Chapter 4

Environmental Aging Effects on the Durability of Electrically Conductive Adhesive Joints

Abstract

The mechanical behavior of electrically conductive adhesive joints exposed to elevated temperature and relative humidity conditions has been investigated, and failure mechanisms of conductive adhesive joints have been determined. Three model, silver-filled, epoxy-based adhesive systems have been studied in conjunction with printed circuit board (PCB) substrates with metallizations of Au/Ni/Cu and Cu. Double cantilever beam (DCB) tests have been adopted to investigate the effects of environmental aging on electrically conductive adhesive joints. This study reveals that conductive adhesives as well as substrate metallizations both play important roles in the durability of conductive adhesive joints. The rate of water attack on the interface of conductive adhesive joints with Cu plated PCB substrates is faster than for those with Au/Ni/Cu metallization. A possible explanation of this phenomenon is based on considerations of surface free energy and interfacial free energy. Following drying of the aged conductive adhesive joints, the fracture energy recovered to some extent. This recovery in the fracture energy could be attributed to the reversible effect of plasticization of the bulk adhesives, as well as the rebonding between the adhesive and the substrate during drying at 150°C. XPS analysis of DCB failure surfaces suggested that diffusion of Cu to the Au surface might have occurred on the Au/Ni/Cu plated PCB substrates during aging. Copper oxide on the substrate surface upon exposure of the conductive adhesive joints to the hot/wet environment has also been observed.

Keywords: Electrically conductive adhesives; double cantilever beam; adhesive joints; environmental aging; durability; fracture energy; gold metallization; copper metallization.

4.1 Introduction

Lead-based solder materials have been used for interconnections in the electronics industry for many decades. However, as public environmental awareness increases, the toxicity of lead has become increasingly important, and great efforts to eliminate environmentally harmful lead are being made in electronic applications. Electrically conductive adhesives (ECAs) provide an environmentally friendly solution for interconnections in electronic applications and are gaining increased interest as potential solder replacements. Numerous studies have shown that joining with electrically conductive adhesives possesses several advantages over conventional solder interconnection technology including improved environmental performance, finer pitch printing, lower temperature processing, and more flexible and simpler processing. However, the replacement of solder by electrically conductive adhesive technology has found limited applicability owing to some drawbacks mainly related to reliability of the adhesive joining. Limited impact resistance [1,2] and increased contact resistance and weakened mechanical strength in various climatic environmental conditions [2,3] are several major obstacles currently preventing ECAs from becoming a general replacement for solders in electronic applications.

Numerous studies have been conducted to investigate the reliability of electrically conductive adhesives technology with an emphasis on electrical reliability aspects. Some interesting work in this area can be found in references 3-6. The reliability of the ECA joining depends on the properties of the conductive adhesives, as well as on the substrate metallization. The degradation mechanisms of conductive adhesive joints with different substrate metallizations have also been discussed [3,5]. Jagt [5] has offered explainations for the increase in the electrical resistance of some ECA joints upon exposure to environmental aging, including oxidation of non-noble metallizations, crack formation/delamination, formation of a silver depleted surface layer in the adhesive, creep of the adhesive, the formation of an intermetallic layer, and processing defects such as undercure, etc. However, failure mechanisms for specific ECA joint systems need further investigation.

Electronics products are now used widely in everyday life, and may be exposed to various environmental conditions such as relatively high temperature, high humidity, and large temperature changes. As a polymeric material filled with electrically conductive fillers, electrically conductive adhesives and their joints may degrade when exposed to these harsh environmental conditions and result in the failure of the adhesive interconnections. Moisture is the most commonly encountered service environment and must be considered a critical factor in determining the long-term reliability of adhesively bonded joints. For many polymeric systems, warm, moist environments can considerably weaken the performance of the adhesive joints. Moisture may affect the behavior of adhesive joints by attacking the bulk adhesive and the adhesive/substrate interface [7]. Moisture can alter the properties of adhesives in a reversible manner, such as plasticization, which can result in depression of the glass transition temperature and weakening of the mechanical strength of adhesives [8,9]. Moisture can also change the properties of the adhesive in an irreversible way by causing further crosslinking [10], chemical degradation [11], inducing cracking or crazing in the adhesive [12,13]. Water can also degrade the adhesive joint by attacking the adhesive/substrate interface. Displacement of the adhesive by water is likely when high surface free energy substrates are utilized and the adhesion between the adhesive and the substrate is mainly due to van der Waal's forces [14]. In addition, water may also hydrate the metal or metal oxide and cause the formation of a weak boundary layer at the interface [15,16]. In light of these possible moisture effects on an adhesive joint, studies of the performance of conductive adhesives and their joints upon moisture attack during exposure to high relative humidity conditions were undertaken in this research. Environmental aging effects on the thermal and mechanical properties of bulk conductive adhesives have been reported in a separate paper [17]. In this work, our efforts are focused on the durability aspect of conductive adhesive joints.

The objective of this work is to experimentally determine the mechanical behavior of conductive adhesive joints when exposed to elevated temperature and relative humidity, and to further investigate failure mechanisms of conductive adhesive joints with different substrate metallizations. Three model, silver-filled, epoxy-based adhesive systems have been studied in conjunction with substrate metallizations of Au and Cu. Double cantilever beam (DCB) tests, which have been used extensively to study the durability of the adhesively bonded joints in the aerospace and automotive industries [18-20], have been successfully adapted to investigate the effects of environmental aging on electrically conductive adhesive joints. The results of this study have significant relevance to the electrical industry. First, the test procedure developed in this study can be used to evaluate newly formulated conductive adhesives. The DCB test used in this study offers several advantages over shear tests, which have been regularly utilized to characterize the mechanical performance of conductive adhesive joints [3-5]. The DCB test has the capability to collect multiple data points from a single specimen in contrast to the shear tests which yields only one data point from each specimen. Moreover, the progressive failure of a DCB specimen makes it easier to observe the failure process of the adhesive joint and to obtain a fundamental understanding of the failure of the adhesive joint. The second importance of this research is that results obtained from the comparative study on the failure mechanisms of different conductive adhesive and substrate metallization combinations may provide the electronics industry with some insights into the selection of electrically conductive adhesives and substrate metallizations for tougher and more durable conductive adhesive interconnections.

4.2 Experimental Procedure

4.2.1 Materials

Three silver-filled, epoxy-based adhesive systems, which were designated as ECA1, ECA2 and ECA3, respectively, were supplied by Emerson & Cuming. They are not commercial products, but rather are model systems specifically formulated for this research. Thermogravimetric analysis results showed that ECA1, ECA2 and ECA3 had silver loadings of 83%, 82% and 86% by weight, respectively, while the epoxy resin, thermoplastic epoxy copolymer, curing agents and other additives accounted for the rest of the adhesive formations. By running differential scanning calorimetry (DSC) scans with a heating rate of 5°C/min on the three conductive adhesives, the glass transition temperatures of the adhesives were found to be: ECA1, 106°C; ECA2, 61°C; and ECA3, 30°C. The T_g was determined from the midpoint of the change in slope of the baseline of the DSC curves [17].

FR-4 printed circuit boards (PCB), with dimensions of 200 x 25 x 1.2 mm, were used as substrates for the DCB specimens. Two different board metallizations, Cu and Au, were utilized in this study. The metals were plated only along the center of the PCB boards with a width of 6.5 mm. The adhesive was applied to these strips to bond two substrates together. The gold plated PCB substrates were made by electroless plating. As a conventional plating process in the industry, a copper layer was first plated on the PCB board as the base metal and then a nickel layer with a thickness of 4~6 μm was made on the copper layer as a diffusion barrier to prevent the copper from diffusing into the gold and vice versa. Finally, a thin layer of gold with an approximate thickness of 0.08~0.2 μm was plated on the top of the nickel layer to prevent oxidation. Gold plated PCB substrates were manufactured by Triad Circuit Inc. located in Round Lake, Illinois. For copper plated PCB substrates, large copper plated

PCB panels were purchased from Triad Circuit Inc and etched at Virginia Tech to obtain the required DCB substrate pattern.

There were several considerations for the selection of the substrate material and geometry in this study. First, FR-4 boards are very representative of actual applications. Second, in contrast to traditional DCB samples in which the adhesive is spread across the entire substrate width, the DCB samples used in this study were bonded by placing the conductive adhesive only at the center along the substrate length. With reduced bonding area of the adhesive joint, the amount of adhesive was greatly reduced for each DCB sample. Hence, the material cost for each specimen was much reduced. Moreover, the reduced adhesive width allows air trapped in the adhesive to escape more easily in the width direction during cure. As a result, porosity problems, which were encountered in joints made with wider adhesive bondlines, were minimized. Another advantage of using the bonded width as some fraction of the specimen width is that the stresses in the substrates are significantly lowered during testing and as a result, the possibility of damage or non-linearity in the FR-4 boards is greatly reduced.

Prior to adhesive bonding, all the substrate surfaces were first cleaned with 75% isopropyl alcohol and then rinsed with deionized water and re-dried at room temperature for one day. All the specimens tested in this study were cured at 150°C for 1h, cooled to room temperature, and then stored in a desiccator prior to testing. The detailed DCB sample fabrication process can be found in a separate publication [21].

4.2.2 Environmental Conditioning

The samples were conditioned in a water bath for periods of up to 50 days. Samples were placed on a rack above the water level, suspending them above the liquid water. Selected samples were periodically removed from the water bath and tested at aging times which were logarithmically separated. The water bath was maintained at 85°C and was tightly closed except when samples were removed for testing. As a result, the relative humidity in the water bath chamber was nearly 100%.

4.2.3 Tensile Testing

Tensile dogbone stress strain specimens of the three conductive adhesives were prepared from uncured adhesives in accordance with ASTM D638-01 [22] Type V. The dogbone samples had a nominal gage length of 9.5 mm and a width of 3 mm. All tensile tests were conducted on a 4505 Instron machine at a crosshead displacement rate of 1 mm/min under ambient conditions. Samples were clamped with flat-faced, pneumatic grips. To prevent slipping during testing, abrasive cloth tabs were used to increase friction on the grip faces.

A non-contact laser extensometer manufactured by Fiedler Optoelektronik GmbH, Germany was utilized to acquire strain data. The laser extensometer consists of a scanner and a receiver and is controlled by the extensometer software provided with the laser extensometer. During testing, a rotating mirror in the scanner continually swept a laser beam between two white marks created at the gage section of each dogbone sample. The reflected light from the sample was collected by the receiver and the deformation between the two marks on the test sample was then calculated by the extensometer software. Both engineering strain and stress were reported in this study.

4.2.4 Double Cantilever Beam (DCB) Testing

To study the durability of conductive adhesive joints exposed to elevated temperature and humidity, quasi-static double cantilever beam (DCB) tests were conducted on a 4505 Instron machine controlled through its GPIB interface using LabVIEW ® software developed by National Instruments. Tests were controlled to make the time-to-failure, t_f, approximately 1 minute, where t_f is the time from the application of the load to that for the onset of crack growth in a fracture test. Load and corresponding displacement information was recorded continuously during the test. Crack length was measured when the crack arrested in each load-hold-unload cycle using a movable magnifier during tests. This test procedure is similar to that described in ASTM D 3433-99 [23].

The strain energy release rate was calculated using the following equation

$$G = \frac{P^2 (a + x)^2}{B(EI_{eff})}$$ Equation 1

where P is the external load, B is the bond width of the specimen, a is the crack length, EI_{eff} is the effective stiffness of the DCB specimens, and x is the apparent crack length offset. Both the effective stiffness EI_{eff} and the crack length offset x can be obtained from the relation between the compliance of the specimen and the crack length. In this study, the maximum and arrest fracture energy, G_{max} and G_{arr} in each load-held-unload cycle were calculated. The peak fracture energy value in each cycle was identified as G_{max}. On the other hand, the arrest fracture energy in each cycle was obtained based on the criterion that the value of the strain energy release rate decreased by less than 1 J/m^2 over a minute while the cross-head was being held constant. Detailed information on the DCB test procedure is given in the literature [18,24].

4.2.5 SEM and XPS Studies

To study the change of the locus of failure of adhesive joints with aging, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were performed on the failure surfaces of the adhesive joints. Scanning electron microscopy was conducted using an ISI Model SX-40 scanning electron microscope. Before being placed in the microscope, all the specimens were sputter-coated in a vacuum chamber with a thin layer of gold to reduce charging.

X-ray photoelectron spectroscopy (XPS) measurements were performed on the failure surfaces of both as-produced and aged conductive adhesive joints using a Perkin-Elmer PHI Model 5400 x-ray photoelectron spectrometer, employing Mg x-rays ($h\upsilon = 1253.6$ eV). Initially, survey spectra were taken over a wide energy range of 0 - 1100 eV to determine the principal elements on the sample surface. After the principal elements were identified, detailed spectra for particular elements were taken over a narrow energy range to determine the chemical nature of the element. The analyzed area was 1 x 3 mm and a typical XPS sampling depth was 40-50 Å thick.

4.3 Results and Discussion

4.3.1 Stress-Strain Results

To characterize the mechanical behavior of the three conductive adhesives, stress-strain tensile tests were performed on the as-produced samples. For each type of conductive adhesive, at least five dogbone stress-strain samples were tested. Figure 4.1 shows typical stress-strain curves obtained on ECA1, ECA2 and ECA3 samples. Note that the conductive adhesives exhibit very different stress-strain behavior. ECA1 and ECA2 exhibit much higher tensile strength and much lower failure strains than ECA3. These differences can be mainly attributed to the viscoelastic nature of the materials. As noted earlier, the glass transition temperature of ECA3 is around room temperature, which means that the polymer chains in the material can move to some extent under mechanical deformation and as a result, the material as a whole shows large tensile elongations. On the other hand, ECA1 and ECA2 both have glass transitions at temperatures well above room temperature. Therefore, at room temperature, the molecular chains in both materials are more restrained and as a result, the materials show stiffer behavior as can be observed in Figure 4.1.

4.3.2 DCB Results

Figure 4.2-4.4 show quasi-static fracture energy as a function of aging time for conductive adhesive joints with gold plated and copper plated substrates. The error bars in the figures are one standard deviation and are obtained from multiple fracture energy values on a single DCB specimens. As the maximum and arrest fracture energy for each conductive adhesive exhibited similar trends with aging time, only the arrest fracture energy values as a function of aging are presented here, and the maximum fracture energy values are attached in Appendix B. The failure mode, based on visual observations, of the samples at different aging times is identified beside each data point in the figures, in which “C” “M” and “I” represent cohesive failure, cohesive/interfacial mixed-mode failure, and interfacial failure, respectively. The general trend is that the fracture energy for each combination of adhesive and substrate metallization decreases significantly during the initial aging periods; as aging continues, the fracture energy values tend to level out, albeit at relatively low values. The fracture surfaces from the aged samples indicated that the failure mode changed in the following manner as a function of aging time:

Pure cohesive failure: initial aging time

Cohesive/adhesive mixed-mode failure: intermediate aging time

Pure adhesive (interfacial) failure: long aging time

Further observation shows that during the mixed mode failure period, the area exhibiting interfacial failure accounted for a greater percentage of the failure surface as the aging time increased, until pure adhesive failure occurred at longer aging time. One point that is noted from the figures is that for as-produced conductive adhesive joints, which showed cohesive failure regardless of the adhesive type and substrate metallization, ECA3 joints showed higher fracture energy than ECA1 and ECA2 at room temperature. This difference is probably due to the viscoelastic nature of the adhesive. As mentioned earlier, the glass transition region of ECA3 is located around room temperature, which means that ECA3 had a better ability to dissipate energy through internal friction created by relative motions of segmental chains during testing. After exposure to the hot/wet environment, however, the fracture energy of all three adhesive systems was reduced significantly. After 50 days of aging, the fracture energy for all three bonded adhesive systems fell to nearly the same low level. These results indicate that none of the three adhesives shows superior long-term durability under this hot/wet environment. These ECAs were model adhesives, however, so their moisture resistance had not been optimized.

One important observation that can be made from Figure 4.2-4.4, in combination with visual observations on the fractured surfaces, is that the rate of water attack on the interfacial region of conductive adhesive joints with copper plated PCB substrates is faster than the rate of water attack on the interfacial region of joints with gold plated PCB substrates. For ECA1/Au joints, the apparent interfacial failure started at 10 days of aging, while for ECA1/Cu joints, the apparent interfacial failure began at 5 days of aging. ECA2/Au showed pure interfacial failure starting at day 2, when the fracture energy exhibited a catastrophic drop. On the other hand, ECA2/Au joints showed mixed mode failure until day 20, at which time pure interfacial failure occurred. ECA3 joints with both gold and copper substrates exhibited interfacial failure one day after aging started and the failure was accompanied by a substantial drop in fracture energy (see Figure 4.4).

The phenomenon observed above may be explained using the concept of surface free energy and interfacial free energy. Zanni-Deffarges and Shanahan [25] reported that water spreads close to the interface of epoxy joints at a faster rate than it diffuses within the bulk polymer. To explain this phenomenon, they have proposed the concept of “capillary diffusion” and suggested that a “three phase” region exists, consisting of substrate, wet adhesive and dry adhesive near the adhesive/substrate interface, as illustrated in Figure 4.5. Analogous to the wetting front of a liquid spreading to a high energy surface, where the solid surface tension provides the driving force that drags liquid to wet the surface, the substrate/dry adhesive interfacial free energy provides the driving force to “pull” the water diffusion front to the interface region. Based on the information about the surface energies of

$$g_{ab} = g_a + g_b - 2(g_a^D g_b^D)^{1/2} - 2(g_a^P g_b^P)^{1/2} \qquad \text{Equation 2}$$

gold and copper [26,27], it is estimated using Equation 2 [28] that the copper/dry adhesive interfacial free energy is greater than the gold/dry adhesive interfacial free energy. This would imply that the adhesive joints using copper metallization have a stronger driving force to enhance water diffusion along the adhesive/substrate interface. As a result, the joint interface with copper metallization can be attacked by water at a faster rate than the joint interface with gold metallization, as observed from the results obtained on the conductive joints.

Further observations of Figure 4.2-4.4 show that the rate of water attack on the interface is different for adhesive joints bonded with different conductive adhesives. Among the three conductive adhesives, ECA3 joints exhibited interfacial debonding just 1 day after exposure to the hot/wet environment, while the rate of interfacial debonding for ECA1 joints was relatively slow in contrast with ECA2 and ECA3 joints, as especially evident for joints with copper metallization. One explanation for this phenomenon is that ECA3, as well as ECA2, exhibits a glass transition temperature below the aging temperature (85°C). Upon exposure to 85°C, segmental motion of the polymer chains are greatly increased. This would permit diffusing water to penetrate more readily into the adhesive and reach the adhesive/substrate interfaces faster than in the adhesives which exhibit higher glass temperature transitions. In addition, it is interesting to see that the fracture energy obtained on adhesive/copper plated substrate joints initially shows a dramatic drop in response to moisture attack to the interfaces. As aging continues, however, an increase in the fracture energy can be observed in the adhesive joints, which is especially pronounced in the ECA2 joint. This phenomenon cannot be explained based on the visual observations on the fractured surfaces. The XPS analysis conducted on the failed surfaces, which will be discussed in the following sections, may provide some clues to explain this phenomenon.

Some DCB joints with copper and gold metallizations were re-dried for 2 hours at 150°C in a vacuum oven after 2 days and 50 days aging. Test results obtained on the re-dried DCB samples, along with results obtained on as-produced and aged samples are summarized in Table 4.1. As extensive bridging was observed on re-dried ECA3 joints for both Au and Cu adherends after 50 days aging during testing, misleading results may have been produced for the joint. Therefore, the fracture energy of the re-dried ECA3 joint after 50 days aging is not included in this discussion, though it is listed in the table. As can be seen from the table, the fracture energy of the adhesive joints with both gold and copper metallizations was partially recovered upon drying after 2 days aging, though the recovery extent is different for each type of adhesive joints. For re-dried adhesive joints after 50 days aging, the ECA1/Au joint showed some increase in the fracture energy in contrast to the joint aged for 50 days without drying, while other re-dried joints after 50 days aging exhibited little change in the fracture energy as compared to the ECA1/Au joint aged for 50 days without drying. Visual observations of the failure surfaces of the adhesive joints revealed that aged joints, which showed an increase in the fracture energy after drying, exhibited relatively more cohesive failure area, compared with the joints aged for the same periods but without drying, as illustrated in Figure 4.6, where the failed surfaces of ECA1 joints after 2 days aging with or without re-drying are presented. In addition, XPS characterization of the failure surfaces of the aged adhesives further revealed that the joints without any recovery in the fracture energy after drying showed failure along the adhesive/copper oxide interface or within the copper oxide (see the next section for details), while joints which regained some fracture energy after drying exhibited cohesive failure in the adhesive or interfacial failure along the adhesive/metal interface. The results obtained from the surface analysis suggest that the fracture energy loss is irreversible for the joints in which a copper oxide exists on the substrate surface as a weak boundary layer. On the other hand, the fracture energy loss can be partly reversible when the joints showed failure in the adhesive or along the adhesive/pure metal interface. Part of the recovery in the fracture energy can be attributed to the reversible effect of plasticization of the bulk adhesives, while some of the recovery may be due to regaining adhesion between the adhesive and the substrate when the joints were re-dried at 150°C. In the re-heating process at 150°C, some of the ingredients in the adhesives may have melted and then re-bonded the substrates. The exact mechanisms of the recovery of the fracture energy, however, need further investigation.

4.3.3 Failure Mechanism of Conductive Adhesive Joints

In the above section, the fracture energy of conductive adhesive joints as a function of aging time was given and visual observations on the failure mode changes during aging were discussed. To identify the exact locus of joint failure and investigate the failure mechanisms of ECA joints with copper and gold substrate metallization, surface analysis was conducted. SEM and XPS analyses were utilized to investigate the failure mechanisms. In this endeavor, an emphasis was placed on ECA2/Cu and ECA2/Au joints combined with gold and copper metallizations. As shown in the above section, all three adhesive systems showed a similar tendency in the change of fracture energy and failure mode as a function of aging time. Therefore, the analysis conducted on ECA2 joints is taken as being representative of the three conductive adhesive joints. In the following sections, all the discussion refers to ECA2 joints, unless specifically named.

4.3.3.1 Copper-Plated Joints

The surface of a PCB substrate with copper metallization prior to bonding was first analyzed using XPS and the survey spectrum is shown in Figure 4.7 (a). This spectrum reveals that carbon, oxygen, nitrogen and copper are present on the copper surface. Carbon, oxygen and nitrogen probably originated from a handling process or environmental contamination. The combination of high resolution Cu 2p spectra and Cu LMM spectra further revealed that copper on the surface of the freshly prepared substrate was elemental copper, and no copper oxide was present.

The locus of failure for the non-exposed ECA2 joint was visually identified as being purely cohesive, occurring along the middle of the adhesive layer. This finding was further confirmed from SEM (See Figure 4.8) and XPS studies conducted on both fracture surfaces of a typical sample. The XPS analysis suggested that the opposite sides of the failure surfaces of the non-exposed sample showed equivalent survey spectra and similar elemental atomic concentration in the conductive adhesive, as listed in Table 4.2. The non-exposed ECA1 joint also exhibited purely cohesive failure, similar to the ECA2 joint. For as-produced ECA3 joints, visual observations, and additional SEM studies (See Figure 4.9), revealed that the failure occurred very close to the adhesive/copper interface, with a thin adhesive layer covering the copper surface. After 2 days aging at 85°C, 100%, the locus of failure of the ECA2 joint was visually assessed as being purely interfacial failure, along the adhesive/copper interface. The specimen was further examined by using XPS analysis of both the adhesive side and the substrate side of the failure surfaces (See Figure 4.10). The XPS results showed that the substrate side of the joints (Figure 4.10 (a)) exhibited a similar spectrum to that of the fresh substrate surface, which is shown in Figure 4.7 (a), and copper on the failure surface was present in its pure state and no evidence of oxidation was obtained. The XPS spectrum of the surface of the adhesive side is shown in Figure 4.10 (b). As can be readily seen, no copper signal was detected on the adhesive side of the failed surface. This finding further confirms the point that the locus of failure for the conductive adhesive joint was predominantly interfacial along the adhesive/copper interface. On the other hand, further observations made from Figure 4.10 (b) reveal that the XPS spectrum of the adhesive side is not at all characteristic of that of the reference bulk adhesive as shown in Figure 4.7 (b). One important difference is that silver, which was detected on the surface of the bulk adhesive, is not present on the surface of the adhesive side of the failed joint. In addition, the high resolution 1s carbon spectrum revealed that carbon on the surface of the adhesive side is mainly associated with hydrocarbon, while in the bulk adhesive, a large amount of the detected carbon was related to epoxy carbon. The indications from these results are that the conductive adhesive adjacent to the interface possesses a different chemical structure compared to the bulk adhesive and there exists a silver-depleted layer between the metallization and the adhesive, as also reported in the literature [29]. The depth profile of the silver-depleted layer, however, needs additional investigation, although the XPS sampling depth implies that the depleted layer is at least 40-50 Å thick.

Visual observations suggested that after 50 days aging at 85°C, 100%RH, all three conductive adhesive joints exhibited interfacial failure along the adhesive/copper interface. However, XPS studies showed that the three adhesive joints actually exhibited different failure loci. The XPS results obtained on both sides of the failed surface of the aged ECA2/Cu joint are shown in shown in Figure 4.11. Of particular note in the figure is that both the adhesive side and the substrate side of the failure surface exhibit copper signals. The high-resolution 2p copper spectra further revealed that the copper detected on both sides of the failed surface was CuO. This conclusion is based on Cu $2p_{3/2}$ binding energy of 933.7eV and the shake-up satellites features occurring in the 2p copper spectra (See Figure 4.12). These results indicate that at longer aging times, copper was oxidized and the locus of failure shifted into the copper oxide layer from the adhesive/copper interface. One possible reason for the change of the failure path is that moisture may have penetrated into the oxide layer and weakened the oxide layer. Figure 4.11 also shows that there are strong carbon signals in the spectra of both sides of the failed surface. One possible explanation is that the adhesive adjacent to the interface, which may possess a different chemical and physical structure from the bulk adhesive, such as lower crosslink density, may have penetrated into the copper oxide and formed an adhesive/copper oxide composite interphase between the adhesive and the underlying copper, though it is well known that a highly crosslinked adhesive generally does not have much mobility. The slight increase in the fracture energy at longer aging time may be attributed to the mechanical interlocking formed within the interphase.

For the ECA1/Cu joint after 50 days of aging, the XPS analysis revealed that the locus of failure occurred principally along the adhesive/copper oxide interface. XPS studies on ECA3 joints after 50 days aging showed that the joints actually failed within the secondary, silver-depleted layer of the adhesive, which is adjacent to the interface. This observation indicates that for ECA3 joints, the secondary layer of the adhesive is always the weakest layer, where the adhesive failure occurred prior to and after aging.

4.3.3.2 Gold-Plated Joints

The XPS spectrum of a PCB substrate with gold metallization prior to bonding is shown in Figure 4.13. The figure reveals that gold, fluorine, carbon, and oxygen are present on the surface. Nickel and copper, which were plated under the gold layer, were not detected on the surface. The fluorine, carbon and oxygen atoms probably originated from processing or environmental contamination.

The as-produced ECA1/Au and ECA2/Au joints showed purely cohesive failure, occurring along the middle of the adhesive layer, while the initial failure for the ECA3 joints occurred very close to the adhesive/copper interface, with a thin adhesive layer covering the gold surface. After 2 days of aging, however, the locus of failure of the ECA2 joints visually appeared to be mainly interfacial along the adhesive/gold interface, accompanied by a small region of cohesive failure at the center of the adhesive joint. XPS studies were conducted at the failure location where interfacial failure was visually identified for the adhesive joint aged for 2 days. The XPS results for the ECA2/Au joint are shown Figure 4.14. The XPS spectrum for the adhesive side is very similar to the spectrum of the adhesive side of the ECA2/copper joint aged for 2 days as shown in Figure 4.10 (b), but unlike that of the reference bulk adhesive (Figure 4.7 (b)). This finding further confirms that an adhesive boundary layer exists adjacent to the adhesive/substrate interface, whose chemical structure is different from that of the bulk adhesive. On the other hand, the XPS results for the substrate side (Figure 4.14(a)) indicated small amounts of silver, nickel and copper (See Table 4.3) elements in addition to gold. Apparently, the silver was from the adhesive layer, while the nickel and copper were from the layers under the gold plating, where nickel and copper were deposited. Earlier studies [30,31] reported that surface silver diffusion can occur at the Ag and Au bonded interface and can result in a silver depletion region in the silver plated substrate at the bond periphery. Pinnel and Bennett [32, 33] revealed that the diffusion of Cu to the Au surface can take place at relatively low temperatures and that the Ni layer only retards the motion of copper to the gold surface but does not totally prevent the diffusion process. They also found that the diffusion time of copper is highly dependent on the thickness of nickel and gold layers, as thin gold and nickel layers can shorten the diffusion time significantly. Chang [34] reported that copper can diffuse to the Au surface even with a Ni layer plated between the Au layer and the Cu layer as a barrier layer to prevent diffusion, and the diffusion can be enhanced by oxygen. Based on the studies cited above and the XPS results conducted in this research, it is apparent in the adhesive systems studied here, that diffusion may occur between Au and Ag, and Au and its underlying metals during curing at 150°C and subsequent aging at 85°C.

Visual observations of failed specimen illustrated that that all three conductive adhesive joints after 50 days aging at 85°C, 100%RH exhibited interfacial failure along the adhesive/gold interface. However, close-up studies using the XPS showed the three adhesive joints actually exhibited somewhat different failure loci. The XPS spectra for both sides of the failed surface of the aged ECA2 joint are shown are shown in Figure 4.15. For the metal side, it is interesting to note that a very weak gold signal and a strong copper signal were detected. This finding indicates that copper diffused via nickel up to the surface of the gold layer with increasing aging time. The high-resolution 2p copper spectra revealed that copper detected on the gold surface was copper oxide and was primarily CuO, based $Cu2p_{3/2}$ peak binding energy (933.7eV) and the shake-up satellite features in the 2p copper spectra. On the other hand, the adhesive side of the joints aged for 50 days exhibited a similar spectrum to that of the adhesive side of the 2 days aged copper joint which exhibited purely interfacial failure along the adhesive/copper interface. The interpretation of the spectra indicated the existence of an adhesive secondary layer adjacent to the adhesive/substrate interface. Hence, one conclusion that can be reached from the XPS studies is that the failure locus for the ECA2/Au sample aged for 50 days was indeed predominantly interfacial along the adhesive/copper oxide interface.

The failure of the ECA3 joint aged for 50 days exhibited interfacial failure along the adhesive/copper oxide interface, a result similar to that formed for the ECA2/Au joint. For the ECA1 joint with gold metallization, however, XPS analysis revealed significant gold, as well as small amounts of silver and copper on the surface of the substrate side, while the adhesive side showed a spectrum very similar to that of the adhesive side of the ECA2 joint aged for 2 days as shown in Figure 4.14(b). This observation suggests that the locus of failure of the ECA1 joint after 50 days aging is mainly interfacial along the adhesive/gold interface.

The elemental atomic concentrations obtained on the substrate side of ECA1, ECA2 and ECA3 joints with gold metallization aged for 50 days are tabulated in Table 4.4. As can be observed from the table, the ECA1/Au joint showed high Au atomic concentration and low Cu atomic concentration on the surface of the metal side, as compared to the ECA2/Au and ECA3/Au joints. These XPS results reveal that the rate of copper diffusion on the gold substrate bonded with ECA1 is slower than with ECA2 and ECA3. One possible reason for this phenomenon is that ECA1 joints may have better resistance to the attack of oxygen which can enhance the copper diffusion [34], compared to ECA2 and ECA3 joints.

4.4 Summary and Conclusions

This research was initiated to study effects of the environmental aging on the durability of the conductive adhesive joints, and to further investigate the failure mechanisms of the adhesive joints. Through this study, the following conclusions can be made:

The fracture mechanics approach-DCB test has been adapted to investigate the effects of environmental aging on electrically conductive adhesive joints. To make the test method more suitable for the electronic industry, a special DCB geometry was developed. Results obtained in this study suggest that the test procedure developed in this study may be a useful tool for evaluating newly formulated conductive adhesive systems.

A hot/wet environment (85°C, 100% RH) can significantly weaken the strength of the conductive adhesive joints studied herein. A comparative study of the durability of different conductive adhesive and substrate metallization combinations showed that the resistance of the adhesive joints to moisture attack is related to the adhesive properties as well as to the substrate metallization. Gold metallization has better resistance to moisture attack than copper metallization. The mechanism for this difference may be explained using the concept of surface free energy and interfacial free energy combined with a three-phase diffusion model near the metal/polymer transition.

The fracture energy of some of the aged adhesive joints recovered to some extent upon re-drying, partly due to the reversible effect of plasticization of the bulk adhesives, as well as partial recovery of adhesion at the interface during reheating at the high temperature. However, the fracture energy of the adhesive joints showed little recovery after the metal surface was oxidized.

XPS and SEM have been used to investigate the failure mechanisms as a result of environmental attack on the conductive adhesive joints. For adhesive joints using copper metallization, water attack on the adhesive joint may be divided into three phases: displacing the adhesive from the substrate, oxidizing copper, and weakening the copper oxide. At the end of aging, the three adhesive joints exhibited different modes of failure. ECA1 joints failed interfacially along the adhesive/copper oxide interface, while ECA2 joints exhibited the locus of failure within the copper oxide layer. For ECA3 joints, the failure occurred within the secondary layer of the adhesive, which is adjacent to the interface and is a silver-depleted layer.

Surface analysis of the adhesive joints using gold metallization revealed that diffusion of silver to gold and diffusion of copper to the surface of gold occurred. After 50 days aging, the conductive adhesive joints exhibited failure along the adhesive/copper oxide interface, except for ECA1 joints, which still showed the failure along the adhesive/gold interface. This finding suggests that the Ni layer deposited between the Au and Cu layers only retards the transport of copper to the gold surface, but does not totally prevent the diffusion process. And optimized thickness of Ni and Au layers may be needed to prevent outdiffusion of Cu to the Au surface.

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