Mechanisms Underlying the Unstable Contact Resistance of Conductive Adhesives

Daoqiang Lu, *Member, IEEE,* Quinn K. Tong, and C. P. Wong, *Fellow, IEEE*

Abstract—One critical obstacle of current conductive adhesives is their unstable contact resistance with nonnoble metal finished components during high temperature and humidity aging. It is commonly accepted that metal oxide formation at the interface between the conductive adhesive and the nonnoble metal surface is responsible for the contact resistance shift. Two different mechanisms, simple oxidation and galvanic corrosion, both can cause metal oxide formation, but no prior work has been conducted to confirm which mechanism is the dominant one. Therefore, this study is aimed at identifying the main mechanism for the metal oxide formation and the unstable contact resistance phenomenon of current conductive adhesives. A contact resistance test device, which consists of metal wire segments and conductive adhesive dots, is specially designed for this study. Adhesives and metal wires are carefully selected and experiments are systematically designed. Based on the results of this systematic study, galvanic corrosion has been identified as the underlying mechanism for the metal oxide formation and for the observed unstable contact resistance phenomenon of conductive adhesives.

Index Terms— Conductive adhesives, contact resistance shift mechanisms, galvanic corrosion, oxide formation, simple oxidation.

I. INTRODUCTION

TIN lead (Sn/Pb) solders have been widely used as interconnecting materials in electronic assemblies for surface mount applications [1]–[4]. Recently, with the clear awareness of the negative effects of lead on human health and environments, several legislative measures have been proposed to ban, tax, or limit the use of lead in solders. This threat has stimulated great industry efforts to identify lead-free alternatives.

Electrically conductive adhesives (ECA's) are an environmentally friendly alternative to lead-bearing solders. ECA's are superior to their counterpart, eutectic Sn/Pb solders, in many respects, including reduced environmental impact, improved processing characteristics, and increased resistance of thermal fatigue [5]–[8]. However, compared to the mature soldering technology, conductive adhesive technology still has limitations and concerns that greatly hinder its wide application. One critical limitation of current commercial ECA's is that contact resistance between the ECA's and nonnoble metal surfaces increases significantly during high

D. Lu and C. P. Wong are with the School of Materials Science and Engineering and the Packaging Research Center, Georgia Institute of Technology, Atlanta, GA 30332-0245 USA.

Q. K. Tong is with the Corporate Research Department, National Starch and Chemical Company, Bridgewater, NJ 08807 USA.

temperature and high humidity aging, particularly 85 °C/85% relative humidity (RH) aging. It is commonly accepted that metal oxide formation at the interface between the ECA and the nonnoble metal surface is responsible for the contact resistance shift [8], [9]–[12]. Oxides such as Cu_2O and Pb oxide were found at the interfaces between ECA's and Cu and Sn/Pb finished components, respectively, after 85 °C/85%RH aging [13]. Two mechanisms, simple oxidation and galvanic corrosion, both of which can cause the formation of metal oxide, were suggested as the possible mechanisms behind the unstable contact resistance phenomenon [5], [8], [11], [14], [15]. Since oxidation and galvanic corrosion are two different processes, different approaches should be employed to prevent them. Therefore, in order to stabilize contact resistance by preventing metal oxide formation, it is essential to identify the dominant mechanism for the metal oxide formation and for the contact resistance shift. However, no prior work has been conducted to identify the main mechanism underlying the contact resistance shift phenomenon, and no prior study has been conclusive. In this study, a series of experiments were carefully designed to differentiate these two mechanisms and elucidate the dominant one responsible for metal oxide formation and contact resistance shift.

II. EXPERIMENTAL

A. Materials

A bisphenol-F type epoxy resin used in this study was supplied by Shell Chemical Company. Hardeners for the epoxy resin were purchased from Aldrich Chemical Company. All the chemicals were used as received. Silver (Ag) flakes were obtained from Degussa Corporation. Nickel (Ni) flakes were obtained from Novamet Company. Metal wires, including Ni, Sn, Cu, Ag, gold (Au), and platinum (Pt) wires, all of which have about 0.25 mm diameter and 99.99% purity, were purchased from Aldrich Chemical Company. Eutectic Sn/Pb wire (0.25 mm diameter) was obtained from Hisco Company. The commercial ECA used in this study is a Ag flake-filled epoxy adhesive, Ablebond 8175A.

B. Study of Contact Resistance Shifts

Contact resistance was measured using an in-house test device that is shown in Fig. 1. This device consists of metal wire segments (about 1 cm long) that are separated by approximately 1 mm gaps. The metal wires were used here to simulate the metallization of printed circuit board (PCB) and surface finish of surface mount components. Conductive

Fig. 1.   In-house contact resistance test device.

| Metal wires	Contact resistance change after aging
Pt	stable
Au	stable
Ag	stable
Sn	unstable
Sn/Pb	unstable
Ni	unstable

Fig. 2.   Contact resistance shifts of a Ni flake-filled ECA with different metal wires (Ni, Sn, Cu, and Ag) during 85 °C/85%RH aging.

adhesive pastes were applied to the gaps to connect the metal wire segments. After cure, the total contact resistance of a specimen was then measured with a Keithley 2000 multimeter. Three specimens were tested for each sample. The specimens were subjected to one of the following test conditions: 85 °C/85%RH (in a temperature and humidity chamber from Lunaire Environmental, model CEO932W-4), and 85 °C/dry (in a Blue M oven). The contact resistance of each specimen was measured periodically during aging. The results of these specimens were reported.

C. Study of Bulk Resistance Shifts

Bulk resistance of conductive adhesives was obtained from specimens with specific dimensions. The dimensions of the specimen were controlled using the following procedures:

1) apply two strips of an adhesive tape on a pre-cleaned glass slide with a 2.54 mm distance between the two strips;
2) spread a conductive adhesive paste on the glass slide within the gap with a doctor blade;
3) remove the adhesive tape and cure the specimen;
4) measure the resistance of the specimen using the Keithley multimeter with a four-point probe.

Similarly, three specimens were tested for each sample. The specimens were aged under one of the following conditions: 85 °C/85%RH and 85 °C/dry. The bulk resistance of each specimen was recorded periodically and the results of these specimens were reported.

III. RESULTS AND DISCUSSION

A. Contact Resistance Shift Phenomenon

A commercial conductive adhesive that is a Ag flake-filled epoxy adhesive was used in this study. Contact resistance between this ECA with different metal wires was studied with the contact resistance test device described in the previous section. Shifts of the contact resistance during 85 °C/85%RH aging were monitored. After 500-h aging, if the increase of the contact resistance is larger than 20%, then the contact resistance is defined as "unstable." But if the increase is less than 20% after 500-h aging, the contact resistance is defined as "stable" [10]. According to this criteria, variations of contact resistance of the ECA with different metal wires are given in Table I. As can be seen from the table, noble metals Ag, Pt, and Au showed stable contact resistance with
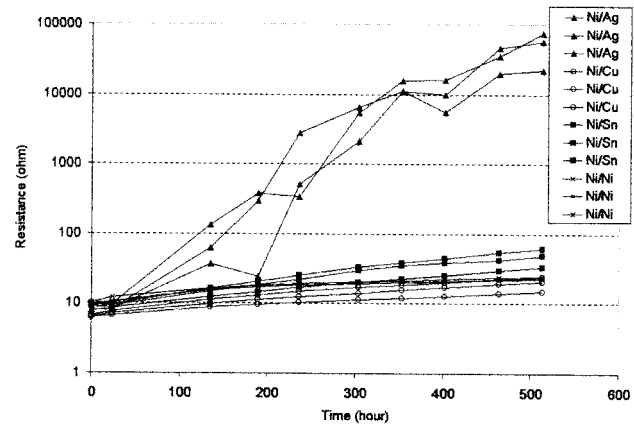
this ECA, but nonnoble metals Ni, Sn, and Sn/Pb showed large resistance shifts. The results are consistent with those from other researchers, which indicates that our in-house test vehicle is valid and reliable [9], [11], [13].

B. Investigation of Mechanisms Underlying the Unstable Contact Resistance Phenomenon

1) Base Resin Formulation: In order to focus on the mechanism study, ECA formulations used in this study were kept as simple as possible. A base resin formulation was composed of just a bisphenol-F type epoxy, a hardener, and a catalyst. Other components such as an adhesion promoter, conductivity enhancer, and diluent were omitted from these formulations.

2) Contact Resistance of a Ni-filled ECA with Different Metals: An ECA was formulated using the above base resin formulation. The filler was a Ni flake, and filler loading was 70 weight percent. Different metal wires, Ni, Sn, Cu, and Ag, were selected and employed in the test vehicles. The contact resistance changes of these samples during 85 °C/85%RH aging are shown in Fig. 2. It was found that all the contact resistance increased with aging time, but the contact resistance with Ag wire increased much more significantly than that with Ni, Sn, and Cu. This result suggested that the contact resistance change is not due to simple oxidation of the nonnoble metals. For if it were, the contact resistance with Ni, Sn, and Cu wires should have increased more dramatically than that with Ag wire.

3) Contact Resistance Shifts during Different Aging Conditions: The ECA used in this study was also a Ni flake-filled epoxy adhesive. By using two different metal wires, Ni and
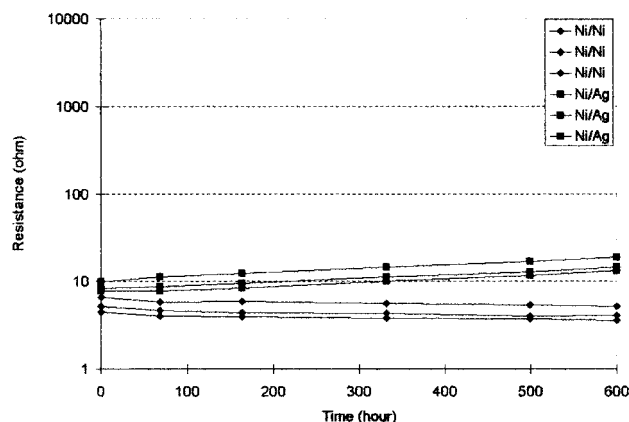
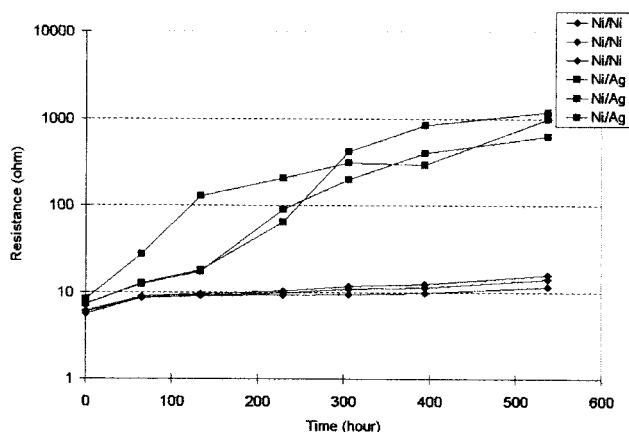Fig. 3. Contact resistance shifts of a Ni flake-filled ECA with Ni and Ag wires during 85 °C/dry aging.

Fig. 5. Bulk resistance shifts of three ECA's with different fillers during 85 °C/dry aging.

Fig. 4. Contact resistance shifts of a Ni flake-filled ECA with Ni and Ag wires during 85 °C/85%RH aging.

ble metals is not dominant at 85 °C. Under the aging condition of 85 °C/85%RH, both simple oxidation and galvanic corrosion can happen. If simple oxidation dominated, then the Ni/Ni combination should have had a larger resistance shift than the Ni/Ag combination. The fact that the Ni/Ag combination showed much significant resistance shifts indicates that simple oxidation of the nonnoble metals is not a dominant mechanism for contact resistance shifts during 85 °C/85%RH aging.

4) Bulk Resistance Shifts under Different Aging Conditions: Three conductive adhesives (ECA-1, ECA-2, and ECA-3) were formulated with the base resin formulation mentioned in the previous section. These three ECA's are exactly the same except for the fact that their fillers were different. ECA-1 was filled with Ni flake. ECA-2 was filled Ag flake. ECA-3 was filled with a mixture of the Ni flake and the Ag flake (weight ratio of the Ni flake and the Ag flake was 95:5). Again, six specimens were tested for each sample. Three of them were exposed to 85 °C/dry and the other three were aged under the condition of 85 °C/85%RH. Bulk resistance of each specimen was measured periodically during the aging. Results of these three specimens for each sample were reported. Shifts of bulk resistance of these samples under 85 °C/dry and 85 °C/85%RH conditions are shown in Figs. 5 and 6, respectively. It can be seen that:

1) during 85 °C/dry aging, all of the samples showed relatively stable resistance;
2) under the aging condition of 85 °C/85%RH, ECA-3, which was filled with the mixture of Ni and Ag flakes, had much larger resistance increase than ECA-1 and ECA-2.

Based on the results from Section III-B3 and Section III-B4, it can be summarized that:

1) under the aging condition of 85 °C/dry, regardless the metals involved, all samples showed relatively stable resistance, even though the metals involved included an easily oxidizable metal such as Ni;
2) under the aging condition of 85 °C/85%RH, if only one type of metal was involved, the samples showed stable resistance, even for commonly known oxidizable metals such as Ni.

Ag, simple oxidation and galvanic corrosion mechanisms could be differentiated. Therefore, two different samples were tested here: Ni flake-filled ECA with Ni wire (referred as Ni/Ni combination in later sections) and Ni flake-filled ECA with Ag wire (referred as Ni/Ag combination). Six specimens were fabricated for each sample. The specimens were aged under two different conditions: 85 °C/dry (dry) and 85 °C/85%RH (wet). Three of the specimens were exposed to 85 °C/dry and the other three were exposed to 85 °C/85%RH. The contact resistance of each specimen was collected periodically during the aging. The results of these specimens were reported for each sample. The resistance changes of the samples during 85 °C/dry and 85 °C/85%RH aging are shown in Figs. 3 and 4, respectively.

As can be seen from Fig. 3, upon exposure to 85 °C/dry, both Ni/Ni and Ni/Ag combinations showed no significant contact resistance change. From Fig. 4, it was found that during 85 °C/85%RH aging contact resistance of Ni/Ni combination was relatively stable, but contact resistance of the Ni/Ag combination increased dramatically. Under the 85 °C/dry aging condition, galvanic corrosion is negligible; therefore, simple oxidation of the metals is the only possible mechanism. Insignificant contact resistance shifts for both samples after 85 °C/dry aging indicated that simple oxidation of the nonno-
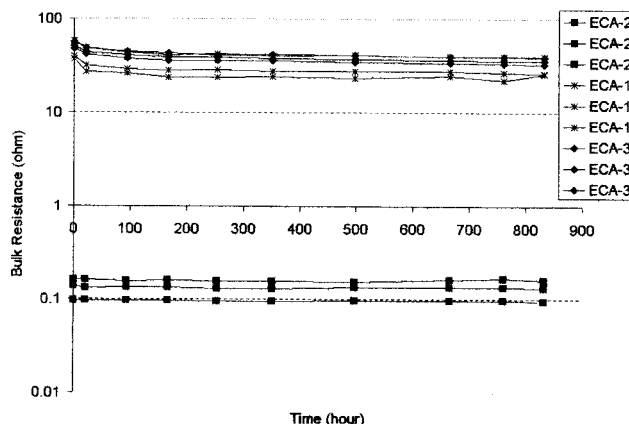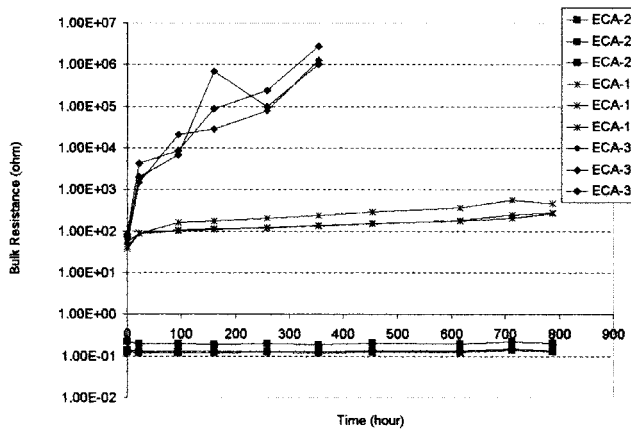
Fig. 6. Bulk resistance shifts of three ECA's with different fillers during 85 °C/85%RH aging.
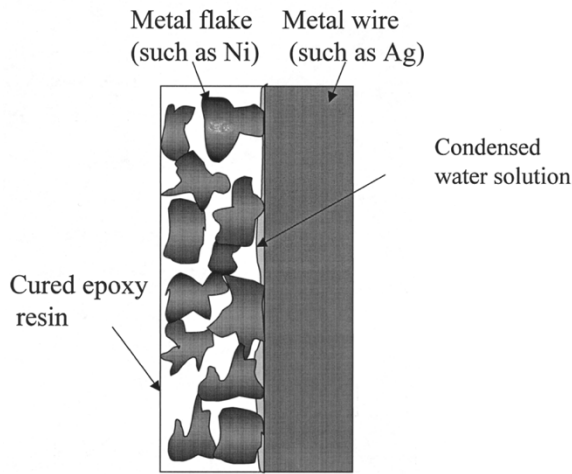

Fig. 7. Schematic explanation of galvanic corrosion at the interface between metal flake (such as Ni) and metal wire (such as Ag) during 85 °C/85%RH aging.

However, the resistance increased dramatically if two different metals were involved. These results strongly indicate that galvanic corrosion rather than simple oxidation was the dominant mechanism for the unstable contact resistance phenomenon during high temperature and high humidity aging.

The experimental results of Section III-B3 and Section III-B4 are consistent with galvanic corrosion mechanism [16]. A schematic explanation is given in Fig. 7. When a Ni flake contacts with a Ag wire or a Ag flake, particularly under wet condition, moisture and oxygen diffuse into the interface and then the moisture condenses into water. The accumulated water could dissolve some impurities from the resin and form an electrolyte solution. All the requirements for a galvanic corrosion are met. Therefore, micro galvanic cells are formed at the interface. The less noble metal Ni acts as an anode, loses electrons, and becomes Ni^{+2}. The reaction can be represented as $Ni - 2e^- = Ni^{+2}$. The noble metal Ag acts as a cathode and the reaction on this electrode is $2H_2O + 4e^- + O_2 = 4\,OH^-$. Ni^{+2} combines with the OH^- and form a nickel hydroxide that is usually unstable and becomes nickel oxide. As a result, a layer of Ni oxide is formed at the interface. Because this

TABLE II
NORMAL POTENTIALS OF SOME ELECTRODE REACTIONS [17]

Electrode Reaction	Normal potential (volt) (Normal hydrogen scale)
$Au - 3e = Au^{3+}$	1.50
$Pt - 2e = Pt^{2+}$	1.20
$Ag - 1e = Ag^+$	0.80
$2H_2O + O_2 + 4e = 4OH^-$	0.40
$Cu - 1e = Cu^1$	0.34
$Cu - 2e = Cu^{2+}$	0.52
$Pb - 2e = Pb^{2+}$	-0.13
$Sn - 2e = Sn^{2+}$	-0.14
$Ni - 2e = Ni^{2+}$	-0.25

oxide layer has much higher resistance than the nickel, the contact resistance increased significantly after aging.

The contact resistance shift results of Ablebond 8175 on different metals (in Section I) can be explained with similar methodology. Galvanic corrosion can happen only if the potential of a metal which acts as an anode is lower than the potential of the cathodic reaction, $2H_2O + 4e^- + O_2 = 4OH^-$, which is 0.4 V under standard conditions [16]. According to Table II, normal potentials of Ag, Au, and Pt are higher than the potential of the cathodic reaction. No galvanic corrosion occurs and thus no metal oxide is formed at the interface. As a result, the contact resistance between the Ag filled ECA with these noble metals remained stable during aging. In contrast, the other metals, Ni, Sn, and Sn/Pb all have lower potentials than the cathodic reaction. Galvanic corrosion happens and the nonnoble metals are corroded to form insulating metal oxides at the interface. Therefore, the contact resistance between the Ag flake-filled ECA with these metals increased dramatically upon aging.

All of the above results indicated that shift of the contact resistance between an ECA and nonnoble metals is mainly due to the metal oxide formation which is caused by galvanic corrosion of the nonnoble metal at the interface.

IV. CONCLUSION

Results from this systematic study strongly suggested that galvanic corrosion rather than simple oxidation of a nonnoble metal was the dominant mechanism for the metal oxide formation and for the unstable contact resistance between conductive adhesives and the nonnoble metal finished surface mount components.

REFERENCES

[1] H. H. Manko, *Solders and Soldering, Materials, Design, Production, and Analysis for Reliable Bonding*, 2nd ed., McGraw-Hill, 1979, pp. 1–123.
[2] R. J. K. Wassink, *Soldering in Electronics*. Ayr, U.K.: Electrochemical Publ., 1984.
[3] F. N. Sinnadurai, *Handbook of Microelectronics Packaging and Interconnection Technologies*. Ayr, U.K.: Electrochemical Publ., 1985.
[4] L. P. Lambert, *Soldering for Electronic Assemblies*. New York: Marcel Dekker, 1987.
[5] G. Nguyen, J. Williams, F. Gibson, and T. Winster, "Electrical reliability of conductive adhesives for surface mount applications," in *Proc. Int. Electron. Packag. Conf.*, 1993, pp. 479–486.
[6] G. Nguyen, J. Williams, and F. Gibson, "Conductive adhesives: Reliable and economical alternatives to solder paste for electrical applications," in *Proc. ISHM*, 1992, pp. 510–517.
[7] J. C. Jagt, "Reliability of electrically conductive adhesive joint for surface mount applications: A summary of the state of the art," *IEEE*

Trans. Comp., Packag., Manufact. Technol. A, vol. 21, pp. 215–225, June 1998.

[8] J. C. Jagt, P. J. M. Beric, and G. F. C. M. Lijten, "Electrically conductive adhesives: A prospective alternative for SMD soldering?," *IEEE Trans. Comp., Packag., Manufact. Technol. B*, vol. 18, pp. 292–298, May 1995.

[9] M. A. Gaynes, R. H. Lewis, R. F. Saraf, and J. M. Roldan, "Evaluation of contact resistance for isotropic electrically conductive adhesives," *IEEE Trans. Comp., Packag., Manufact. Technol. B*, vol. 18, pp. 299–304, May 1995.

[10] M. Zwolinski, J. Hickman, H. Rubon, and Y. Zaks, "Electrically conductive adhesives for surface mount solder replacement," in *Proc. 2nd Int. Conf. Adhesive Joining Coating Technol. Electron. Manufact.*, Stockholm, Sweden, June 3–5, 1996, pp. 333–340.

[11] H. Botter, "Factors that influence the electrical contact resistance of isotropic conductive adhesive joints during climate Chamer testing," in *Proc. 2nd Int. Conf. Adhesive Joining Coating Technol. Electron. Manufact.*, Stockholm, Sweden, June 3–5, 1996, pp. 30–37.

[12] C. P. Wong, D. Lu, S. Vona, and Q. K. Tong, "A fundamental study of electrically conductive adhesives," in *Proc. 1997 1st IEEE Int. Symp. Polymeric Electron. Packag.*, Norrkoping, Sweden, 1997, pp. 80–85.

[13] J. Liu, K. Gustafsson, Z. Lai, and C. Li, "Surface characteristics, reliability and failure mechanisms of tin, copper and gold metallizations," in *Proc. 2nd Int. Conf. Adhesive Joining Coating Technol. Electron. Manufact.*, Stockholm, Sweden, June 3–5, 1996, pp. 141–153.

[14] K. Gilleo, "Evaluating polymer solders for lead free assembly, part I," *Circuits Assembly*, pp. 50–51, 1994.

[15] ———, "Evaluating polymer solders for lead free assembly, part II," *Circuits Assembly*, pp. 51–53, 1994.

[16] U. R. Evans, *The Corrosion and Oxidation of Metals: Scientific Principles and Practical Applications*. London, U.K.: Edward Arnold, 1960.

[17] G. Milazzo, *Electrochemistry: Theoretical Principles and Practical Applications*. New York: Elsevier, 1963, p. 157.

Daoqiang Lu (M'99), for a photograph and biography, see this issue, p. 207.

Quinn K. Tong, for a photograph and biography, see this issue, p. 207.

C. P. Wong (SM'87–F'92), for a photograph and biography, see this issue, p. 201.