Thermal Effects on Lifetime Evaluation of Adhesiveless Copper–Polyimide

Kuo-Hua Huang* and Jeng-Gong Duh

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 300, Taiwan

Adhesiveless materials are commonly used for electric or portable products that require high flexibility during operation. This structure incorporates a copper substrate and polyimide film. For life-time studies, the key aspect to evaluate is the effect of the thermal factors. In general, techniques to measure the life-time of the materials involve storing samples over a long term period in order to monitor changes; however, this is time-consuming. The aging test is an alternative method to predict and evaluate the changes in the mechanic properties over a short term period; yet the test conditions influence the accuracy of the results. The temperature and relative humidity (RH) are the major parameters for the test, and the test conditions of 85°C/85% RH and 150°C will be discussed in this paper. It is observed that the lifetime of rolled-annealed copper foil with polyimide film is significantly higher than metal films produced by other common methods, and the results are explained using the analysis of the fracture mechanics. From comparing the test data with samples stored for three years, the best prediction was achieved with conditions of 85°C/85% RH, with errors of less than 5%. The best flexibility was achieved when the optimum thickness of the copper and polyimide was determined. [doi:10.2320/matertrans.M2015041]

(Received January 26, 2015; Accepted April 7, 2015; Published June 5, 2015)

Keywords: life-time, adhesiveless, long term aging, Cu/PI composite, debonding

1. Introduction

Polyimide is used in the fabrication of electronic circuitry because of its low dielectric constant, high thermal stability, and high bulk resistance, as indicated by Fig. 1. The adhesion between polyimide and metals, particularly copper, plays a key role in the fabrication of such electronic circuitry.1) Recently, a process in order to enhance the adhesion between the polyimide and weakly interacting copper has been reported. The process involves the intermixing of the coated polyimide onto the substrate when the process temperature attains a critical value. Other efforts to improve the adhesion of the metal layer involve increasing the roughness of the surface of the polyimide by methods such as sputtering, chemical treatment, and reactive ion etching.

Previous studies on copper-polyimide interactions have been conducted using vacuum deposited metals. Recently, a novel process in order to coat polyimide with weakly interacting metals, such as copper, has been reported.2) This process is based on the pyromellitic dianhydride-oxydianiline (PMDA-ODA) varnish of polyimide. This varnish is initially coated on the copper foil during roll manufacturing by exposure to the N-methylpyrrolidinone (NMP) solvent. This could result in dramatically lower fabrication costs since roll-to-roll processing is steady-state and avoids many of the handling complications that are associated with traditional batch processing, and thus enables a higher throughput.3) This semi-finished material of copper-polyimide reduces the amount of residual NMP solvent produced during the heat treatment process. The construction of this material incorporates copper and polyimide film without any resin. This can minimize the thickness and reduce the amount of defects produced during the operation.4)

As illustrated Fig. 2, the typical construction incorporates a copper substrate and a polyimide film. The polyimide film usually has a thickness in the range of 12 µm to 25 µm, and the thickness of the copper foil is between 9 µm and 35 µm. Using this construction, an adhesion value of 1.08 N/mm was obtained under ambient conditions. However, the adhesion value increases to greater than 1.16 N/mm when the samples are subjected to the solder float test at a temperature of 288°C for 10 min.

In this study, a modified process that incorporates a thermal treatment step and the development of a novel method for the lifetime prediction of this material will be discussed in this paper. The investigations were conducted in an attempt to understand the aforementioned process, and the results of a

*Corresponding author, E-mail: rich1231kimo@yahoo.com.tw
long term aging study on coated polyimide under humid and high temperature environments were demonstrated.

2. Experimental Methods

Polyimide purchased from DuPont (USA) was synthesized to varnish status. A seed of copper (35 µm) was rolled, annealed, and treated with nickel, cobalt, and other metallic powders. Following the coating in rolled copper foil and air drying, the polyimide seeded with copper was heated to a temperature of 380°C for 60 min in a nitrogen gas oven. The heat treated Cu/PI was subsequently treated for 5 min in 5 M of nitric acid to etch away the traces of copper oxide and then rinsed with deionized water. Subsequently, adhesion and long term aging studies were conducted on the samples, as described in the following sections. The samples for the adhesion measurement studies were prepared with seed copper with a thickness between 12 µm and 18 µm, depending on the tests.

The long term aging experiments on the Cu/PI film were conducted at a temperature of 85°C at 85% relative humidity (RH) and tests were also conducted at a temperature of 150°C in an air environment. Subsequently, the adhesive force of the composite was evaluated following a period of 240 h. Under the 85°C/85% RH testing conditions, the Cu/PI performed poorly. This was likely to be attributed to the high reactivity (corrosive nature) of copper, which is known to accelerate in the presence of ionic impurities. The thermal effects on this composite at a high temperature, 150°C was also observed. This test method can assist in evaluating the stability of the major properties of the material over a few years after its fabrication. During this test, the effect of the constant loading force on the mechanical behavior of the material was evaluated. It is assumed that residual stress existed at the interface between the Cu and PI, causing crack growth on the Cu side and thus reducing the life-time. The samples for this study were prepared by reducing the thickness of the textured copper to 18 µm, and the thickness of the PI film was set as 20 µm. The relative humidity or moisture may reduce the adhesive ability at the interface of the composite and thus needs to be controlled during the operation and the storage of the materials.9) A relative humidity of 85% was selected to reflect the strict storage conditions. A greater level of moisture can dehydrate the polymer film, destroy functional groups, and affect the combined force. Thus, the humidity needs to be considered during testing. The polyimide plated copper was initially dried in air and subsequently dried at 200°C for 30 min in a heat oven. The sample was masked using 3.2 mm wide masking tape. The sample was immersed in an aqueous 3 M FeCl3 solution in order to etch the exposed metal. Following thorough rising, the masking tape was removed and a 90° peel test was performed according to the Institute for Interconnecting and Packaging for Electronic Circuits (IPC) test method 650–2.4.9 in order to characterize the adhesive force between the copper and the polyimide film. The material was subjected to the solder float test (IPC test method 650–2.4.9) and the 90° adhesion measurement was immediately performed.10)

To determine the performance of the adhesiveless Cu/PI film during thermal aging testing under conditions of 85°C/85% RH and at 150°C, the 90° peel test was conducted at various time intervals. Cracking behavior is the mode of failure for the Cu/PI film, and the de-bonding of the coating film is characterized by a critical thickness value. The coating de-bonds from the substrate if its thickness exceeds a critical magnitude.11, 12) In general, the critical thickness of the coating on the copper composite is in the range of 12 µm to 18 µm. In this study, the thicknesses of the coating films are 12 µm, 20 µm and 25 µm, depending on the samples. During this study, a QC-104 COMETECH test machine was used. It has a rotation angle of ±135°, a radius of 0.8 mm or 0.38 mm, a speed of 175 rpm, and a weight loading of 10 gf/10 mm W, as indicated in Fig. 3. The number of cycles to failure can be defined using the lifetime test. During testing, strain cycling exhibits a cumulative effect on the sample. It may cause a crack on the copper side of the sample and thus cause a loss in the electric continuity or produce defects when it is fabricated into circuit boards.13) Therefore, the test will incorporate a sensor to monitor the electric resistance of the copper and the machine will be shut down when the resistance is over a predetermined point. In this case, the value of the predetermined point is 10% greater than the initial status. This is the point at which the number of cycles to failure is determined. An onset of the de-bonding process was observed with this composite. Figure 4 shows a schematic drawing of a coating de-bonding from a substrate.

3. Results and Discussion

3.1 Adhesion study

When the 18/20 Cu/PI film sample was subjected to the 90° peel test, adhesion values of 1.04 to 1.13 N/mm were obtained under ambient conditions. For the polyimide coated
on copper foil, the adhesion remained between 1.11 and 1.20 N/mm following the solder float test. This high adhesion is believed to be predominantly attributed to the mechanical interlocking which is facilitated by the textured copper substrate.\textsuperscript{14}

### 3.2 Long term aging study

The peeling strength is the average load per unit width of bond line required to separate bonded materials where the angle of separation is 90°. This measurement was used to evaluate the adhesive ability during this program. Figure 5 shows the 18 µm Cu/20 µm PI sample under compression when exposed to temperature and humidity conditions of 85°C/85% RH and 150°C after 240 h. Three groups of samples were tested and the mean values were measured each time. It is revealed that the peeling strength under the 85°C/85% RH condition is lower than that at 150°C.

Following 240 h, the product stability can be confirmed when there is no significant difference between the initial and final status observed. The most common aging method to evaluate the lifetime of products involves subjecting the samples to 85°C/85% RH and 150°C for a period of three years. The above methods can be used to predict the lifetime following a period of three years. The errors were less than 5%, and this correlates with the true situation.\textsuperscript{15} As illustrated in Fig. 6, samples with the same structures were maintained at room temperature and normal relative humidity for a period of three years. Subsequently, three samples were inspected and the mean values were calculated every quarter. The mean values of the peeling strength were 1.004 Kgf/m and 1.048 Kgf/m with a standard deviation of 0.0794 and 0.0691. Based on the same Cu/PI structure, the results are close to those obtained for the 85°C/85% RH conditions, and other methods involve checking the critical parameters at a temperature of 150°C. The above methods can be used to predict the lifetime over a short term period only. However, this method has been used to understand the changes that occur during operation or storage in real situations.\textsuperscript{15} As illustrated in Fig. 6, samples with the same structures were maintained at room temperature and normal relative humidity for a period of three years. The errors were less than 5%, and this correlates with the true situation.

The initial crack on the copper surface caused the crack propagation that resulted in the final failure. However, the polyimide film did not break and still remained satisfactory. This may be attributed to the soft intrinsic properties of the polyimide. Figure 7 presents the number of cycles to failure for the samples with a fixed thickness of Cu and various thicknesses of PI. Five samples of each structure were examined; the mean value of the cycles to failure for the 18 µm Cu/12 µm PI, 18 µm Cu/20 µm PI and 18 µm Cu/25 µm PI samples were 415, 1375 and 1000 and the standard deviations were 27.2, 83.4, and 106.4, respectively. It is apparent that if the PI is too thin the structure becomes fragile, e.g., PI with a thickness of only 12 µm. If the thicknesses of the Cu and PI are equal or relatively close, the structure exhibits the greatest rigidity, and demonstrates the greatest amount of cycles to failure. However, if the PI becomes too thick, e.g., 25 µm, then the sample tends to weaken as the number of cycles to failure decreases slightly.

The application of a thinner copper substrate is a new trend in the rapidly developing electronics industry. It should be noted that samples with a different radius are required to test thinner copper substrates. The number of cycles to failure for the 18 µm Cu/12 µm PI sample is 329 and the standard deviation is 38.2, while the respective values are 858 and 134.7 for the 12 µm Cu/12 µm PI sample, as shown in Fig. 8. Following testing on samples with identical PI thicknesses, it is evident that a thinner copper substrate will achieve improved results. The characteristics of copper are more significant than those of polyimide for this type of structure.

When the 18 µm Cu/20 µm PI sample was subjected to ageing tests under conditions of 85°C/85% RH for 240 h, the number of cycles to failure was 1317 and the standard deviation was 96.3. At a temperature of 150°C, the respective values were 997 and 121.5. For the composite with the same temperature and normal relative humidity for a period of three years.

![Peel strength test](image1.png)

**Fig. 5** The trend of the peel strength tested at 150°C and 85°C/85% RH for 240 h.

![Change in peel strength](image2.png)

**Fig. 6** Change in the peel strength following storage under normal conditions for a period of three years.

![Number of cycles to failure](image3.png)

**Fig. 7** A comparison of the number of cycles to failure for the different structures (same Cu thickness).
structure stored under normal conditions (25°C/60% RH) for three years, the number of cycles to failure was 1261 with a standard deviation of 114.8. When compared to the sample under conditions of 85°C/85% RH, there is only a difference of less than 5.0%.

3.3 De-bonding study

It is assumed that the crack grows along the surface between the coating and the substrate.\(^{16}\) The following deviation is based on an energy balance analysis which is similar to that used by Griffith. The elastic energy released by the de-bonding of the coating is shown below in eq. (1):

\[
dU_e = \frac{s^2}{2E}whdL
\]  

(1)

Where \(s\) is the tensile stress of the coating, \(E\) is the Young’s modulus of the coating, \(dL\) is an increment in the de-bonding length, \(h\) is the thickness of the coating, and \(w\) is the width of the coating. The energy used to de-bond the coating from the substrate is:

\[
dU_t = GwdL
\]  

(2)

Where \(G\) is the fracture toughness of the de-bonding. The coating de-bonds from the substrate if the released elastic energy, \(dU_t\), is greater than the dissipated energy, \(dU_e\).

\[
s > (2GE/h)^{1/2}
\]  

(3)

Equation (3) is similar to the Griffith criterion, and the thickness of the de-bonding coating is analogous to the length of a crack in the Griffith criterion. The de-bonding process is caused by a 90° rotation of a crack in the coating and its growth along the coating/surface substrate.

However, in ductile metal the value cannot be higher than the yield stress of the coating material. The critical value decreases with an increase in the coating thickness.\(^{17}\) The de-bonding fracture toughness can be determined from eq. (4).

\[
G = s^2h^+ / 2E
\]  

(4)

Where \(s\) is the tensile stress of the coating and \(h^+\) is the critical coating thickness for this study. The magnitude of the stress in the coating material is not known, but can be roughly estimated. The lower estimate for the yield stress of the substrate is 12,240–15,300 Kgf/m. The Young’s modulus of copper is 918,000 Kgf/m. By substituting the values of 13,770 Kgf/m, 918,000 Kgf/m, and 8 µm into eq. (4), one obtains \(G \approx 8.3\) J/m². All the values are approximately hundred-times higher than the de-bonding values for metal films manufactured by the commonly used sputter deposition method. This implies that the adhesion of an adhesiveless copper-polyimide composite is significantly higher.

4. Conclusions

(1) An adhesiveless composite which consists of copper and polyimide exhibits high flexibility and long lifetimes for applications in electronic-related fields.

(2) The adhesiveless Cu/PI exhibits a favorable performance which is required for good reliability and adhesion capabilities in order to withstand a variety of thermal and environmental conditions. The aging test at 85°C/85% RH is effective in order to predict the life-time of the material in the short term, with an error less than 5%.

(3) A layer featuring identical or similar thicknesses of Cu and PI can enhance the strength of the structure to endure the high stresses that occur during the process.

(4) Classical methods as sputter deposition and chemical vacuum deposition do not provide appropriate levels of adhesion. Moreover, such methods are relatively expensive and require excessive amounts of energy. The production of adhesiveless Cu/PI can reduce these costs. Hence, the products can be used widely, not only in the electronic engineering field but also in space, energy, and microelectronics applications.

REFERENCES