Effects of Metal Surface Conditions on Interfacial Characteristics between Metal and Epoxy Resin

Michiya Matsushima*, Yuta Kato, Yusuke Takechi, Shinji Fukumoto and Kozo Fujimoto

Graduate School of Engineering, Osaka University, Suita 565–0871, Japan

Conductive adhesives are alternatives to solder joints and are of interest because of their high bonding strength, low thermal resistance, and low electrical resistance. In this paper, we focused on the dependence of the metal surface conditions on the surface processing and clarified the effect of different metal surface finishes on the bonding strength and thermal characteristics. The effects of air exposure and silane coupling agent processing on the adhesive strength between the metal and resin were investigated. The thermal resistance after repeated bending was measured to determine the effect of different metal surface finishes on the thermal resistance.

1. Introduction

The demand for power modules, which are key components of energy conservation, is increasing because of the social demand for global environment protection. Power modules are used in various products ranging from consumer electronics to industrial equipment. To attain higher performance, the modules become smaller and the current density increases. Therefore, a heat-resistant joining method is required for power modules.

The restriction of hazardous substances (RoHS) prohibited the use of certain hazardous substances, including lead, in electronic equipment. However, high-melting-temperature solders containing 85% lead were exempted from this restriction because there are no acceptable alternatives. However, the exemptions are set to expire in 2017, and finding an alternative joint material is an urgent need.

One possible alternative to high-lead solder is conductive adhesive. Conductive adhesives are complex with metal fillers for electrical/thermal conductivity and a thermoset resin for structural strength. Epoxy resin is the typical resin used for conductive adhesives. Silver, copper, aluminum, nickel, and gold are used for the metal fillers.

Adequate structural strength and electrical and thermal conductivity are required for joints of electric devices such as power modules. The interfacial properties between the resin and metal are considered critical for these properties and depend on the surface conditions of the metals. Therefore, the relationships between the surface conditions and interfacial strength, thermal resistance, and electrical conductivity should be clarified.

The joining mechanisms are known to be mechanical anchoring, chemical bonding, and bonding with van der Waals forces. Mechanical bonding depends on the bonding area. The bonding strength in a certain area must be improved. The van der Waals force is smaller than that of a chemical bond.

In this paper, the effect of chemical processing of the metal surface on the interfacial properties between the metal and resin is investigated. The surface conditions of the metal parts were measured using the contact angle of a water drop, and the shear strengths of the joint of the resin and metal parts were also measured.

In a conductive adhesive joint, the increase of the thermal resistance caused by the delamination of the resin and metals, such as electric terminals or metal fillers, is presumed to be suppressed by higher interfacial strength. Conductive adhesive joints using combinations of different surface processes on the copper plate and fillers were repeatedly bent, and the thermal resistances of the samples were measured.

2. Specimens and Experimental Method

2.1 Materials

A 99.96% copper sheet with dimensions of 20 mm × 20 mm × 1.5 mm and a 99.96% copper rod with dimensions of φ5 mm × 8 mm were used for the bonded materials. The shear strengths of the interfaces of the resin and other metals such as aluminum and silver were measured for comparison. The resin consisted of a one-component thermosetting bis-phenol F-type epoxy resin with aromatic amine as the curing agent (Fujikura Kasei Co., Ltd.). This resin and φ1 μm 99.9+% copper fillers were compounded to fabricate the thermal resistance specimens.

2.2 Surface processing of metals

The surface condition of the metal is considered to affect the bondability of the resin and metals. As a pre-processing step for the metal surface process, the metals were polished using #120 to #4000 emery paper. The samples were pickled with 5% hydrochloric acid and wash with ethanol for 180 s. The polishing process was skipped for the metal fillers.

The effects of air exposure and the silane coupling process were investigated. For the air exposure, the samples were exposed to air for 0, 1, 24, and 200 h. For the silane coupling process in this experiment, 3-aminopropyltriethoxysilane was used. The silane coupling agent is an organosilicon compound with an organic functional group and alkoxy group in one molecule. The silane coupling process causes the following reaction. The alkoxy group is hydrolyzed to hydroxyl and chemically bonded to the hydroxyl on the metal surface. Therefore, the organic functional group is coated on the metal surface, and the hydroxyls of the organic function group and...
epoxy resin form covalent bonding. The silane coupling process consisted of soaking of the metal parts in 2 mass% silane coupling solution for 60 s after pre-processing followed by drying the parts in a 110°C oven for 180 s.

2.3 Measurement of contact angle

The chemical bond of the metal and resin interface is considered to be affected by the functional group on the metal surface. The silane coupling agent reduces the metal surface hydrophilicity9). Therefore, the measurement of contact angle of water is used as an index of the surface condition change caused by the silane coupling process. The contact angle is denoted as $\theta$ in Fig. 1(a) and is represented by eq. (1):

$$\gamma_S = \gamma_L \cdot \cos \theta + \gamma_{SL}$$  \hspace{1cm} (1)

$\theta$: contact angle
$\gamma_S$: surface tension of the solid
$\gamma_L$: surface tension of the liquid
$\gamma_{SL}$: interfacial tension of the solid-liquid interface.

The contact angle was measured from an optical microscope image using the sessile drop method10). If the size of the water drop is sufficiently small, the effect of gravity is negligible, and the water drop is considered to be a part of a sphere. The $\theta$ shown in the Fig. 1(b) was determined using eq. (2). The water drop was 2 $\mu$l, and the measurements were performed 4 times for each sample.

$$\theta = 2 \tan^{-1} \frac{h}{r}$$  \hspace{1cm} (2)

$\theta$: contact angle
$h$: height of the water drop
$r$: radius of the water drop

2.4 Shear test

Figure 2 presents a schematic diagram of the shear test specimen. The copper rod was bonded with the epoxy resin on copper, silver, or aluminum plates. The bonding height was controlled by mixing 5 vol% of $\phi150$ Ni fillers as a spacer in the epoxy resin. The pre-processed copper rod with the epoxy resin was placed on the surface-processed metal plate before heating the specimen to 150°C for 90 minutes.

A shear speed of 0.05 mm/s and shear height of 0.15 mm were used in the testing. The shear direction was vertical to the polished direction. The fracture surfaces were examined using an optical microscope, and the fracture areas were measured. The shear strength was calculated based on the fracture area and breaking load.

2.5 Measurement of thermal resistance

Figure 3 shows the specimen used to measure the thermal resistance. To form the conductive adhesive, 50 vol% of $\phi1 \mu$m copper fillers and 5 vol% of $\phi150 \mu$m Ni fillers were mixed with epoxy resin. The conductive adhesives were used to bond two copper plates with dimensions of 20 mm $\times$ 20 mm $\times$ 1.5 mm. The copper plates and fillers were pre-processed and silane coupling processed using the following combinations:

(A) Both the copper plate and fillers were only pre-processed.
(B) The copper plate was silane coupling processed, and the fillers were only pre-processed.
(C) Both the copper plate and fillers were silane coupling processed.

The conductive adhesives kneaded in a vacuum was placed on the surface-processed copper plate and degassed in vacuum for 30 min. The coated surfaces of the two copper plates faced each other and were bonded with heating at 150°C for 90 min.

The thermal resistance was measured using the steady-state method11) with the equipment shown in Fig. 4. Figure 4(a) presents a schematic illustration of the equipment, and Fig. 4(b) shows an example of the measured temperature gradient. One side of the specimen was heated and the other side was cooled to generate a steady-state temperature gradient. The thermal resistance was calculated from the heat flux. The origin of the axis was set at the top of the rod, and assuming linear steady-state heat conduction, the temperature at each position was determined using eq. (3).
The temperature at the rod edge \( T_A(0) \) and the temperature gradient \( \frac{dT}{dx} \) were approximated using the least squares method based on the temperatures \( T_{A0}, T_{A1}, T_{A2}, \) and \( T_{A3} \) at the positions \( x_{A0}, x_{A1}, x_{A2}, \) and \( x_{A3} \), respectively.

\[
T_A(0) = \sum_{i=0}^{3} x_{Ai} T_{Ai} - \sum_{i=0}^{3} x_{Ai} \sum_{i=0}^{3} x_{Ai} T_{Ai}
\]

\[
\frac{dT}{dx} = \frac{\sum_{i=0}^{3} x_{Ai} T_{Ai} - \sum_{i=0}^{3} x_{Ai} \sum_{i=0}^{3} x_{Ai} T_{Ai}}{4 \sum_{i=0}^{3} x_{Ai}^2 - (\sum_{i=0}^{3} x_{Ai})^2}
\]

Based on eq. (3), the estimated temperature at the sample side edge of the upper rod \( T_A(x_{As}) \) was calculated using eq. (6):

\[
T_A(x_{As}) = \frac{4 \sum_{i=0}^{3} x_{Ai} T_{Ai} - \sum_{i=0}^{3} x_{Ai} \sum_{i=0}^{3} x_{Ai} T_{Ai}}{4 \sum_{i=0}^{3} x_{Ai}^2 - (\sum_{i=0}^{3} x_{Ai})^2} x_{As}
\]

\[
+ \frac{\sum_{i=0}^{3} x_{Ai}^2 \sum_{i=0}^{3} x_{Ai} T_{Ai} - \sum_{i=0}^{3} x_{Ai} \sum_{i=0}^{3} x_{Ai} T_{Ai}}{4 \sum_{i=0}^{3} x_{Ai}^2 - (\sum_{i=0}^{3} x_{Ai})^2} x_{As}^3
\]

If \( k_A \) is inserted as the thermal conductivity of the upper rod, the heat flux in the upper rod \( q_A \) is

\[
q_A = -k_A \left( \frac{dT}{dx} \right)_A
\]

The temperature of the edge of the lower rod \( T_D(x_{Ds}) \) and heat flux \( q_D \) were also calculated in the same manner. The thermal conductivity \( k_s \) was determined using eqs. (3)–(7) and the sample thickness \( d_{ts} \):

\[
k_s = \frac{1}{2} \left( \frac{1}{k_A} + \frac{1}{k_D} \right) d_{ts}
\]

The thermal resistance value was calculated by averaging the measured values at 871 to 900 s from the start of heating.

2.6 Cyclic bending test

The effect of the surface processing on the increase of thermal resistance with fatigue loading was investigated. A bending load was repeatedly applied to the thermal resistance measurement specimen shown in Fig. 3, and the thermal resistance change is measured. For each bending condition, 500, 1000, 2000, and 4000 bending load cycles were applied. Figure 5 presents a schematic diagram of the cyclic bending test. The sample was supported by stainless steel rods placed at 3 mm from the sample edges and repeatedly loaded down and unloaded with a plate-shaped tool. To prevent local plastic deformation, 0.5-mm-thick stainless steel sheets were inserted at both the upper and lower side of the specimen. The displacement was 0.2 mm, and the speed was 0.2 mm/s. The delamination was examined using scanning acoustic tomography (SAT).

3. Experimental Results

3.1 Effect of air exposure

The surface condition change of the metal is considered to affect the bondability of the resin and metals. Air exposure is a simple method to change the surface condition. The copper, silver, and aluminum plates were exposed to air in an evacuated desiccator at room temperature for 0, 1, 24, and 200 h, and the shear strength was measured.

Figure 6 plots the shear strength as a function of air exposure time. The shear strength of the copper sample increased upon increasing the air exposure time from 0 to 24 h. The shear strength of the 200-h air exposure sample was almost the same as that of the 24-h air exposure sample. The air ex-
posure generated an oxidation layer on the copper surface\(^{12}\). The oxidation is considered to have improved the bonding strength. However, the aluminum sample only showed improvement of the shear strength at 1 h. Other factors such as contamination of the metal surface may have been responsible for the decrease of the shear strength. The shear strength of the silver showed no significant change with air exposure. The oxidation layer of silver rapidly became stable and thin\(^{13}\). The silver oxide layer does not appear to be as effective in improving the bondability as the other metals.

### 3.2 Effect of silane coupling process

The copper, silver, and aluminum plates and rods were exposed to the silane coupling process and bonded. The water drop contact angles on the processed surfaces were measured, and the bonded samples were shear tested. Figure 7 and Fig. 8 show the contact angle of water droplet and shear strength of the silane coupling processed samples, respectively. The results for the bonded samples directly after pre-processing are also presented for comparison.

The water drop contact angles increased for the specimens that underwent the silane coupling process in every case. The process is thought to change the hydroxyl group on the metal surface to a different group. Otherwise, the shear strengths of the copper and aluminum samples improved with the silane coupling process. The strength of the silane-coupling-processed copper sample reach 150% of that of the unprocessed sample. The shear strength of the aluminum sample improved with the silane coupling process; however, the strength was less than that of the sample exposed to air for 1 h. No significant effects of the silane coupling process were observed in either the contact angle or shear strength for the silver sample.

### 3.3 Cyclic bending test

#### 3.3.1 Thermal resistance after cyclic bending test

The effect of metal surface processing on the thermal characteristics under fatigue loading was investigated by measuring the thermal resistance after cyclic bending testing. Copper filler, which had been clarified as effective for the silane coupling process on the shear strength, was used as the conductive adhesive.

As mentioned in section 2.5, copper materials with three different combinations of surface processing were used for the conductive adhesives. The bonded samples were loaded for 500, 1000, 2000, and 4000 cycles, and the thermal resistances were measured. The displacement was 0.2 mm, and the speed was 0.2 mm/s.

Figure 9 shows the relationship between the thermal resistance per unit area of the conductive adhesive layer and the bending load cycles. No significant differences were observed in the thermal resistance for the samples with different surface processing. The thermal resistance of sample A without the silane coupling process increased 1.4 times compared with the initial value after 1000 cycle and 2.5 times after 2000–4000 cycles. The thermal resistance of sample B with the silane coupling process only on the copper plate increased 1.7 times compared with the initial value after 2000 cycles. No significant increase of the thermal resistance was observed for sample C with the silane coupling process on both
the fillers and plates. The silane coupling process on the copper surface is thought to have prevented the delamination of the resin and metal interfaces and suppressed the thermal resistance increase.

### 3.3.2 Scanning acoustic tomography results

After the cyclic bending tests, the samples were examined using SAT to monitor the delamination of the conductive adhesive. The observation was performed after 1000 and 4000 cycles for samples A, B, and C. Figure 10 shows the observation direction. Figure 11 presents an SAT image of the initial sample directly after bonding. The gray part represents the bonded area, and the white part represents the void or delaminated area. Figure 12 presents SAT images of samples A, B, and C after the cyclic bending tests. Delamination is observed from the left edge to 5–6 mm after 1000 cycles for specimen A. The delamination propagated to the center of the sample after 4000 cycles. A small amount of delamination appears at 6–7 mm from the edge after 1000 cycles for sample B. The delamination propagated to the left edge after 4000 cycles. No delamination was observed after 1000 cycles for sample A, and a small amount of delamination appeared at 5 mm from the left edge after 4000 cycles.

The silane coupling process delayed the delamination, and processing of both the fillers and plate was more effective. The suppression of the delamination by the silane coupling process is effective in preventing an increase in the thermal resistance.

### 4. Conclusion

This paper focused on the resin–metal interface of conductive adhesives, which is thought to affect their properties. The effect of metal surface processing on the interfacial strength and thermal resistance after cyclic bending tests was investi-
gated, and the following conclusions were drawn:

(1) The oxidation on the copper surface by the air exposure improved the shear strength of the bonded resin. The shear strength was 42.3 MPa after 200-h air exposure compared with 33.9 MPa without air exposure. The shear strength was largest after 1-h air exposure for the aluminum plate. No improvement of the shear strength with air exposure was observed for the silver plate.

(2) The silane coupling process increased the water drop contact angles on the surfaces of copper, silver, and aluminum. The shear strength of copper and aluminum were improved by the silane coupling process. The shear strength of the copper was improved to 52.8 MPa from 33.9 MPa.

(3) The initial thermal resistance was not affected by the silane coupling processing; however, the silane coupling processing on the plate prevented the thermal resistance from increasing after exposure to cyclic bending load. The silane coupling processing on both the filler and plate was more effective in suppressing the increase of the thermal resistance after cyclic bending loading.

(4) The SAT observations revealed the suppression of delamination after cyclic bending loading with the silane coupling processing on the copper plate and fillers.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 15K18222.

REFERENCES