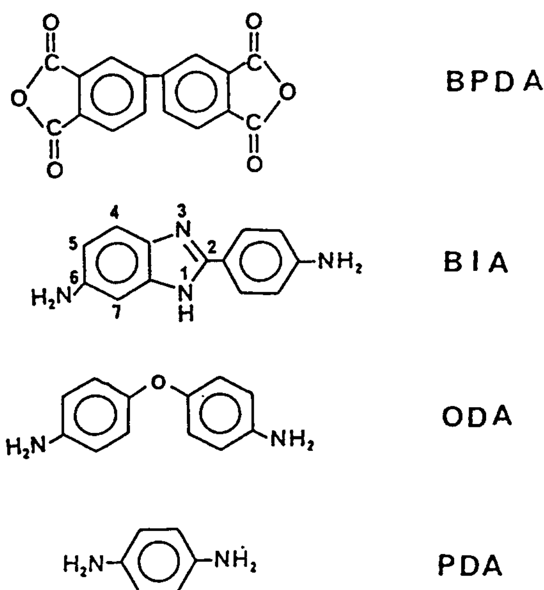

Figure 2 The molecular structures of the polyimide monomers.

jugated planar molecule. ODA is a bent molecule. Benzimidazole (BIA) is an unsymmetrically extended conjugated molecule with the imidazole group having an active hydrogen on one of the nitrogen (N1) and a Lewis base at the other nitrogen (N3) due to the presence of an unshared pair of electrons. All these compounds (PDA, ODA, and BIA) can react with BPDA to form polyamic acid. A rod-shape rigid polyimide of high packing density is formed from the reaction of BIA or PDA with BPDA, and a flexible polyimide is obtained from the ODA/BPDA system.

The Effect of Diamine Structure on Physical Properties

The flexible nature of the ODA polyimide and the rigidity of the PDA and BIA polyimides lead to the usage of diamine mixtures composed of both ODA and BIA or PDA in imidization in order to obtain

Table II Thermal Properties of Polyimide Films

	PI-1	PI-2	PI-3	PI-4	PI-5
C.T.E. (ppm/°C)	41.9	18.0	30.0	22.4	11.0
T_g (°C)	275	358	337	367	384

polyimide with adjustable physical properties. Thus, different polyimides were synthesized with ODA (PI-1), ODA/PDA (PI-2), ODA/BIA (PI-3 and PI-4), and BIA as diamines. Their mechanical and thermal properties are listed in Tables I and II. It was found that the polyamic acid viscosity and tensile strength, glass transition temperature (T_g), and thermal stability of the polyimide films are highly affected by the molecular structure of the diamines.

ODA diamine is a bent molecule where the two phenyl rings can rotate freely. It can produce polyamic acid of low viscosity (0.42 dL/g) and flexible polyimide film with 14.6 kg/mm^2 tensile strength, 60% elongation, low T_g value (275°C), and low thermal stability (PI-1).

PDA diamine is a conjugated aromatic planar molecule. When used in mixture with ODA (PI-2), the viscosity of the polyamic acid increases to 0.48 dL/g, the tensile strength of the polyimide film increases to 17.0 kg/mm^2, the elongation drops to 15%, and the T_g value is raised to 385°C.

BIA diamine with its unsymmetrically extended conjugated molecule gives rise to high-viscosity polyamic acid (0.58 dL/g) and polyimide film with high tensile strength (17.5 kg/mm^2), low elongation (10%), high glass transition temperature (T_g 384°C), and high thermal stability (570°C) (see PI-5). However, all these properties are affected by the incorporation of ODA into the diamine mixture as in PI-3 (0.3 BIA, 0.7 ODA) and PI-4 (0.6 BIA, 0.4 ODA). The viscosity of the polyamic acid decreases with the increase of ODA content, and for the resulting polyimide film, the tensile strength and T_g

Table I Physical Properties of Polyimides Made from BPDA

	PI-1	PI-2	PI-3	PI-4	PI-5
Diamines	ODA	0.8 PDA 0.2 ODA	0.3 BIA 0.7 ODA	0.6 BIA 0.4 ODA	BIA
Inherent viscosity η_{inh} (dL/g)	0.42	0.48	0.55	0.56	0.58
Tensile strength (kg/mm^2)	14.6	17.0	15.2	15.8	17.5
Elongation (%)	60	15	32	21	10

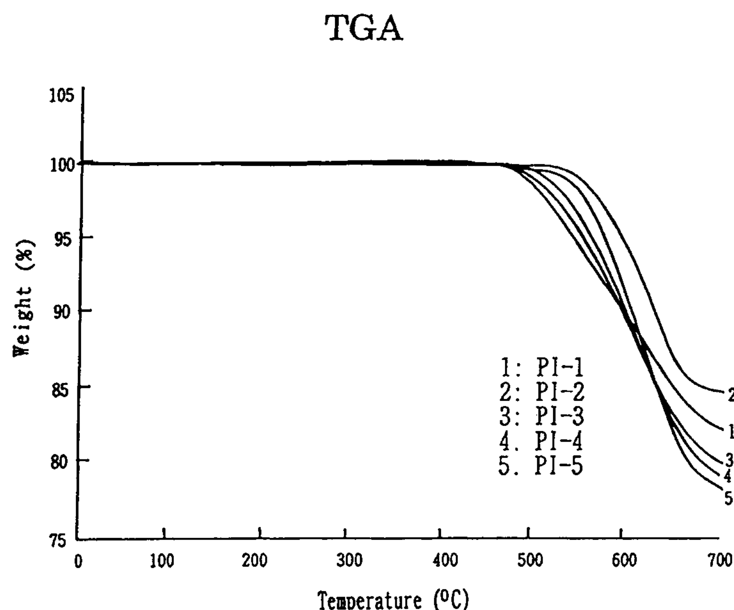

Figure 3 Thermogravimetric analysis for a series of polyimides.

value decrease and the elongation value increases with increase in the ODA content.

For the PI studied in this article, the polymers' weight loss measured by thermogravimetric analysis (TGA) at such a high temperature may be due to polymer decomposition, which is strongly related to chemical structure, because thermal stability is primarily a function of bond energy. When the temperature increases to the point where vibrational energy causes bond rupture, the polymer degrades. Since benzimidazole is an extended conjugated molecule, with delocalized electrons distributed all over the molecule, the polyimide made from BIA is highly thermally stable until 570°C, which is higher than those made from ODA or from both BIA and ODA. Polyimide made from 80% PDA–20% ODA copolymer is thermally stable until 580°C, because PDA is a conjugated aromatic molecule, which is also very stable (Fig. 3).

Polyimide/Copper Adhesion

Although the nature of the adhesion mechanism of polyimide/metal remains to be understood, it is generally accepted that the interfacial interaction of polyamic acid and metal may lead to chemical bonding at the interface. We postulate that such reactions do occur with BIA and ODA polyamic acids. It is well known that BIA can react with metal oxide to form a metalazole complex and has been employed as a corrosion inhibitor of transition metals.[19] Recently, it was reported that by pretreating the copper surface with benzimidazole solution a better copper/polymer adhesion can be achieved because of the formation of copper imidazolate inner complexes that provide active sites for coordinating interfacial bonding.[20] Improved copper adhesion has also been reported for ODA polyimide.[11] The results of the adhesion strength (measured by the 90° peel test) for polyimides studied in this article are shown in Table III. As expected, the flexible structure of ODA and the chemical nature of BIA result in laminates with high adhesion strength as well as those made from ODA and BIA diamine mixture. The peel strength is low for laminate made from 80% PDA and 20% ODA.

Curl-free Polyimide/Copper Laminate

The thermal expansion coefficient (C.T.E.) of polymer is dependent on its chemical structure with polymer having high packing density and a rigid molecular chain exhibiting a low thermal expansion

Table III Adhesion Strength of Polyimide/Copper Laminate

	PI-1	PI-2	PI-3	PI-4	PI-5
90° peel strength (lb/in.)	8.2	1.7	7.2	9.0	4.8

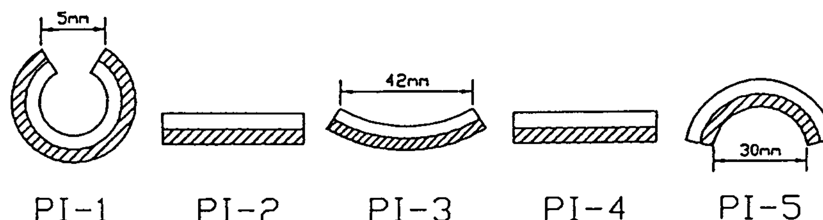

Figure 4 The side view of polyimide/copper laminates: (□) polyimide; (▨) copper.

coefficient. Consequently, the thermal expansion coefficient of polyimide made from ODA (PI-1) should be larger than that for polyimide made from BIA (PI-5), PDA, or diamine mixtures (PI-2, PI-3, PI-4) because of the flexibility of the ODA diamine. Our experimental results comply with the aforementioned postulation (Table II). Curling is the result of the differences in the thermal expansion coefficient of each component (polyimide and copper as in this study) when cooled after imidization. Material with a large thermal expansion coefficient will shrink more after being cooled, with curling inward for the component having a larger thermal expansion coefficient. The thermal expansion coefficient of polyimide made from BIA is smaller than that of copper (11 ppm/°C < 17.6 ppm/°C) and the thermal expansion coefficient of polyimide made of ODA is larger than that of copper (41.9 ppm/°C > 17.6 ppm/°C). Therefore, when interfaced with copper, the direction of curling for the PI film is opposite, as shown in Figure 4. The thermal expansion coefficient of the copolymer made from 30% BIA and 70% ODA (PI-3) is also larger than that of copper (30 ppm/°C > 17.6 ppm/°C); therefore, the laminate made from this polyimide also slightly curls inward toward the polyimide, as shown in Figure 4. The thermal expansion coefficient of the other two copolymers made from 80% PDA and 20% ODA (PI-2, 18 ppm/°C) and 60% BIA and 40% ODA (PI-4, 22.4 ppm/°C) is nearly equal to copper. Therefore, when interfaced with copper, both laminates are dimensionally stable and free from curling. However, as mentioned above, the peel strength is low for laminate made from 80% PDA and 20% ODA. Thus, the ideal diamine mixture for high peel strength, curl-free laminate should be composed of 60% BIA and 40% ODA (PI-4).

CONCLUSIONS

The polyimide film made from BIA as the diamine component has the following characteristics because BIA is an extended conjugated molecule forming a high packing density, rodlike shape rigid polyimide:

1. High tensile strength (17.5 kg/mm^2).
2. High glass transition temperature (T_g = 384°C).
3. High thermal stability (5% weight loss at 570°C).
4. Low coefficient of thermal expansion between 50 and 250°C (11.0 ppm/°C).
5. Low elongation (10%).

When this polyimide interfaces with copper, a high-adhesion laminate can result because the active hydrogen in the imidazole group of BIA can form chemical bond with copper oxide at the interface. However, the polyimide side of the laminate curls outward because the thermal expansion coefficient of this polyimide is smaller than that of copper.

The thermal expansion coefficient of a copolymer made from 60% BIA and 40% ODA is nearly equal to that of copper. A high adhesion curl-free polyimide/copper laminate has been obtained by using 60% BIA and 40% ODA as diamines in the preparation of polyamic acid.

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