

Degradation Mechanism of Conductive Adhesive/Sn Interface under High Humidity

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Abstract

Ag-epoxy conductive adhesives have been proposed as one of the ecological alternatives to lead-bearing solders in electronic industries. Although Ag-epoxy conductive adhesives possess many advantages as the alternative, they have still several drawbacks to be clarified. One of the drawbacks is the poor compatibility with Sn-plated components in a humid atmosphere. The humid environment sometimes brings the interfacial degradation of Ag-epoxy conductive adhesive on Sn surface. This degradation has been reported to be attributed to one sort of corrosion, i.e., galvanic corrosion; however, neither definitive explanation nor proof has been achieved yet. The present study focuses on the degradation mechanism of the interface between Ag-epoxy conductive adhesive and Sn plating under a humid condition. The degradation characteristics of the interface were examined in detail by use of transmission electron microscope (TEM). As the results of TEM analyses, two different types of oxide layers, SnO and SnO₂ phases, were found to be formed at the interface. These Sn-oxides were mainly formed at the interface where the surface of Sn plating was close to Ag fillers in the conductive adhesive and they became thicker and larger with humid exposure time. Many voids were also found at the interface. Thus, the formation of Sn-oxides and voids at the interface is the root cause of the interfacial degradation. The formation of these defects can be explained by galvanic corrosion in a humid atmosphere.

Key words: Ag-epoxy conductive adhesive, ICA, Degradation mechanism, Interfacial microstructure, Sn-oxide, TEM, and Galvanic corrosion

Introduction

Lead-bearing solders, such as Sn-Pb alloys, have been dominantly used as interconnection materials in the electronic industries. However, their environmental issues caused by toxicity of lead require the development and research of ecological solder materials as the substitutes of them [1-5]. Electrically conductive adhesives (ECA) and lead-free solders have been attracting attention as the representative substitutes. Among the substitutes, conductive adhesives with the Ag-epoxy system have been recognized as one of the alternatives to lead-bearing solders. The conductive adhesives offer many advantages over conventional soldering, such as flexible and simple processing, fine pitch printing, and low temperature processing [4-6]. In addition, they can be adopted as an interconnection material even in high temperature assemblies, which is attributed to their excellent heat-resistance [7-11]. However, they still have several drawbacks related to joint reliability in unfavorable environments, such as unstable electrical resistance and poor impact strength [4, 5].

Considering the joint reliability, one of the important issues is the interfacial degradation of the conductive adhesive joints in a high temperature and

humidity condition [12, 13]. Above all, Ag-epoxy conductive adhesives possess poor compatibility with Sn-plated components in a humid environment. This characteristic reveals the degradation of conductive adhesive/Sn interface under the humid condition, resulting in higher electrical resistance and lower joint strength.

As one of the degradation factors in a humid environment, it has been reported that the insulating oxides formed at the conductive adhesive joints mainly causes the increase of electrical resistance [4, 5, 14-17]. In addition, as the possible mechanism, it has been proposed that the oxide formation could be caused by either simple oxidation or corrosion of non-noble metal surfaces, i.e., galvanic corrosion [6, 15-17]. However, recent studies on the degradation mechanism almost indicate that the oxide formation is mainly attributed to galvanic corrosion rather than simple oxidation [4, 5, 14]. Although there are many arguments on the interfacial degradation mechanism, the definitive explanations and proofs are still insufficient. Particularly, regarding the detrimental microstructure of the conductive adhesive joints, no detailed information at the nano scale has been achieved yet. In case of oxide formation at the conductive adhesive joints, it is uncertain about the

oxide type, morphology, and its relation to the degradation properties. In addition, it is necessary to investigate the existence of other interfacial defects, besides the oxides, through microstructural studies. Since the interfacial defects detrimental to the joint reliability are formed with a small size at the conductive adhesive joints, therefore, microstructural examination can be obtained in detail through various nano-scale studies such as transmission electron microscopy (TEM).

The objective of the present study is the clarification on the degradation mechanism of the conductive adhesive/Sn interface under a high humidity environment. To investigate degradation factors, the interfacial microstructure was examined in detail by TEM. The degradation mechanism was considered through the microstructural variation of the conductive adhesive/Sn interface with exposure time of the humid test.

Experimental Procedure

The interfacial degradation mechanism in the present study was investigated by modeling samples. Fig. 1 shows a schematic diagram of the modeling sample for the conductive adhesive/Sn interface and its corresponding initial microstructure. The preparation process of the modeling samples is as follows. First, the conductive adhesive with Ag-epoxy system was printed on the Sn-plated Cu substrate. This modeling sample was cured at 150°C for 30 minutes. Next, the high temperature and humidity test was carried out at the 85°C/85% relative humidity (RH) condition up to 1000 hours.

The microstructure of the interface between

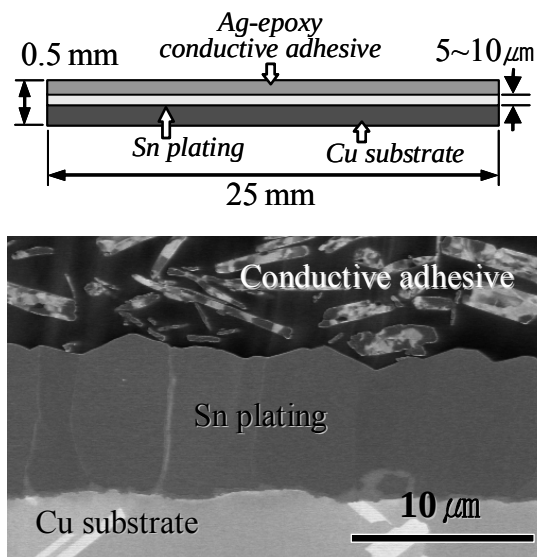


Fig. 1. Schematic diagram of the modeling sample for the conductive adhesive/Sn interface and its corresponding initial SIM image.

conductive adhesive and Sn plating with exposure time of the humid test was examined in detail by scanning ion microscopy (SIM, FB-2100) and TEM (JEM-2100). Elemental analyses of the interface were performed by electron probe micro analyzer (EPMA, JXR-8800R). The cross-sectional specimens, used for various analyses in this study, were prepared by cross-section ion polisher (CP, SM-09010), which enabled to obtain clear and accurate microstructural information of the interface. TEM specimens were prepared by focused ion beam system (FIB, FB-2100). Phase identification was performed in detail by various TEM works, such as electron diffraction pattern, conventional-TEM, and high resolution electron microscopy (HREM).

Results and Discussion

Interfacial microstructure between conductive adhesive and Sn plating

Fig. 2 shows cross-sectional SIM images on the microstructural variation of the conductive adhesive/Sn interface with exposure time of the humid test. It is clearly observed that a secondary layer is formed at the interface under the humid test for 100 hours or more, as indicated by arrows in Fig. 2(a)-(d). This secondary layer was never found at the interface of initial modeling sample, as shown in Fig. 1. Therefore, the formation of secondary layer seems to be caused by the humid atmosphere. Considering the formation of secondary layers, it must be noted that they are observed mainly at the interface close to Ag fillers in the conductive adhesive, as shown in Fig. 2(a) and (b). In addition, it gradually becomes thicker and larger with humid exposure time, as shown in Fig. 2(a)-(d). The long hours of humid exposure accelerates more the growth of secondary layer at the interface. Another point to notice is that many voids are observed in the secondary layer, as shown in Fig. 2(c) and (d). The voids are sure to be introduced simultaneously with the formation of secondary layer during the humid test. Therefore, it can be said that the humid exposure in this study causes the formation of secondary layers with many voids at the conductive adhesive/Sn interface. The formation of secondary layers with many voids is likely to be related to the degradation of conductive adhesive/Sn interface in a humid atmosphere. To investigate the interfacial degradation factors, the secondary layer was analyzed in detail as follows.

At first, elemental mapping was performed by EPMA to examine the secondary layer formed at the conductive adhesive/Sn interface. Fig. 3(a) shows a SEM image of the interface where a secondary layer is formed after the humid test for 500 hours. EPMA mapping images of Fig. 3(b)-(d) show elemental distribution of Ag, Sn, and O, respectively, and they all correspond to Fig. 3(a). As indicated by

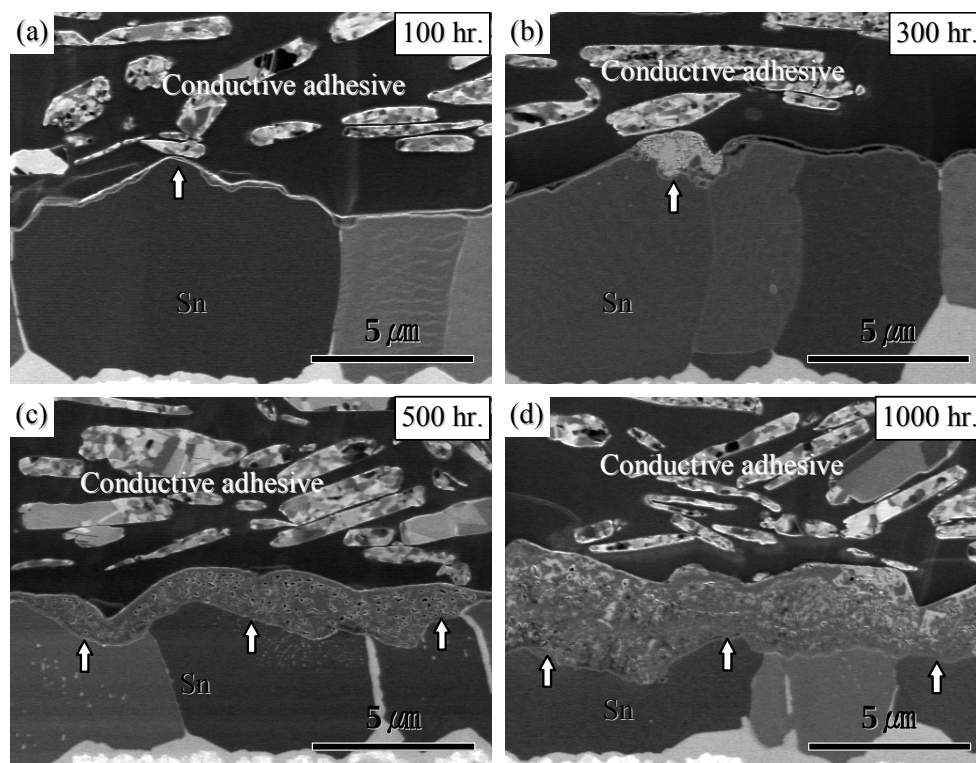


Fig. 2. Cross-sectional SIM images of the conductive adhesive/Sn interface with humid exposure time: (a) 100, (b) 300, (c) 500, and (d) 1000 hours.

arrows in Fig. 3(c) and (d), both Sn and O elements were concurrently detected from the region of secondary layer in Fig. 3(a). This result indirectly indicates that the secondary layers are Sn-oxide phases.

The secondary layers at the conductive adhesive/Sn interface, i.e., Sn-oxides, were identified in detail by TEM works. Fig. 4(a) shows a bright-field (BF) TEM micrograph of the modeling sample exposed to the humid test for 100 hours. There is a

Sn-oxide layer with about 100nm in thickness formed at the conductive adhesive/Sn interface. Fig. 4(b) is the selected area diffraction pattern (SADP) obtained from the Sn-oxide layer in Fig. 4(a). The noticeable point is that many diffraction spots with ring types are observed in the SADP of Fig. 4(b). It indicates that the Sn-oxide layer in Fig. 4(a) consists of nanosized polycrystalline phases. In addition, the ring types of diffraction spots were identified as those of stannic oxide (SnO_2) with the rutile structure, as shown in Fig. 4(b).

Fig. 5(a) is a HREM image taken from the Sn-oxide layer in Fig. 4(a). Polycrystalline lattice fringes of the Sn-oxide are clearly observed in Fig. 5(a), which confirms polycrystalline structure of the Sn-oxide, like the SADP result of Fig. 4(b). Fig. 5(b) and (c) show the fast Fourier transform (FFT) pattern and the noise-filtering image, respectively, taken from the Sn-oxide region by computer-aided image processing using digital micrograph software. The FFT pattern of Fig. 5(b) is correspondent with $[\bar{1}11]$ incidence of SnO_2 phase, which also confirms the SADP result of Fig. 4(b). Lattice arrangements of SnO_2 phase are more clearly observed in the noise-filtering image of Fig. 5(c). From the results of Fig. 5 and 6, it can be said that nanosized polycrystalline SnO_2 phases are formed at the conductive adhesive/Sn interface during the humid test for 100 hours.

Fig. 6(a) shows a BF-TEM micrograph of

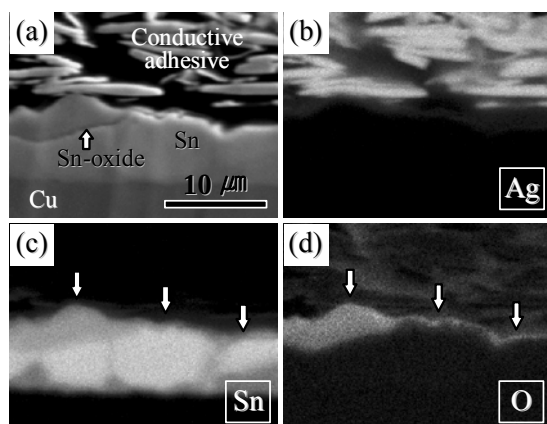


Fig. 3. (a) SEM image of the interface where a Sn-oxide layer is formed after the humid test for 500 hours and corresponding EPMA mapping image of (b) Ag, (c) Sn, and (d) O elements, respectively.

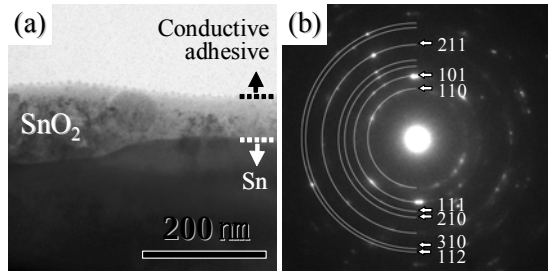


Fig. 4. (a) BF-TEM micrograph and (b) SADP taken from the region where a SnO_2 layer is formed after the humid test for 100 hours.

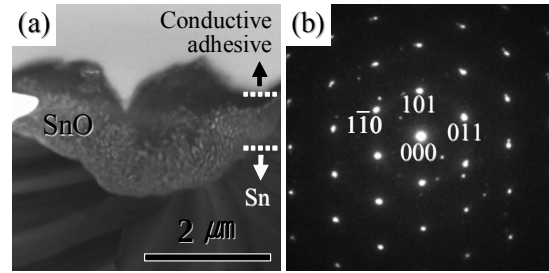


Fig. 6. (a) BF-TEM micrograph and (b) SADP taken from the region where a SnO layer is formed after the humid test for 1000 hours.

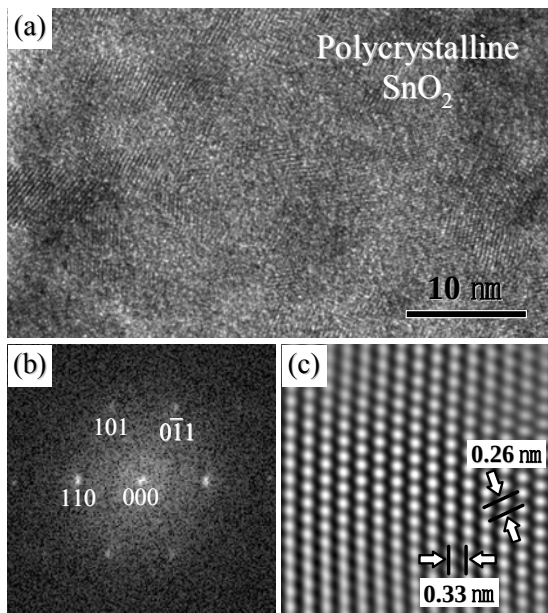


Fig. 5. (a) HREM micrograph, (b) FFT pattern, and (c) noise-filtering image taken from the SnO_2 region of Fig. 4(a).

the modeling sample exposed to the humid test for 1000 hours. A Sn-oxide layer with the thickness over 1 μm is observed to be formed at the conductive adhesive/Sn interface. The growth of Sn-oxide with the increase of humid exposure time was observed also through TEM works, like the results of Fig. 2. The Sn-oxide layer was identified as stannous oxide (SnO) with the litharge structure, from the analysis on the corresponding SADP of Fig. 6(b) which was taken with the incident beam parallel to $[11\bar{1}]$ direction of SnO phase. In the TEM results of Fig. 4-6, SnO and SnO_2 phases were found to be formed at the conductive adhesive/Sn interface under the humid test, though exposure time was different. However, there was no phase selection of Sn-oxides according to humid exposure time in this study. This is because both SnO and SnO_2 phases are observed to be formed inhomogeneously at the conductive adhesive/Sn interface under the humid test for 100 hours or more, with no relation of exposure time.

Effect of Sn oxide formation on joining properties

In the present study, the formation of Sn-oxides, SnO and SnO_2 , is probably related to the interfacial degradation between conductive adhesive and Sn plating. In case of SnO_2 , for many years, it has been widely used as a transparent conducting oxide film due to its high transmittance and conductivity in electronic devices [18, 19]. Electrical resistivity of pure SnO_2 was in the range of 10^{-1} - 10^{-3} Ωcm , while that of pure Sn was 1.26×10^{-5} Ωcm [19-22]. Pure SnO_2 possesses relatively high conductivity, but its resistivity value is still higher than that of pure Sn. Furthermore, SnO is an insulating phase [23, 24]. Therefore, it is clear that the SnO and SnO_2 layers formed at the conductive adhesive/Sn interface cause the increase of interfacial electrical resistance. In other words, the Sn-oxide layers formed at the interface can interfere with electrical contact between Ag filler and Sn plating, because they all possess higher electrical resistivity than that of Sn plating.

Considering the interfacial degradation caused by a humid environment, besides the increase of electrical resistance, the joining strength is also significantly weakened [12, 25]. In the present study, the mechanical degradation of conductive adhesive/Sn interface was investigated through the separated interfacial microstructure of modeling samples after the humid test. The conductive adhesive/Sn interface after the humid test was easily separated by external stress, while the same failure of initial modeling samples hardly occurred.

Fig. 7(a) and (b) show the cross-sectional SIM images of the conductive adhesive/Sn interface where the failure occur. The separated interfacial microstructure in Fig. 7(a) and (b) was taken from the modeling sample subjected to external stress after the humid test for 100 and 1000 hours, respectively. The inserted microstructure in Fig. 7(a) was taken from other region of the same modeling sample. The interfacial failure in this study was classified into the following two types. First, as indicated by white arrows in Fig. 7(a), the separation occurred at the Sn-oxide/Sn interface. It seems that the separation is

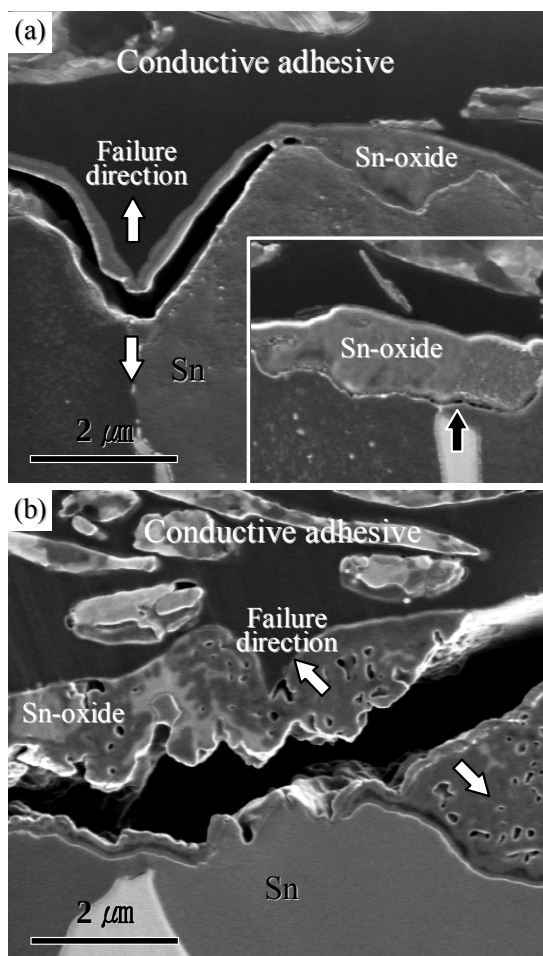


Fig. 7. Cross-sectional SIM images of the failed interface by external stress after the humid test for (a) 100 and (b) 1000 hours, respectively.

caused by interfacial voids formed at the Sn-oxide/Sn interface after the humid test, as indicated by black arrows in the inserted figure. Second, the separation occurred at the inside of Sn-oxide layers, as shown in Fig. 7(b). This separation seems to be caused by many inside voids of Sn-oxides layers. From these results, the factor in both interfacial failures was summarized to be ascribed to the voids, though the separation through the voids depended on their formation areas. As stated above, the voids are sure to be introduced concurrently with Sn-oxide formation during the humid test. Therefore, it can be said that the humid environment leads to the formation of both Sn-oxides and voids at the same time, resulting in the interfacial degradation.

Mechanisms of Sn oxide and void formation in a high humidity environment

As the results in the present study, two different types of Sn-oxide layers, SnO and SnO₂ phases, were formed inhomogeneously at the conductive adhesive/Sn interface. In addition, many voids were formed at either the Sn-oxide/Sn interface

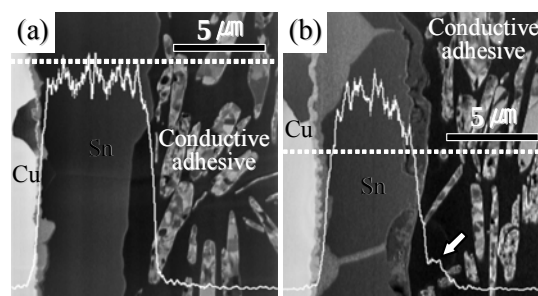


Fig. 8. EPMA line analysis and corresponding SIM image of (a) initial and (b) aged modeling sample for 500 hours in the humid test, respectively.

or the inside of Sn-oxide. The formation of Sn-oxides and voids is sure to be the root cause of interfacial degradation in a humid atmosphere. The formation of these defects can be explained by galvanic corrosion. Because the Sn plating as an anode possesses a lower potential than that of the cathodic reaction ($2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2 = 4\text{OH}^-$) on the Ag fillers, galvanic corrosion easily occurs at the conductive adhesive/Sn interface in a humid atmosphere [14]. Through this electrochemical reaction, the surface of Sn plating near Ag fillers is corroded and then Sn-oxide layers, such as SnO or SnO₂ phases, are finally formed at the interface.

During the galvanic reaction, many voids also can be formed at either the inside of Sn-oxide or the Sn-oxide/Sn interface. Fig. 8 shows the cross-sectional SIM image and the line analysis result on the Sn elements by EPMA. The results in Fig. 8(a) and (b) were taken from an initial and an aged modeling sample for 500 hours in the humid test, respectively. The strength curves on Sn content correspond to the dotted line in Fig. 8(a) and (b). The point to notice is that there is an increase of Sn content from the Sn surface toward the conductive adhesive only after the humid test, as indicated by arrows in Fig. 8(b). The increase of Sn content can be explained by galvanic corrosion: Sn ions attributed to the anodic reaction of Sn surface can migrate toward the Ag filler which acts as a cathode during the humid test. From this point of view, many voids can be formed at the region where the depletion of Sn occurs. This is because Sn ions participate in forming Sn-oxides and migrate into the conductive adhesive in galvanic cell.

From these results, it is concluded that galvanic corrosion mainly induces the formation of defects between conductive adhesive and Sn plating, such as Sn-oxides and voids in this study. In addition, those defects are to be the main causes of the interfacial degradation, resulting in the increase of electrical resistance and the decrease of adhesive strength.

Conclusion

In the present study, the degradation mechanism of the conductive adhesive/Sn interface in 85°C/85%RH condition was examined in detail by various microstructural analyses. As the results of microstructural analyses, two different types of Sn-oxide layers, SnO and SnO₂ phases, were formed inhomogeneously on the surface of Sn plating. These Sn-oxides were found to be formed at the interface between conductive adhesive and Sn where the surface of Sn plating was close to Ag fillers and they became thicker and larger with humid exposure time. Many voids were also found to be formed at either the Sn-oxide/Sn interface or the inside of Sn-oxide. The formation of these defects, i.e., Sn-oxides and voids, are the root cause of interfacial degradation, because they enable to increase the electrical resistance and decrease the joining strength. In addition, their formations are caused by galvanic corrosion between Ag filler and Sn plating. This can be explained by the results: the Sn-oxide formation close to Ag fillers and the increase of Sn content from Sn surface toward conductive adhesive under the humid test. Therefore, it is concluded that galvanic corrosion at the conductive adhesive/Sn interface mainly causes the interfacial degradation in a high temperature and humidity environment.

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