Adhesiveless Copper on Polyimide for Flexible Circuit, HDI and Microvia Applications

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Abstract

A new class of adhesiveless substrate materials has emerged for the production of flexible circuits, chip scale packages and HDI products. A typical construction includes a polyimide base film, a thin metal tiecoat, a copper seedcoat, and a layer of electrodeposited copper. The manufacture of these materials makes use of continuous vacuum techniques for tiecoat and seedcoat, and special roll to roll electrodeposition methods for copper build-up. The elimination of the adhesive layer substantially reduces weight and thickness, offering advantages in portable applications. In addition, copper as thin as 5 µm is routinely provided, with copper layers as thin as 0.2 µm available for semi-additive approaches. The availability of very thin copper facilitates manufacture of fine-line circuit features, and traces as narrow as 25 µm are possible for HDI applications.

Data will be presented on component material properties and the effects of environmental factors such as temperature and humidity on adhesion performance. Polyimide base films offer good thermal and chemical stability with a low dielectric constant. Microvias can be easily formed through the use of plasma, lasers, or wet etching and are facilitated through the elimination of the adhesive layer. Small copper grain size and good tensile strength, ductility, and flexural endurance offer advantages in flexible circuit and chip scale packaging applications. Selection of an appropriate tiecoat material provides good copper adhesion to the base film after exposure to severe environmental and processing conditions. This paper also discusses manufacturing methods and availability of material types for this new class of substrate material.

Introduction

Flexible polyimide film based laminates have been used extensively for flexible and high density electronic interconnection applications. Until fairly recently, the primary market for these materials was in military or defense applications. However, new generations of portable commercial products such as laptop computers, camcorders, cell phones, and pagers have dramatically changed the market and technical requirements for both flexible and rigid-flex circuits. Additionally, the need for fine lines and small vias on the surface of high density boards has led to the need for non-reinforced surface layers having very thin copper.

A new class of substrate materials based on adhesiveless copper on polyimide has emerged to meet the demanding needs of such applications. For these materials, the copper conductor is directly metallized onto the polyimide substrate. In one product variation, the underlying polymer substrate may include a layer of adhesive opposite the copper layer in order to enable high density multilayer and microvia applications. These emerging substrate technologies enable the manufacture of circuits that are lightweight, thin, and highly reliable. In this paper, key technical considerations involved in the use of adhesiveless laminates for flexible circuit and high density multilayer applications are reviewed.

Technology Overview

In standard adhesive based products, an adhesive is used to bond copper foil to a flexible substrate. Polyimide film is the substrate used for the most reliable and thermally stable products. The copper used can be either electrodeposited or rolled foil. Traditionally, rolled and annealed foils have been used for flexible circuits because of their good elongation and ductility properties. However, recent advances in electrodeposited foils have made these materials perform as well as the rolled annealed foils[1].

Adhesive based flexible laminates are manufactured either by roll-to-roll techniques, or by static pressing of sheets. The adhesives required for roll-to-roll lamination are often inferior in properties to the adhesives used for static pressing. The static pressed laminates also have better dimensional and other properties compared to the roll laminated products. On the other hand, roll laminated products facilitate the manufacture of flexible circuits in continuous form.

The weak link in the adhesive based substrates used for flexible circuits has typically been the adhesive used to bond the copper to the polyimide film. Most flexible adhesives have Tg about 80°C or less, which can lead to undesirable effects for flex circuit applications. In addition, the adhesive adds to the thickness and weight of the final circuit.

Direct vacuum metallization techniques eliminate the need for adhesive altogether. The result is an adhesiveless flexible laminate material. As illustrated in Figure 1, a typical construction includes a polyimide substrate, a thin metal tiecoat, a copper seedcoat, and a layer of electrodeposited copper. The base substrate of choice is polyimide film having a thickness in the range 12.5 µm to 125 µm. More commonly, thickness is either 25 µm or 50 µm. Adhesiveless flexible laminates can have single or double-sided metallization, and are often provided in roll format to streamline subsequent processing.

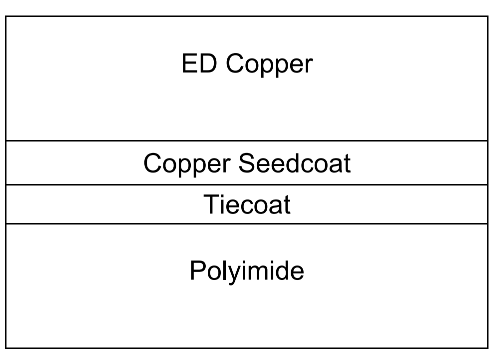

Figure 1: Typical Construction of Adhesiveless Copper on Polyimide Substrate

Tiecoat and seedcoat metallizations are typically applied using vacuum deposition techniques. The process begins with a plasma pretreatment of the polyimide. The pretreatment cleans and chemically modifies the surface to enhance adhesion. After the pretreatment, tiecoat metals are deposited using a sputter deposition process. Other vacuum deposition techniques can also be used. Tiecoat materials include chromium and nickel based alloys. Tiecoat layers can be as thick as several hundreds of angstroms and as thin as a few angstroms. Providing sufficient tiecoat thickness and selecting an appropriate tiecoat metal help to provide adhesion retention performance after environmental exposure, as will be discussed in further detail below.

Copper seedcoats are about 2000 Å thick and are also applied using a sputtering process. The seedcoat serves to provide sufficient electrical conductivity to permit electroplating to final copper thickness. The electrodeposited copper layer can be 18 µm or thicker, although thinner copper is preferred. Copper on either side of the substrate can have different thickness, which increases the number of circuit design options. In some instances, electrodeposited copper on the laminate can be eliminated altogether to provide very thin copper. Final copper thickness can then be achieved additively farther downstream in the board manufacturing process.

Up to this point, the substrate materials discussed typically are applied to flex circuit based applications. However, high density multilayer boards can benefit from some of the unique properties of these materials, while at the same time they can have additional requirements. For example, a mechanism is required to adhere outer surface layers to core innerlayers. Also, the need for interconnection between layers requires the ability to form vias in the surface layers, usually with lasers or plasma. This latter step is more readily accomplished if no glass cloth is present. For this reason, copper foil coated with resin has become available.

Resins used for resin coated copper may consist of a single B-staged layer, or of both a B-staged and a C-staged layer. The C-stage layer of the two-layer construction serves to provide a known minimum thickness between the surface copper layer and the next layer of circuitry after lamination. Copper thickness is normally 18 µm, but copper as thin as 9µm is possible. The thinner copper facilitates fine line formation.

A variety of resin systems are used for resin coated copper products, but most are epoxy materials with Tg ranging from 140°C to 180°C. Usually the resins are brominated in order to meet the UL 94V-0 specification.

The application of an adhesiveless copper on polyimide product as an alternative for these resin coated foils will be discussed in a later section of this paper. The adhesiveless copper on polyimide product offers both thinner copper and a more thermally stable surface than are presently available.

Material Properties

Selected properties of three commonly used polyimide films are given in Table 1[2]. Polyimide films have a high degree of thermal stability, permitting them to withstand processing at elevated temperatures. They have low shrinkage and a coefficient of thermal expansion (CTE) close to copper over a fairly wide temperature range. Because polyimide CTE is close to copper, mechanical stresses induced in copper during thermal excursions are minimized. While polyimides are flexible, they have reasonably high strength and modulus. This enhances handling during board processing, especially for very thin materials. The dielectric constant for polyimide is between 3.2 and 3.5, which is less than that of a typical adhesive material. They also have low dissipation factor and good dielectric strength. Consequently, polyimides provide advantages in electrical performance for high speed applications relative to adhesive based systems. Finally, polyimide materials are chemically stable, and withstand harsh chemical environments associated with circuit board processing.

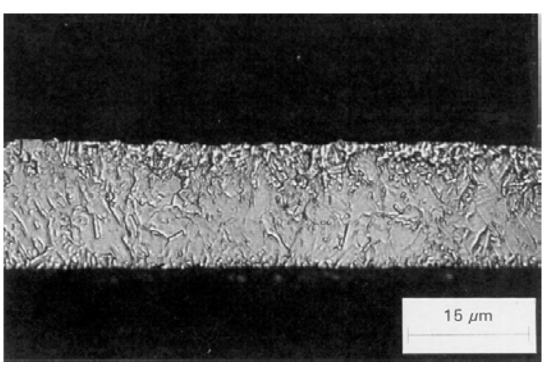

Figure 2: Cross-Section of Copper from Adhesiveless Flexible Laminate

A cross-section of an example of copper plate-up from an adhesiveless laminate is shown in Figure 2. Twin traces and columnar morphology, both of which can be present with some electrodeposited coppers, are largely absent. Copper grain sizes for adhesiveless material are typically small, ranging from about 2 µm to as low as about 0.2 µm[3]. For the most part, individual grains are equiaxed, although slight extension in the growth direction may be present for some grains.

Copper mechanical properties for an adhesiveless laminate are compared to those of other types of copper in Table 2[1,4]. For the adhesiveless copper, the data were determined after chemically etching away the polyimide substrate from the adhesiveless laminate. In each case, the copper was 18 µm thick. Tensile strength and elongation for the adhesiveless plate-up copper are comparable to the same properties for the electrodeposited foil. The adhesiveless copper has lower tensile strength than the as-formed rolled foil, but elongation is significantly greater. The plate-up copper provides elongation comparable to grade 8 rolled foil even after the rolled foil is annealed. The good combination of strength and elongation exhibited by the adhesiveless copper helps to withstand stresses that are

Property	Kapton*-E	Upilex**-S	Apical***-NP
I. Thermal			
CTE, ppm/°C, 50-200°C	16	12	16†
Heat Shrinkage, %	0.05 (200 °C1hr)	0.07 (250 °C 2hr)	0.08 (200 °C 2hr)
II. Mechanical (1 mil)			
Tensile Strength, ksi, @ 25 °C	45	57	44
Tensile Modulus, ksi, @ 25 °C	700	1280	600
Elongation, %, @ 25 °C	55	30	90
III. Electrical (1 mil)			
Dielectric Constant, @ 1 kHz	3.2	3.5	3.3
Dissipation Factor, @ 1 kHz	0.0015	0.0013	0.001
Dielectric Strength, V/mil	7200	6800	8000
IV. Chemical			
Water Abs., 24 hrs. 23 °C, %	1.8	1.2	2.1
Chemical Etch	Yes	No	Yes
V. Other			
Laser Ablation	Yes	Yes	Yes

Table 1: Selected Properties of Polyimide Films[2]

* Kapton is a registered trademark of the E.I. DuPont de Nemours & Co.
** Upilex is a registered trademark of Ube Industries, Ltd.
*** Apical is a registered trademark of Kaneka
† 100 - 200ºC range

Copper Type	Tensile Strength Room Temperature (kpsi)	Elongation Room Temperature (%)
Adhesiveless Plate-Up[4]	52	11
Grade 3 Electrodeposited[1]	51	14
Grade 8 Rolled, As formed, Longitudinal[1]	65	1.5
Grade 8 Rolled, Annealed 225 °C for 10 min., Longitudinal[1]	28	10

Table 2: Copper Mechanical Properties for Adhesiveless Laminate and Copper Foils

induced during flex-to-install, and high strain, low cycle, bending operations.

For many applications, flexible circuits must undergo repetitive bending operations, rather than a single bend. Imposed strains can vary, but in some instances the strains can be very low and large numbers of bend cycles are required. One technique for evaluating performance under such conditions is the Bell flex-fatigue test. With this test, a sample that includes a copper layer is positioned between two vertically aligned mandrels. Electrical contact is established on both sides of the sample. During the test, the mandrels are repetitively displaced vertically, and the copper is stressed alternately in tension and compression. Over time, there is a cumulative effect of strain cycling, or fatigue. Cracks form, grow, and ultimately cause electrical continuity to be lost. The number of cycles to failure, or fatigue life, is determined at this point.

Copper that is present on adhesiveless flexible laminate exhibits good fatigue performance over a range of mandrel diameters[5]. As might be expected, the number of cycles to failure increases with mandrel diameter because imposed strains are lower for larger mandrels. Crack growth across a sample surface and through a sample thickness is impeded at a grain boundary[6,7]. Hence, the small equiaxed grains present in copper of adhesiveless materials promote fatigue life during repetitive flexing conditions. Fatigue life increases with reduced copper thickness, with the improvement due to smaller strains at the copper surface[5]. Consequently, adhesiveless materials with thin copper can facilitate longer fatigue life.

Adhesion

Adhesion is a key performance requirement for copper on polyimide materials. Excellent initial peel strength can be achieved by plasma pre-treating the polyimide film prior to metallization[8]. The peel strength of 35 µm copper on 2 mil Kapton-E substrate is typically 7 lb/in (1225 N/m). For 18 µm copper, peel strength is about 5 lb/in (875 N/m). The choice of tiecoat metal has little impact on as-received peel strength[8].

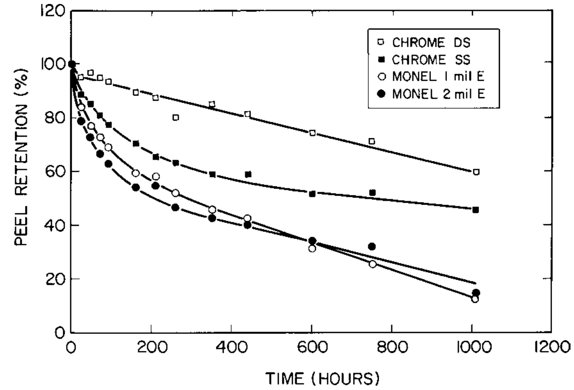

Figure 3: Peel Strength Retention for Adhesiveless Laminates with Monel and Chromium Tiecoats after Exposure to 85°C / 85%rh[9]

While initial adhesion is important, exposure to severe environmental conditions can degrade adhesion between metallization layers and the polyimide substrate. Figure 3 compares peel strength retention, after exposure to 85 °C / 85% relative humidity for up to 1000 hours, of monel and chromium tiecoats for 18 µm copper on Kapton-E substrate[9]. The material with chromium tiecoat exhibits three times the peel strength retention than does the material with monel tiecoat. Figures 4 and 5 compare peel strength retention, after exposure to 121 °C and 2 atmosphere pressure at 100% relative humidity for up to 168 hours, for materials without tiecoat and those with varying thickness of chromium tiecoat[10]. With no tiecoat, virtually no adhesion remained even after small exposure times. However, materials with chromium tiecoat performed remarkably well given the severity of test conditions. Above 75 Å in thickness, chromium thickness had little impact on peel strength retention. In contrast to initial adhesion, results from the humidity durability experiments demonstrate that thin metal tiecoats, and especially chromium, provide improved performance under such conditions.

Other environmental stresses that can be encountered during circuit fabrication include gold plating and elevated temperatures. Adhesion losses for Kapton-E based laminates exposed to a neutral cyanide gold plating bath are significantly reduced when a chromium tiecoat is used[11]. Nickel alloy tiecoats can also improve peel strength retention, but not to the

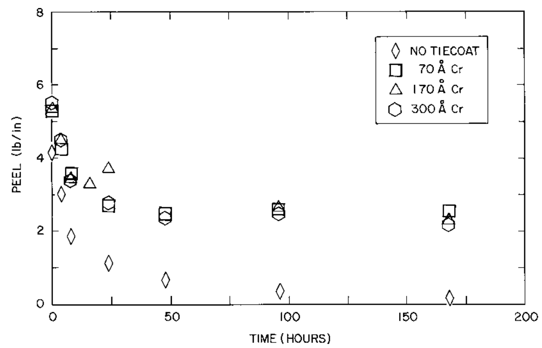

Figure 4: Peel Strength as a function of PC exposure time for Kapton-E laminate with Chromium Tiecoats and 18 µm Copper[10]

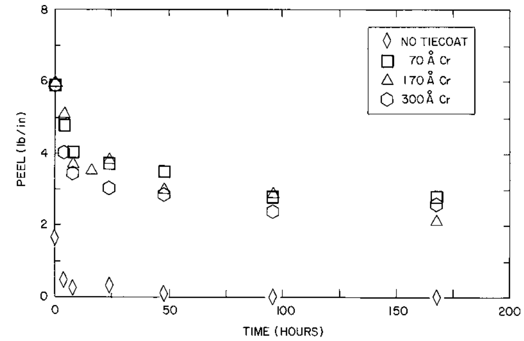

Figure 5: Peel Strength as a function of PC exposure time for Upilex-SGA laminate with Chromium Tiecoats and 18 µm Copper[10]

same degree as chromium. After exposures to elevated temperatures, chromium and nickel alloy tiecoats also significantly reduce adhesion losses[11]. Hence, as with humidity, adhesion losses from thermal or severe chemical environments can be reduced by selecting an appropriate tiecoat material.

Handling and Processing

Adhesiveless substrates have the potential of providing copper and polyimide films that are extremely thin. Consequently, handling can be more difficult than for conventional, thicker, adhesive based laminates. Care must be taken to avoid mechanical damage to these parts. Handling of the copper surface can cause pinholes or other types of damage to the copper surface unless gloves are worn. The copper surface is typically protected from oxidation during shipment and storage, but the anti-tarnish is readily removed in a mild preclean prior to photoresist application.

Generally, normal printed circuit manufacturing techniques can be used to fabricate circuits on adhesiveless substrates. Etching can be done in any of the conventional etchants such as ferric chloride, cupric chloride, or alkaline solutions. Depending on the tiecoat material, one or two etching steps may be required. Monel readily etches in cupric chloride and ferric chloride etchants, and a single etching step can be used. On the other hand, chromium requires a second etch step. Permanganate is a commonly used etchant for chromium tiecoat.

New portable products require very fine lines and spaces in the finished circuit. A major advantage of the adhesiveless materials is the availability of very thin copper, which facilitates fabrication of fine features. Direct metallized materials with copper as thin as 0.2 µm are readily available, while the difficulty of preparing and handling very thin copper foils makes copper thinner than 9 µm virtually unavailable for adhesive based laminates. With fully subtractive methods, the use of 5 µm thick copper on adhesiveless laminate permits the formation of lines less than 50 µm wide. When semi-additive methods are used, even finer lines and spaces can be produced. Adhesiveless materials also have advantages in fine-line fabrication because the interface between metallization and polyimide substrate is smooth. Additional etch time to remove the last vestiges of foil treatment are unnecessary.

Plating of traces where the polyimide-copper interface is exposed is normally not a problem. In some cases with a monel tiecoat, gold plating can cause undercut of the copper traces. This is especially severe with plating chemistries that include high cyanide concentrations. Undercut is not a problem when a chromium tiecoat is used.

Multilayer and High Density Boards

Adhesiveless copper on polyimide substrates have a number of properties that are desirable for multilayer applications. The combination of very thin copper for fine lines, along with the excellent thermal and electrical properties of polyimide, are among the most compelling. There is a new materials approach which can provide the advantages of adhesiveless copper on polyimide substrates to high density multilayer and microvia circuit board applications. A typical construction is shown in Figure 6.

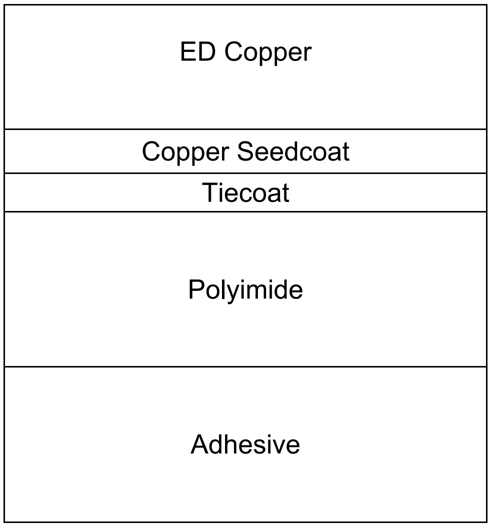

Figure 6: Typical Construction of Copper on Polyimide Substrate with Back-Side Adhesive Layer

As shown in the figure, the product consists of a standard single-sided adhesiveless laminate with an adhesive layer attached to the polyimide side. The adhesive layer, which can be between 25 µm and 75 µm thick, serves to bond the polyimide and metallization layers to the outer surface of a circuit board. Additional prepreg or bond-ply layers are not required. The adhesive has a Tg of approximately 180 °C and will pass the UL 94V-0 specification.

The polyimide film provides a layer of controlled thickness between the surface copper and the next layer of circuitry. The controlled polyimide thickness and smooth metal-polyimide interface, along with the low dielectric constant and dissipation factors of polyimide, provide for excellent electrical performance. High temperature processes such as gold to gold wire bonding do not provide difficulties because polyimide has a high degree of thermal stability.

Fabrication of small surface vias and very fine lines is facilitated by the material construction. Vias can be formed easily by laser ablation or plasma etching due to the absence of the glass fibers found in conventional prepreg. In cases where it is desired to lase through the copper, the availability of thin copper on the order of 2µm is a major advantage. Thin copper is also the key attribute for achieving fine lines, as indicated above.

Conclusions

Technical considerations involved in the use of adhesiveless flexible laminates for flex circuit and high density multilayer applications were reviewed. Polyimide substrates exhibit good thermal, mechanical, electrical, and chemical properties. A good combination of copper strength and elongation reduces the possibility of cracking during high strain, low cycle and flex-to-install applications. Small grain size and thin copper contribute to good fatigue life during repetitive flexing. Adhesiveless materials exhibit the excellent adhesion performance required for stringent processing demands and good reliability. The selection of a chromium, or to a lesser degree, nickel alloy tiecoat can enhance adhesion performance after exposure to severe environmental conditions. A product consisting of a standard single-sided adhesiveless laminate with an adhesive layer attached to the polyimide side enables and provides benefits for high density multilayer and microvia applications. The product provides the features of adhesiveless flex materials including thermal stability, thin, fine-grained copper, and good adhesion after thermal, chemical, and environmental exposure. In addition, the material facilitates the formation of small vias and fine line features.

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