Characteristics of electrically conductive adhesives filled with silver-coated copper

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Abract

Conductive adhesives have been investigated for use in microelectronics packaging as a lead-free solder substitute due to their advantages, such as low bonding temperature. However, high resistivity and poor mechanical behavior may be the limiting factors for the development of conductive adhesives. The metal fillers and the polymer resins provide electrical and mechanical interconnections between surface mount device components and a substrate. As metal fillers used in conductive adhesives, silver is the most commonly used due to its high conductivity and the stability. However the cost of conductive adhesives with silver fillers is much higher than usual lead-free solders and silver has poor electro-migration performance. So, copper can be a promising candidate for conductive filler metal due to its low resistivity and low cost, but oxidation causes this metal to lose its conductivity.

In this study, electrically conductive adhesives (ECAs) using surface modified copper fillers were developed. Especially, in order to overcome the problem associated with the oxidation of copper, copper particles were coated with silver, and the silver-coated copper was tested as a filler metal. Especially the effect of silver coating on the electrical resistance just after curing and after aging was investigated. As a result, it was found that the electrical resistance of ECA with silver-coated copper filler was clearly lower and more stable than that of ECA with pure copper filler after curing process. And, during high temperature storage test, the degradation rate of electrical resistance for ECA with silver coated copper filler was quite slower than that for ECA with pure copper filler.

Key Words : electrical conductive adhesives, copper fillers, silver coating, electrical resistance

1. Introduction

Electircally conductive adhesives (ECAs) have been investigated for use in microelectronics packaging and interconnections as a lead-free solder substitute due to such advantage as low curing temperature. They are usually composed of conductive metal fillers and polymer resin. The metal fillers and the polymer resins provide electrical and mechanical interconnections between surface mounted device components and a substrate. For polymer resins, thermosetting resins such as epoxy, polyimide and polyurethane are commonly used. As the metals fillers used in conductive adhesives, gold (Au), silver (Ag), copper (Cu) and nickel (Ni) in various sizes and shapes are used. Among them, silver is the most commonly used due to its high conductivity and stability. However, the cost of conductive adhesives with silver fillers is much higher than the conventional lead-free solders. Therefore, current ECAs still have some limitations in terms of cost as well as electrical and mechanical properties as replacements for solder.

Many research efforts have been focused mainly on the improvement of electrical conductivity and the reliability performance of ICA joints [1-5]. Additionally, the replacement of expensive Ag fillers by other metal fillers or new materials has been examined for wider applications of ICAs [6-8]. Copper is a promising candidate for conductive filler metal due to its low resistivity, low cost and good electro-migration performance. However, a problem for copper fillers is oxidation of the copper surface and deterioration of the electrical properties of ICAs. There are basically two approaches for the surface treatment of copper fillers to prevent the oxidation of the metal surface. One is an inorganic material coating and the other is an organic coating. However, the thermal stability of the coatings is a concern because most lose their effectiveness when exposed to the curing conditions and various environmental conditions.

In this study, ECAs using surface-modified copper fillers were developed. In particular, to overcome the problem of high electrical resistance associated with the oxidation of copper, copper particles were coated with silver, and the silver-coated copper was tested as a filler metal. The effect of silver coating on the electrical resistance of ICAs just after curing and after reliability tests was investigated.

2. Materials and Experiment

To investigate the effect of silver coating for Cu particle on the electrical properties of conductive adhesive, three different types of conductive adhesives were prepared. Their components are shown in Table 1. Conductive adhesive A was mainly comprised of pure Cu fillers with spinous shape and phenol resin. Conductive adhesive B was mainly comprised of silver coated copper fillers with spinous shape and phenol resin. Conductive adhesive C was mainly composed of silver coated Cu fillers with spherical shape and phenol resin. Figure 1 shows SEM images of cooper fillers used in this study. In all adhesives, total content of metal fillers was fixed at 80.6 mass%.

Table 1 Basic composition of conductive adhesiv es used in this study.

Conductive adhesive	A	B	C
Metal filler	Pure Cu	Silver-coated Cu	Siver-coated Cu
Shape of metal filler	Spinous	Spinous	Spherical
Metal content (mass%)	80.6%		
Polymer	Phenol resin		

Figure 2 shows the schematic diagram of a test piece. The conductive adhesive (24×5×0.1mm) was spread on the FR-4 substrate using the mask. The conductive adhesive samples were cured at 448 K for 1 h in a convection coven. Then, specimens cured under this condition were subjected to high-temperature exposure at 398 K up to 2000 h in air. For another specimens cured, temperature/humidity test at 358 K/85 % RH was conducted up to 1500 h. After those, the four-point probe method was applied to evaluate the electrical resistance of conductive adhesives and the thermal stability of the electrical resistance.

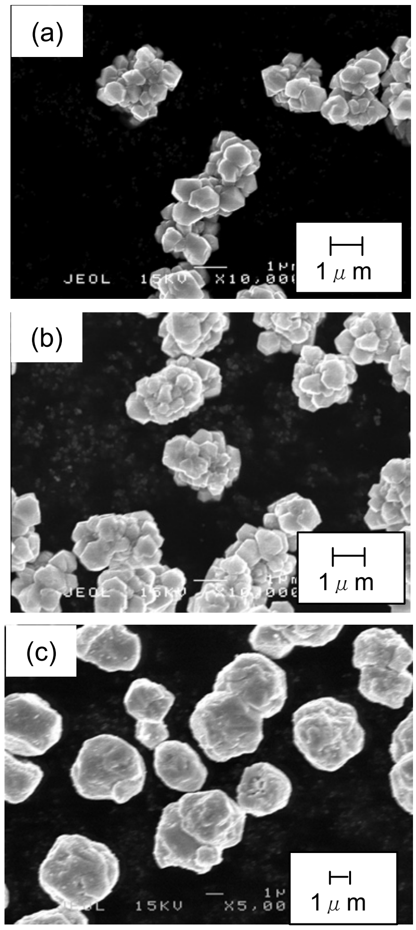

Fig. 1 SEM images of Cu fillers used in this study. (a) Spinous Cu particles (b) Spinous Ag-coated Cu particles (c) Spherical Ag-coated Cu particles

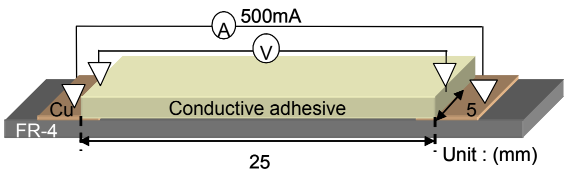

Fig. 2 Schematic illustration of test sample.

3. Results and Discussion

Figure 3 shows the appearance of the specimens before and after curing. As stated above the curing temperature was 448 K and the curing time was 1 h. In the case of conductive adhesive A, the color of the specimen was light brown before curing and, after curing, it turned dark brown. The color change seems to be caused by the oxidation of copper particle filled with the conductive adhesive. On the other hand, in the case of conductive adhesive B and C, the color of the specimen practically remained unchanged during the curing process.

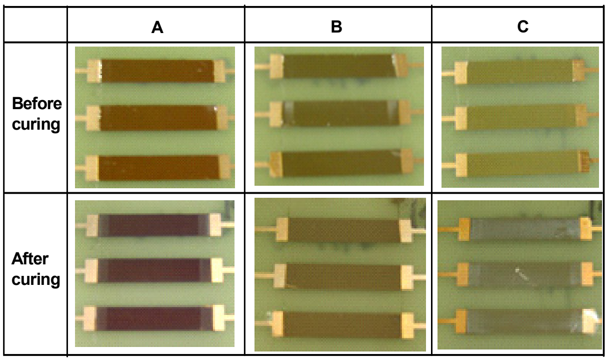

Fig. 3 Appearance of specimens before and after curing.

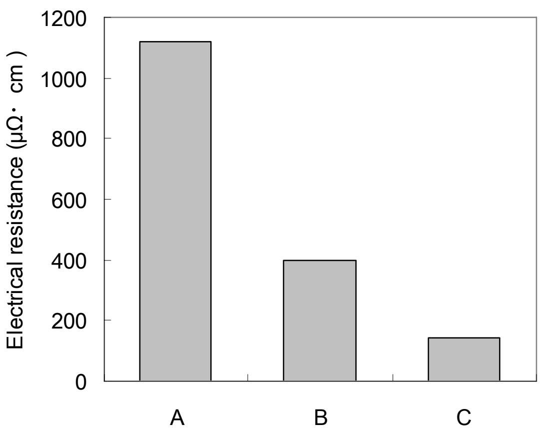

Fig. 4 Effect of silver coating for copper particle on electrical resistance of conductive adhesives just after curing.

Figure 4 shows the effect of silver coating for copper particle on the electrical resistance of the conductive adhesive just after curing. The curing temperature was 448 K and the curing time was 1 h. Regardless of particle shape, the electrical resistances of conductive adhesive B and C used silver-coated copper were much lower thanthat of conductive adhesive A used pure copper. In the case of silver-coated copper particle, the electrical resistance of conductive adhesive C filled with silver-coated copper with spherical shape was lower than half that of conductive adhesive B filled with silver-coated copper with spinous shape. The electrical resistance of cured conductive adhesives are strongly affected the surface condition and the shape of filler metal.

Figure 5 shows the change rate of the electrical resistance of the conductive adhesives as a function of the high-temperature exposure time. The exposure temperature was 398 K. In this figure, as the test time increases, the electrical resistance of

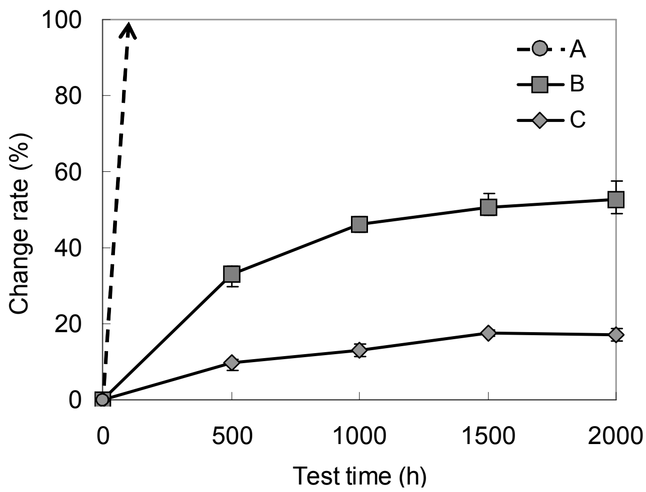

Fig. 5 Change rate of electrical resistance of conductive adhesives as a function of the high-temperature exposure time at 398 K.

conductive adhesive A shows a significant increase only after 100 h and the change rate of the electrical resistances of conductive adhesive B and C was much slower. Especially, after 1000 h, the electrical resistances of conductive adhesive B and C were comparatively stable. This is due to the oxide formation on the surface of the pure cupper particle. The change rate of electrical resistance of conductive adhesive C was slower than that of electrical resistance of conductive adhesive B. In other words, the conductive adhesive C filled with spherical silver-coated copper showed much more stable electrical resistance than the conductive adhesive B filled with spinous silver-coated copper.

About the change rate of the electrical resistance of conductive adhesives during 358 K and 85 % RH aging test, as well as high-temperature exposure, the electrical resistance of conductive adhesive A remarkably increase d with increasing aging time and, only after 100 h, and the resistance could not be measured. On the other hand, the change rate of the electrical resistance of conductive adhesive B and C was much slower. The conductive adhesive B and C filled with silver-coated copper improved the stability under the 358 K and 85 % RH aging when compared to the conductive adhesive A with pure copper. This may be due to the anti-oxidation capability of silver-coated copper at elevated temperature and humidity condition.

4. Conclusion

In order to overcome the problem associated with the oxidation of copper filler, the silver was coated with copper particle, and the silver-coated copper was evaluated as a filler metal. Especially the effect of silver coating on the electrical resistance of conductive adhesive just after curing and after reliability tests was investigated. The main results obtained in this study are summarized as follow.

(1) Just after curing process at 448 K for 1 h, the electrical resistance of conductive adhesive used silver-coated copper as a filler metal was much lower than that of conductive adhesive used pure copper.

(2) During the high temperature exposure test and the 358 K and 85 % RH aging test, the change rate of the electrical resistance of conductive adhesive used silver-coated copper filler was much lower and the conductive adhesive showed improved stability when compared to the conductive adhesive used pure cooper.

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