Reliability and Failure Mechanism of Isotropically Conductive Adhesives Joints

Li Li and J. E. Morris
Department of Electrical Engineering, State University of New York at Binghamton, Binghamton, NY 13902-6000

Johan Liu, Zonghe Lai, Lars Ljungkrona and Changhai Li*
IVF-The Swedish Institute of Production Engineering Research, Argongatan 30, S-431 53 Molndal, Sweden
*Department of Engineering Metals, Chalmers University of Technology, Gothenborg, Sweden

Abstract--Three recently developed silver filled isotropic electrically conductive adhesives from different manufacturers were selected for study. This work was focused on the use of isotropically conductive adhesives for joining surface mount devices (SMD) on printed circuit boards for potential solder replacement. The purpose of this study is to evaluate the reliability and failure mechanism of the adhesive joints in humid environments. 0805 chip components with pre-tinned terminals were attached using the conductive adhesives to printed circuit board (PCB) test boards with passivated copper and tin/lead metallizations. Shear strength and electrical resistance of the adhesive joints were measured initially after assembly and after 85°C/85%RH constant humidity exposure at different time intervals. Electrical resistance of the adhesive joints increases and shear strength decreases dramatically for one adhesive after the humidity exposure while the others showed relatively smaller changes. Microstructure investigations by optical and scanning electron microscopy (SEM) reveal adhesive cracks initially after the cure, and crack development after the humidity exposure. Adhesive joint thickness and adhesive wetting properties to the component leads and PCB pad metallizations were also observed. Different silver flake sizes, distributions and orientations were also investigated. Transmission electron microscopy (TEM) shows different degrees of oxidation of the PCB pad metallizations due to moisture penetration

I. INTRODUCTION

Electrically conductive adhesives (ECAs) have drawn more and more attention in electronics manufacturing as alternative interconnection methods for SMT and other microelectronics applications. ECAs offer several advantages over solder. They are environmentally friendly, eliminating the lead and flux associated with normal soldering processes, and offer lower temperature processing and less process steps. Research and development during the past few years has evaluated the reliability of these materials for specific electronic packaging processes [1-6]. However, the adhesive technology is still in developmental stages in comparison with the mature solder technology. There are many challenges still to be answered, and insights to be gained.

The failure mechanism of the adhesive joints under environmental exposure is a multi-faceted problem. The reliability of the conductive adhesive joints can be influenced by many different factors. These can be moisture absorption by the polymer matrix, corrosion and oxidation of the bonding interfaces, and mechanical stress variation caused by coefficient of thermal expansion (CTE) mismatches of the substrate to component leads and joints. Moisture can be a severe factor causing changes in mechanical and electrical performances of the adhesive joints. It is evident that oxide formation is an important result of the moisture attack in a humid environment. Moisture penetration can cause swelling of polymers, oxidation and corrosion of metal fillers, interconnection terminals and pad metallizations.

The purpose of this work is to study the mechanisms of moisture penetration into the adhesive joints and of oxidation of the interconnection pads. The relationship between processing, the adhesive's rhoelogical properties, and its reliability performance are to be established, along with the correlation of the mechanical bonding strength to the electrical properties of the adhesive joints under humidity exposure.

II. EXPERIMENTAL PROCEDURES

Test Materials and Assemblies

Three isotropically conductive adhesives from various leading manufacturers of conductive adhesives were selected based on previous experimental results [7]. They are all silver loaded epoxies, in one or two component versions. Their physical properties supplied by the manufacturers are summarized in Table 1. The viscosity data are obtained by the vendors under different test conditions and may only be used for relative reference.

Table 1: Physical and rheological properties of the adhesives

Adhesives	Volume resistivity (ohm•cm)	Glass transition (Tg, °C)	Viscosity (Kcps)	Cure schedules
A	$1 \cdot 10^{-3}$	80 °C	310-350	120°C, 10min
B	$1\text{-}3 \cdot 10^{-4}$	90 °C	150-200	150°C, 5min
C	$2 \cdot 10^{-4}$	80 °C	73	150°C, 3min

The layout of the test board is shown in Figure 1. 0805 chip resistors (jumpers) were attached to the PCB test boards with two different conduct pad metallizations, i.e., pre-tinned and passivated copper. The quad flat pac (QFP) sites were not used. PCBs with copper metallization were protected by an organic, azole-based passivation layer (Tolytriazale). The pre-tinned finish was maintained at about 10 µm thickness by using hot-air solder-leveling (HASL). The layout dimensions of the 0805 chip component are shown in Figure 2 with L=110mil, W=70mil and B=40mil. The component terminal finish was solder plating with a nickel barrier.

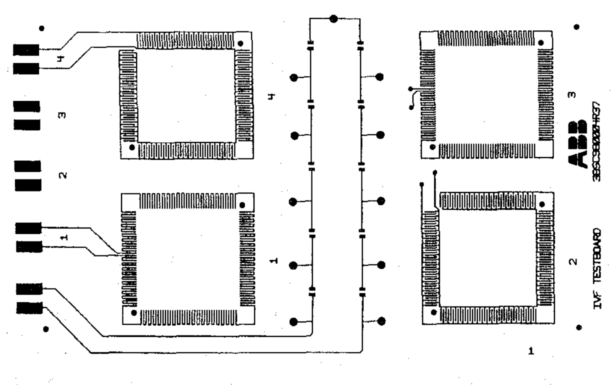


Figure 1: Layout of the test board used.

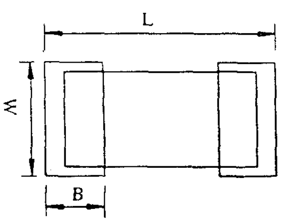


Figure 2: Layout dimensions of 0805 chip component.

The adhesives were stencil printed to the PCB pads with a semiautomatic Conergo screen printer. The stencil printing parameters are summarized in Table 2. Test boards were cleaned in 75% isopropyl alcohol for 30 minutes. The apertures of the stencil were chosen as 80% of the pad size of the component. During the experiment, the rubber squeegee used was found to be too soft to produce high quality printing. A rigid steel squeegee is recommended for future work. Components were manually mounted using a pick-and-place work station equipped with vacuum tweezers. The components were subjected to a light pressure, controlled by a micro-switch in the vacuum nozzle head to provide consistent values each time. Curing of the adhesives was performed in a separate convection box oven. The curing schedule is according to the manufacturers' recommendations, (but 4 min. was added to let the board achieve its cure temperature according to the measured temperature lag experienced when test boards were inserted in the hot box oven). For Adhesive B, the actual cure schedule used in this study was 7 min, based on initial data, but the material specification received later was for 5 min.

Table 2: Stencil printing parameters

Stencil thickness	100 µm
Squeegee material	Rubber, 80 shore
Squeegee speed	45 mm/s
Squeegee angle	45°
Squeegee pressure	125 kpa
Stencil to substrate distance	0

Reliability Tests

Ten chip components were mounted on each test board. All the test assemblies were tested at a constant temperature of 85°C and at a relative humidity of approximately 85% for 1000 hours. The test chamber used was a Tabai LHU-212, which holds a maximum sample volume of 100 liters. Samples were placed vertically on test racks in the test chamber. Electrical resistances of the individual component and the total ten components in series were measured after initial assembly before the humidity exposures, and at five different times afterwards (68, 158, 236, 500, 1000 hours). A HP 34401A Multimeter was used to measure the resistance of the adhesive joints. The mechanical shear tests of the individual chip resistors were performed after the resistance measurements, and standard deviations obtained. The shear force is the average value of the total 10 chip resistors. Shear tests were performed on a Dage BT-22 microtester. The load cell used for the shear testing could handle 5kg. The PCB substrate pads were studied after the shear test under an optical microscope to identify adhesive or cohesive failure of the joints. Crossections of the adhesive joint samples were prepared. Optical and a JEOL JSM-840A SEM were used to investigate the microstructures of the adhesive joints. Composition of the joint terminals, pads and the adhesives were studied with Energy Dispersive Spectroscopy (EDS). Transmission electron microscope (TEM) samples were prepared by cutting the crossection samples into small blocks to fit into the microtone fixture. An ultracut microtone was used to prepared the thin TEM specimens. An analytical electron microscopy, JEOL 2000 FX, with a Link AN 10000 EDS system was used to study the microstructure of the oxide layer of metallization pads. Oxide was detected with windowless EDS analysis. Selected area electron diffraction (SAD) was used to determine the crystal structure of the oxide layer. Reference samples of the bare PCB conduction pads before and after humidity exposure were prepared to measure the oxide thickness using a Perkin-Elmer PHI 660 Scanning Auger Microprobe to compare with the oxide layer of the adhesive joint interfaces.

III. RESULTS AND DISCUSSIONS

Mechanical Strength

The mechanical strengths of the adhesive joints were evaluated by shear test of the 0805 chip components. Figures 3-5 show the shear force to completely shear the component off the PCB boards. Figure 3 is the shear force of the three different adhesives bonded to the copper passivated PCB pads. The values presented here are the averages of the ten samples on each board. Adhesive C had the highest shear force initially, but it decreased rapidly after 68 hours of humidity exposure. Adhesive B showed minor shear force variation throughout the humidity test, except a relatively larger decrease in shear force at 158 hours . The shear force increased again and then leveled off. Adhesive A had the lowest initial shear force, which experienced little decrease during the humidity exposure. The up and down shear force variation during the whole environmental exposure may be caused by moisture absorption saturating at certain exposure times of the epoxy matrix. This phenomenon with the resistance variations was also noticed by other investigators [8]. There might be several factors affecting the total mechanical performance. Figure 4 is one example of the measurement data for Adhesive A on copper pads, and gives the value of standard deviation of the test data. Figure 5 shows the test results on the pre-tinned PCB metallization, which gives similar trends to those on the copper passivated PCB pads. The shear force of Adhesive C dropped dramatically from the highest values to very low after 1000 hours exposure. This may be caused by the degradation of the epoxy matrix of Adhesive C after moisture absorption. For Adhesive A and B, there were small changes for the shear forces after environmental exposure.

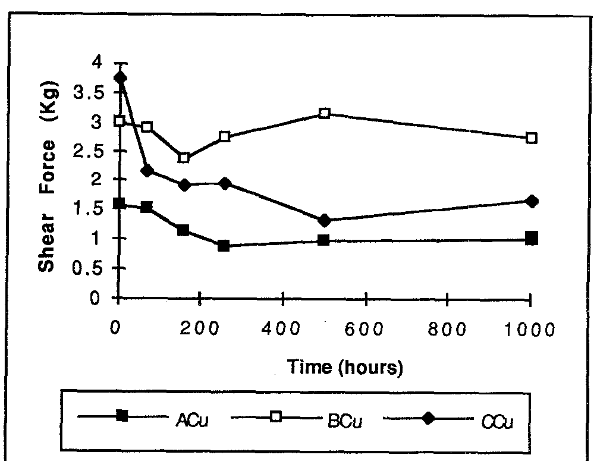


Figure 3: Shear force of the adhesive joints on Cu PCB pads vs. humidity exposure times.

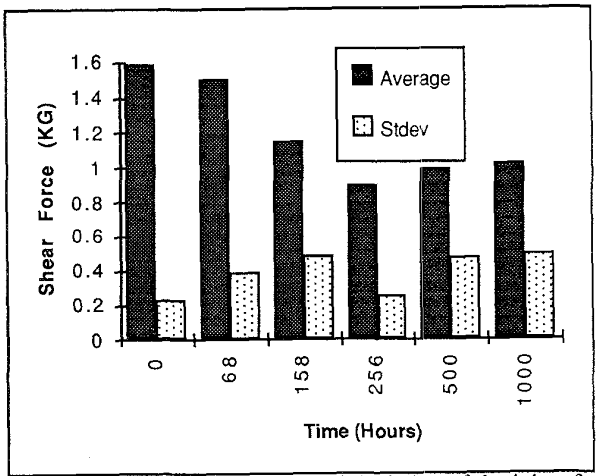


Figure 4: Shear force and standard deviation of the joints for Adhesive A on Cu PCB pads vs. humidity exposure times.

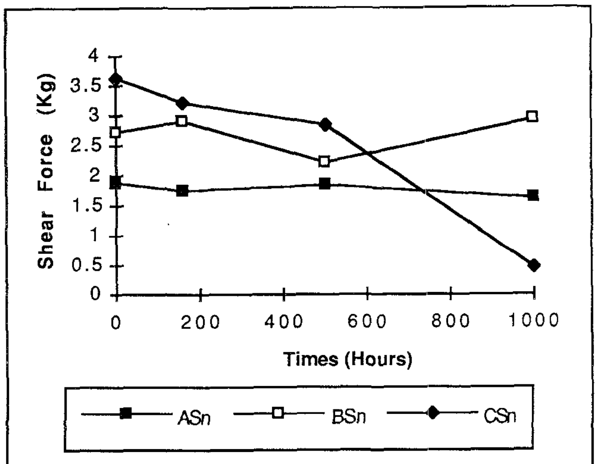


Figure 5: Shear force of the adhesive joints on pre-tinned PCB pads vs. humidity exposure times.

Joint Resistance

Joint resistance of the chip component was measured individually to correlate with the shear force measurement and the microstructural investigation. The total of ten chip components in series was also measured. Figure 6 is the initial total resistance of the ten chip components and the standard deviation of the 8 test boards for each category. Adhesives A showed the highest resistance, matching the relatively high resistivity specified. Adhesive joints of Adhesive A on pre-tinned PCB metallizations showed lower resistances than those on copper PCB metallizations. Adhesive C showed the largest variation of data from the standard deviation calculation. This may be caused by the difficult stencil printing characteristics of the material and the uneven thickness of the adhesive layer which resulted on the boards after printing. Microstructural investigation of the adhesive joints showed such effects, which will be discussed in the next section. Only one set of stencil printing parameters was selected, as shown in Table 2 and based on the previous study [7]. However, this may be unsuitable for the rheological properties for different adhesives. Future work has been done to select the optimum stencil printing parameters for different adhesives on a more advanced stencil printing machine. From the material point of view, the rheological properties of the adhesives should be tailored to meet the fine pitch printing requirement. Adhesive B showed low resistance and small standard deviation of the data.

Figure 7 shows the average joint resistance value of one chip component vs. humidity exposure times. Adhesive B showed small resistance increase with humidity exposure times, about a 27% increase for the pre-tinned metallization and a 127% increase for the copper PCB metallization after 1000 hours humidity exposure. Adhesive B showed its compatibility with both pre-tinned terminals and pre-tinned pads. Adhesive A showed larger resistance increases after the environmental exposure. Adhesive A on a pre-tinned PCB showed a relatively higher resistance increase than that on a passivated copper PCB substrate, although initial resistance trends were opposite . Figure 8 shows that the resistance of Adhesive C increases sharply with the environmental exposure. The data was the average resistance of the components tested. Actually some of the joints failed (10-3000 ohm) after 1000 hours 85°C/85% humidity conditions. These joints also had very lower shear forces. The severe failure may be caused by the stencil printing quality of Adhesive C, which has been shown in Figure 6 to have the large variation of the initial resistance. In order to have reliable adhesive joints, the adhesive rheology must be suitable to the process, either stencil printing or dispensing. The cure parameters are also critical. Adhesive B which cured at 150°C, 7 min (2 min longer than the manufacturer's data) shows relatively stable properties during the reliability tests.

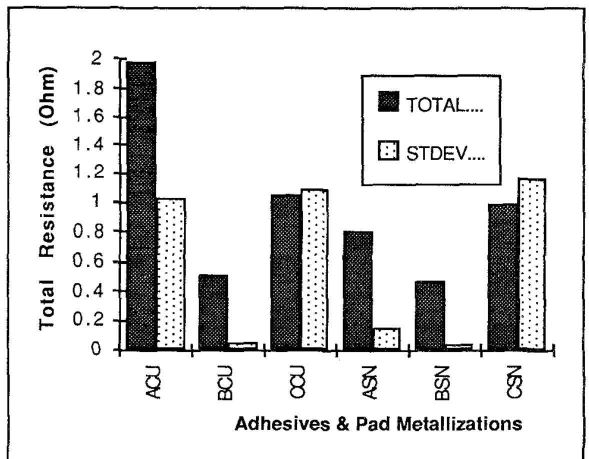


Figure 6: Initial adhesive joint resistance of the ten chip components on Cu and pre-tinned PCB pads.

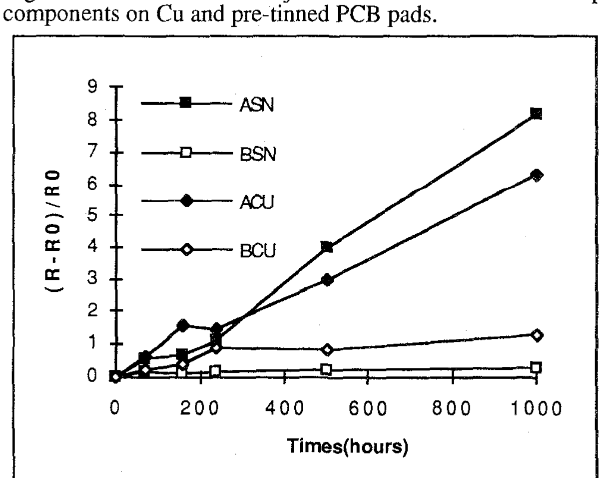


Figure 7: Joint resistance vs. humidity exposure times for Adhesive A and B on Cu and per-tinned PCB boards.

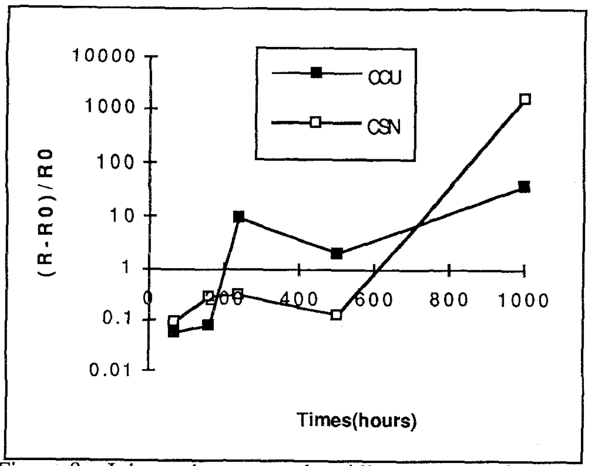


Figure 8: Joint resistance vs. humidity exposure times for Adhesive C on Cu and per-tinned PCB boards.

Microstructural Investigation

Crossections of the adhesive joints before and after humidity exposure were studied under the optical microscope and SEM. Figure 9(a)-(d) shows joints of different adhesives. The measured joint resistances are also included in Figure 9 for comparison and analysis. Figure 9(a) shows a representative low quality print of Adhesive C, although this joint does have a initial resistance reading, and $(R-R_0)/R_0=0.16$ after 68 hours of humidity exposure. Several joints of Adhesive C like this were observed, and it is easy to anticipate failure after prolonged environmental exposure for these cases. Their higher incidence at the center of the board was attributed to a warpage problem with the board. From these pictures, the wetting properties of these adhesives on PCB board pads and component terminals can also be studied. From Figure 9(b), Adhesive C displayed normal stencil printing quality, and wetted the component terminal lead at a triangle. This joint has a resistance increase of only 5% after 500 hours of humidity exposure. Figure 9(c) is a typical crossection for Adhesive B, which has a higher viscosity than Adhesive C. Adhesive B wetted the component terminal at a rectangle shape. Figure 9(c) also shows that Adhesive B sometimes does not wet the copper PCB pads well. Cracks were observed in the adhesive to copper PCB pad interfaces. Figure 9(d) is the joint of Adhesive A. This adhesive has the highest viscosity; the wetting shape of the component lead had a similar shape as Adhesive B. Defects on the PCB pad metallization were also noticed throughout the experiment.

Figures 10(a)-(c) are SEM micrographs, which show the silver flake sizes, shapes and orientations. Figure 10(a) is Adhesive A on a copper pad after 500 hours humidity exposure. Cracks along the terminal lead are noticeable. Adhesive A has very small silver particles less than 1μm in diameter. There are lots of large black spots in the Adhesive A matrix, which are believed to be the flexible agency added by the manufacturer to increase the reliability of the adhesive. The windowless EDS analysis of these spots showed C, Si, O. The adhesive fillers were all identified by EDS analysis to be silver. The pre-tinned component terminal is actually 95%Sn/5%Pb analyzed by EDS. Figure 10(b) is an Adhesive B joint on copper pads; cracks and small voids can be seen here. The silver flakes have bimodal size ranges around 5-8 μm and 1μm. Figure 10(c) is the Adhesive C joint on a pre-tinned pad; agglomerated flakes were seen in the joint. Adhesive C has its flakes oriented differently; flake faces can be seen from the crossection. The size range of these flakes is about 8-10 μm.

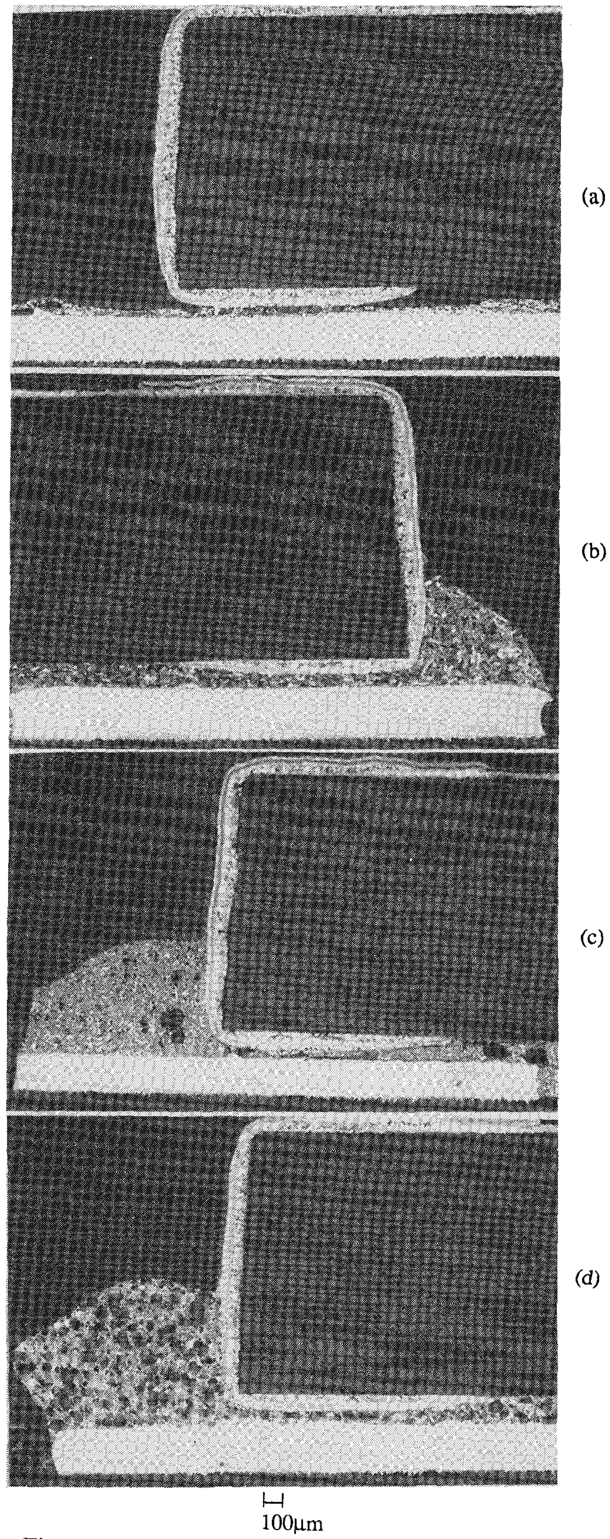
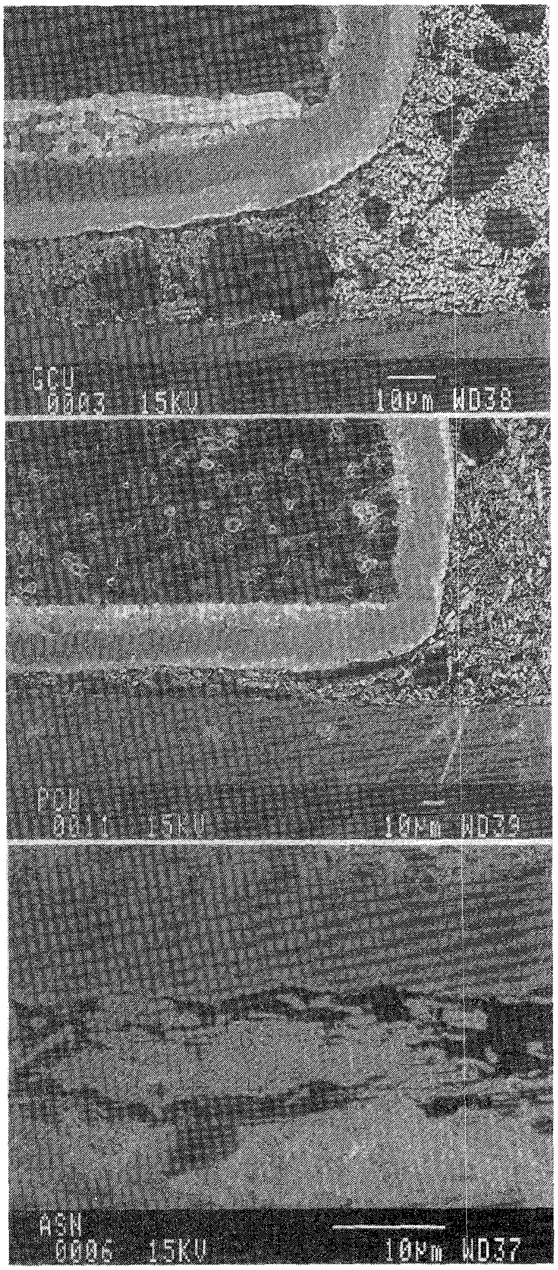


Figure 9: Micrographs of the joint crossections. (a) Adhesive C on pre-tinned pad after 68 hours exposure (R=0.09Ω, $\Delta=(R-R_0)/R_0=0.17$). (b) Adhesive C on copper pad after 500 hours exposure (R=0.068Ω, Δ=0.05). (C) Adhesive B on copper pad after 158 hours exposure (R=0.071Ω, Δ=0.16). (d) Adhesive A on pre-tinned pad after 158 hours exposure (R=0.184Ω, Δ=1.022).



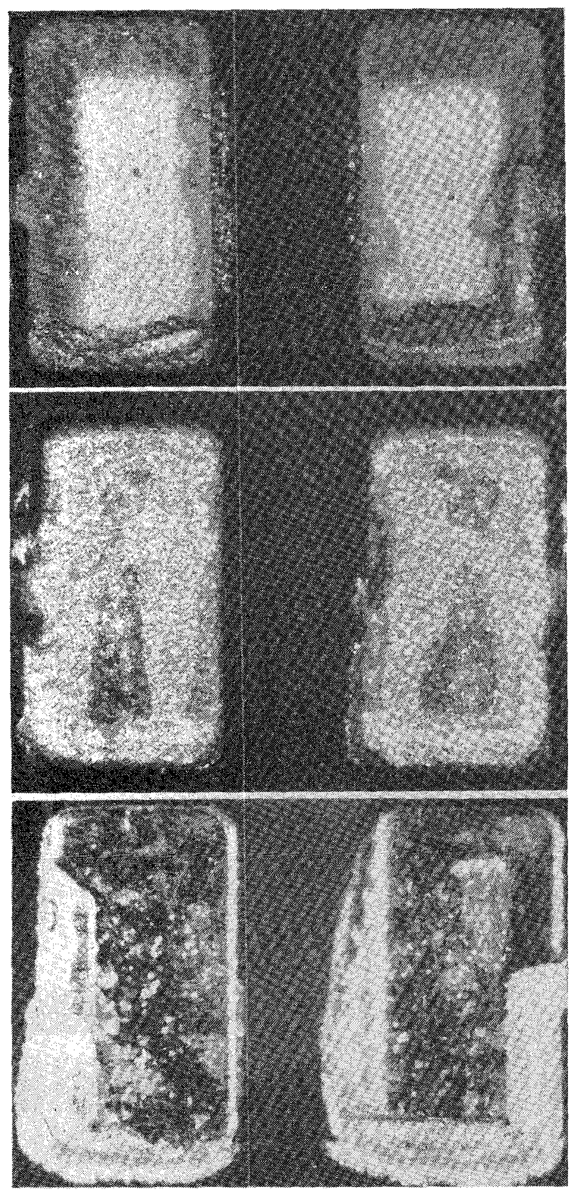
(a)

(b)

(c)

Figure 10: SEM micrographs of the joints after 500 hours exposure. (a) Adhesive A on copper pad. (b) Adhesive B on copper pad. (c) Adhesive C on pre-tinned pad.

The surfaces of the PCB pad metallizations after shear tests were investigated by optical microscopy. Minimum and maximum shear force samples were selected on each board for pictures. The minimum shear force samples had high percentage resistance increases after humidity exposure compared with the maximum shear force samples, when the resistance and shear force data of these individual chip components were compared. Figures 11(a)-(d) show representative photos of different adhesives after humidity exposures. Figure 11(a) is the surface of the highest shear force sample (3.45Kg, $(R-R_0)/R_0=0.197$) for Adhesive C on copper PCB pads after shear testing at 236 hours of humidity exposure. Figure 11(b) is the surface of another Adhesive C joint on the same board with the lowest shear force(0.05Kg), and a resistance failure ($(R-R_0)/R_0=77.52$). Figure 11(a) shows the failure occurred at the PCB pad/adhesive interface. Figure 11(b) on the other hand shows the failure at the component lead/adhesive interface. The adhesive here may be too thin to hold the component. The stencil printing thickness of the adhesive is critical for the adhesive bond. Figure 11(c) is a surface picture of the Adhesive B sample on a pre-tinned PCB metallization after 500 hours of humidity exposure, which had the maximum shear force on the test board. Figure 11(d) is Adhesive A after 158 hours exposure, after the typical failure mode of this material, which occurs at the component lead terminal/adhesive interface. The Adhesive A group had the lowest shear force as shown in Figures 3-5. General observations of the pad surfaces after shear testing were related to the shear force value and resistance change. Adhesive A usually had a combination of cohesive failure and adhesion failure between the lead and adhesive. Adhesion failure between the PCB pads and adhesive were observed on the pre-tinned metallizations for Adhesive B. Adhesive C shows different failure modes at different sites even for a single exposure time.



(a)

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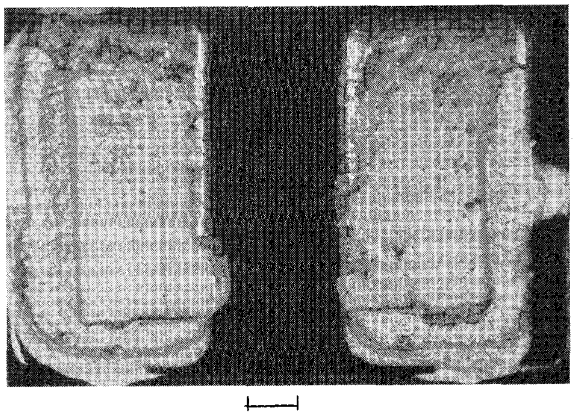


(d)

Figure 11: Micrographs of the surface of the PCB pad after shear test. (a) Adhesive C on copper pad after 256 hours exposure (3.45kg, R=0.073Ω, Δ=0.20). (b) Adhesive C on the same board as (a), (0.05kg, R=22.38Ω, Δ=77.52). (c) Adhesive B on pre-tinned pad after 500 hours exposure (3kg, R=0.074Ω, Δ=0.25) (d) Adhesive A on pre-tinned pad after 158 hours exposure (1.25kg, R=0.11Ω, Δ=0.39)

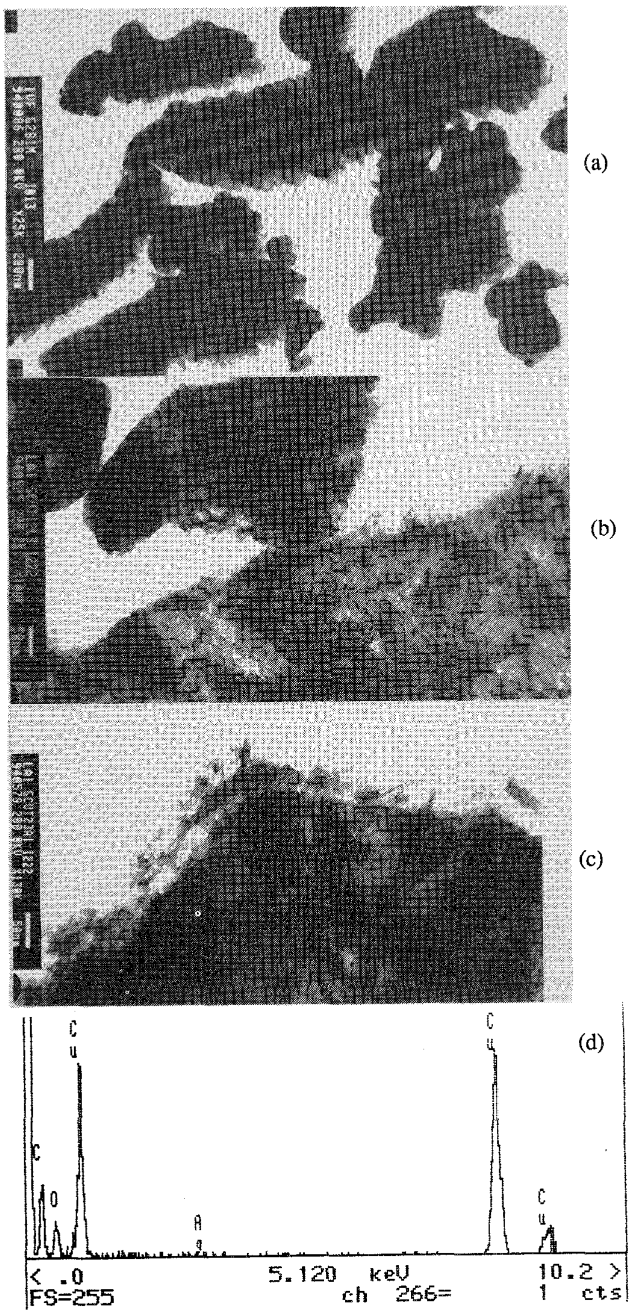
TEM and Auger Studies

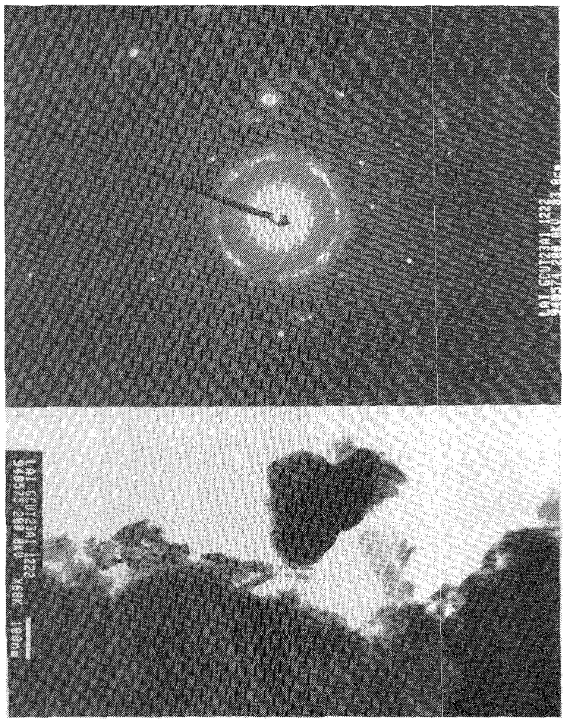
TEM studies were performed mainly to investigate the silver flake morphology and interface oxidation. Figures 12(a)-(b) show how the silver flakes actually touch each other and how they touch the PCB pads. Figure 12(a) is of Adhesive A which has small size particles. The edge of the particles appears to be rough, which may be advantageous to electrical conduction. Figure 12(b) shows how one flake touches the copper PCB pad and another flake. Figure 12(c) shows an oxide layer around 100nm thick formed on the copper PCB pad for Adhesive A after 1000 hours at 85°C/85%RH. Oxide was detected by windowless EDS analysis and figure 12(d) is the EDS spectrum of the copper oxide layer. Selected area electron diffraction (SAD) was used to determine the crystal structure of the copper oxide. The diffraction pattern is shown in Figure 12(e). The index of the pattern shown in Table 3 indicates the Cu_2O cubic structure. Figure 12(f) shows how the flake is actually separated from the copper metallization pad by the oxide layer. The adhesive A samples were investigated along the copper pad and adhesive interface after 68 hours exposure. The EDS spectrum of an apparently thin layer did not show any oxygen peak indicating that the sample has no noticeable oxide layer. The oxide layer on the copper substrate grows with the humidity exposure time. The Cu_2O oxide layer has a resistivity around 10 to 50 ohm-m [9], which is about 1000 times the resistivity of copper and silver. This interface oxide layer growth during humidity exposure will decrease the electrical performance of the adhesive joint. Because of the difficulty of preparation of these TEM specimens, there is not a regular sequence of data at different humidity exposure times. Better methods for preparing samples will be developed for the future interface investigation. For adhesive samples on pre-tinned pads, oxides were detected on the lead(Pb) phases for the 158 and 500 hour exposures. The structures of the oxide need to be studied further.

Auger depth profile analysis was used to determine the reference sample oxide thickness. Bare passivated copper and pre-tinned PCB metallizations were tested before and after the humidity exposure . Almost no oxide was formed on the passivated copper layer. About 7nm of tin oxide layer thickness was detected on the pre-tinned PCB pad. Thick oxide layers about 300nm thick (as determined from the sputtering rate of standard samples) were formed on the copper PCB metallizations after 500 hours of humidity exposure.

Table 3 The index of diffraction pattern (Cu_2O, a=4.261Å)

Experimental data			Crystallographic data	
Ring No.	Radius (mm)	Spacing (Å)	Spacing (Å)	Lattice plane
1	9.5	2.5	2.46	111
2	11.2	2.1	2.13	200
3	13.5	1.7	1.74	211
4	15.6	1.5	1.51	220
5	17.0	1.4	1.42	300
6	18.7	1.2	1.23	222





(e)

(f)

Figure 12: TEM micrographs. (a) Silver flakes in Adhesive A. (b) Silver flake with the copper pad for Adhesive B. (c) Copper pad oxidation layer for Adhesive A after 1000 hours humidity exposure. (d) EDS spectrum of the oxide layer. (e) SAD pattern of the oxide layer. (f) Silver flake separated from the copper pad by the oxide layer.

IV SUMMARY

Electrical and mechanical test results give the degradation of the adhesive joint properties after humidity exposure. Adhesive B showed the smallest variation and good stencil printing properties. Adhesive A had the lowest shear force and highest joint resistance initially; but resistance increases several times the initial value after 1000 hours at 85°/85%RH. TEM investigations of these joints reveal Cu_2O oxide layer formation on the copper PCB metallization and lead(Pb) oxide formed on the pre-tinned pads, which increased the resistance of the adhesive joint. Adhesive C had the worst property changes under humidity. Adhesive joint failure has occurred with high resistance after the humidity exposure. The shear force also dropped quickly with the humidity exposure time. Part of the reason may be the difficulty of the printing properties of this material, or that the stencil printing parameters selected were not the optimum parameters for this material. The process parameters are important to ensure a reliable adhesive joint. Not only resistivity of the ECAs, but also the processing properties and cure kinetics will all contribute to a good and reliable material.

SEM studies show there are different flake size ranges and distributions in these materials. Adhesive A has the smallest flakes and lots of dark spots in the epoxy matrix. TEM investigations show the flakes actually touch at the sharp edges and that some flakes also touch the substrate at certain spots. Oxide layer thickness on the PCB increased with the humidity exposure times.

V ACKNOWLEDGMENTS

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