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Electrical Characteristics of a New Class of Conductive Adhesive

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Conventional conductive adhesives are composed of micro-sized filler metal and polymer matrix. Currently, the conductivity of conventional conductive adhesives is generated by small contact points formed among the particles during the curing process and by the tunneling effect. Therefore, conventional conductive adhesives generally exhibit higher electrical resistance than metal solder materials. In this study, a new class of conductive adhesive, composed of nano-particles and micro-particles in epoxy, was developed to improve electrical conductivity. This study used four conventional conductive adhesives (CCA1 to 4) and three hybrid conductive adhesives (HCA1 to 3). Scanning electron microscopy (SEM) observation was used to investigate the configuration of nano-particles and micro-particles. The electrical resistance of HCA1 to 3 was investigated and compared to CCA1 to 4 using a four-point probe method. When 2 mass% of nano-particle content was added to the micro-particle (HCA1), the electrical resistance decreased compared to CCA3. At 4 mass% of nano-particle content (HCA2), the electrical resistance value was similar to CCA3. However, at 8 mass% of nano-particle content (HCA3), the electrical resistance continued to increase, and exceeded that of CCA3.

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Keywords: *hybrid conductive adhesive, electrical path, isolated cluster, nano-particle*

1. Introduction

Conductive adhesives are being actively investigated for microelectronic applications since environmental requirements and user-friendly alternatives to lead-containing solder materials has increased in the electronics industry.[1–3] Not only the environmental issues, conductive adhesives have several advantages compared to conventional solder, such as simpler processing than wave soldering, less thermo-mechanical residual stress, lower processing temperature and high-resolution capability for fine-pitch interconnection.[4–11] The electrical properties of conventional conductive adhesives are generally explained by the percolation theory: when a sufficient amount of conducting filler metals is loaded into an insulating matrix, the composite transforms from an insulator into a conductor. That is, as the filler concentration in the polymer matrix is varied, the conductivity exhibits an insulator-to-conductor transition that is interpreted as a percolation threshold.[12–14] However, the conducting filler metals (micro size) such as, silver, gold, and copper[15] in conventional conductive adhesives are not dissolved in the polymer matrix at curing temperature (423 to 473 K). Accordingly, the current in conventional conductive adhesives passes by the formed small contact electrical path and by tunneling effect, as illustrated in Fig. 1(a). In contrast, soldering is based on solder reflow. Connection is achieved by dissolving the joints on the electrodes. Therefore, one of the drawbacks of conventional conductive adhesives is their higher electrical resistance than metal solder materials.[16–18] The conducting filler metals in conventional conductive adhesives do not form a metal bonding electrical path, as metal solder materials do, but form a small contact electrical path by shrinkage and solvent evaporation during curing process.[19] Furthermore, the electrical resistance of conventional conductive adhesives depends on the filler metal content. That is, as filler metal content increases, the electrical resistance decreases. However, when filler metal content reaches a certain value, the electrical resistance becomes stable and there is no large electrical property improvement even above critical content. Therefore it is difficult to improve the electrical property of conventional conductive adhesives with micro-sized particles only. To reduce electrical resistance of conductive adhesives, a new class of conductive adhesives was developed as illustrated in Fig. 1(b). This new class of conductive adhesives is composed of nano-particles and micro-particles in epoxy to increase the contact area. The new class of conductive adhesives is termed "hybrid conductive adhesive" (HCA) in this paper. Nano-particles exhibit different electrical, magnetic, optical and mechanical properties than bulk materials.[20] In particular, nano-particles below 100 nm diameter are difficult to control during processing because they tend to aggregate to each other to decrease system energy. Moreover, the ratio of nano/micro particles plays an important role in the resistance of conductive adhesives. When the nano-particles are added into the micro-particles properly, it is expected that nano-particles would help to establish the electrical path because they can enter the interstices of micro particles. However, in the cases of low micro-particle content and high content of nano-particle, nano-particles tend to cluster or separate the contacts among the micro-particles, which might decrease electrical paths and contact points resulting in higher bonding system resistance.[21–23] There-

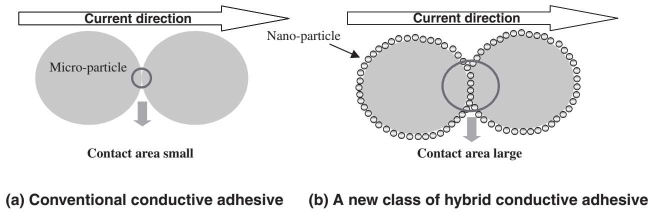

Fig. 1 Conduction model of conventional conductive adhesive and a new class of hybrid conductive adhesives.

fore, it is very important to control the ratio of nano/micro particles in HCA to improve the electrical characteristics of conductive adhesives. This study investigates the most suitable filler metal content in conventional conductive adhesives, and then changes the content of nano-particles and micro-particles at the most suitable filler metal content to decrease electrical resistance. This paper also investigates the proper ratio of nano/micro particles on electrical resistance of HCA and discusses the related conduction mechanism in HCA.

2. Experimental Procedure

To determine the proper content of conventional conductive adhesives (micro-particle only, CCA1–4) for electrical resistance, conventional CCA1 to 4 conductive adhesives were used, and three hybrid conductive adhesives HCA 1 to HCA 3 were used to compare with the electrical resistance of conventional conductive adhesive and investigate proper ratio of nano/micro for electrical resistance in this paper. CCA1 to 4 were composed of an average of 3 µm silver particles (spherical type) and epoxy. The ratio of micro silver particle content of CCA is detailed in Table 1.

HCA were composed of 3 µm silver particles (spherical type), 5 nm of silver particles and epoxy matrix (from Harima Chemical Inc., Ltd.). The ratio of nano/micro particles in HCA are detailed in Table 2. Total content of silver particles (nano-particles and micro-particles) are fixed at 92 mass%, while different composition of nano-particle, namely, 2, 4 and 8 mass% respectively, were considered here. It is difficult to disperse nano-particles uniformly. Therefore, dispersing agent was used in HCA in order to disperse nano-particles uniformly. Dispersing agent covers the surface of nano-particle. Elimination process of dispersing agent during curing is as follows. Firstly, nano-particles were dispersed uniformly due to the presence of dispersing agent before curing. When the curing started, dispersing agent attached on the surface of nano-particles in HCA reacted to epoxy, and was eliminated from the surface of nano-particles. Consequently, the surface of nano-particles tended to be unstable, so that the neighboring nano-particles aggregate and lead to the formation of nano-particle cluster (50–100 nm).

Table 1 Ratio of silver particle in conventional conductive adhesives (CCA) after curing, mass%.

Conductive adhesives	Silver particle (ϕ3 µm)	Resin	Etc.
CCA1	88		
CCA2	90	Epoxy	Curing agent, Solvent
CCA3	92		
CCA4	94		

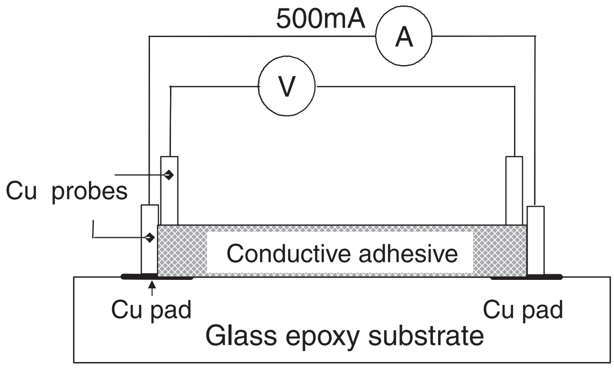

Fig. 2 Schematic diagram of a test piece for four-point probe method.

Differential-scanning calorimeter (DSC) analysis was performed with a DSC-7000M at a heating rate of 10 K/min to investigate the curing profile. The four-point probe method was used to investigate the electrical resistance of conductive adhesives as exhibited in Fig. 2. A metal mask was placed on the FR-4 substrate, and conductive adhesive ($24 \times 5 \times 0.2$ mm) was pasted onto the metal mask. Curing was performed using a convection oven at 423 and 473 K for 1 h. Micro-structures of CCA and HCA for the ratio of nano/micro particles were examined through scanning-electron microscopy (SEM).

3. Results and Discussion

To evaluate the most suitable silver content for conductivity in CCA1 to CCA4, the relationship between electrical resistance and silver content was investigated. Figure 3 depicts the variation of electrical resistance for various silver particle contents and curing temperature in CCA. As the curing temperature increased from 423 to 473 K, the electrical resistance decreased. This can be explained by DSC results of CCA1 to 4 displayed in Fig. 4. The curing reaction peak for these conductive adhesives appeared at 428–444 K. Therefore, at low curing temperature, such as 423 K, the curing reaction of conductive adhesives did not proceed sufficiently. However, at high curing temperature, such as 473 K, the curing reaction of all types of CCA was completed, resulting in a lower electrical resistance than that at 423 K. Moreover, the electrical resistance decreased with an increase of the silver content. The silver content increases from 92 to 94 mass%; however, the variation of electrical resistance is not severe as presented in Fig. 3.

Figure 5 illustrates the surface micro structures of CCA after curing. At low silver particle content (CCA1), Fig. 5(a), a larger tolerance among the silver particles was detected. Following the increase of silver particle content, this tolerance tended to be smaller, as displayed in Figs. 5(b),

Table 2 Ratio of silver nano-particle and micro-particle in hybrid conductive adhesives (HCA) after curing, in mass%.

Conductive adhesives	Nano-particle (ϕ5 nm)	Micro-particle (ϕ3 µm)	Total silver particle	Resin	Etc.
HCA1	2.0	90	92		Curing agent,
HCA2	4.0	88	92	Epoxy	Solvent,
HCA3	8.0	84	92		Dispersing agent

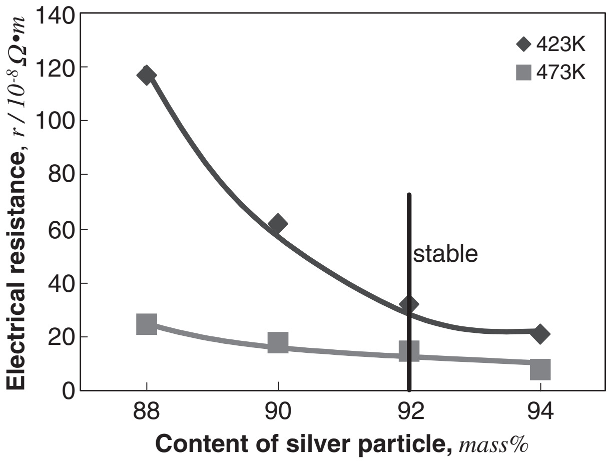

Fig. 3 Relation of electrical resistance and silver particle content, in CCA.

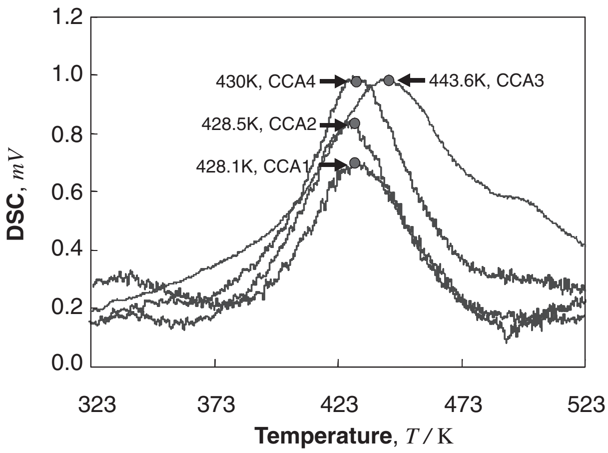

Fig. 4 DSC analysis of conventional conductive adhesives (heating rate: 10 K/min).

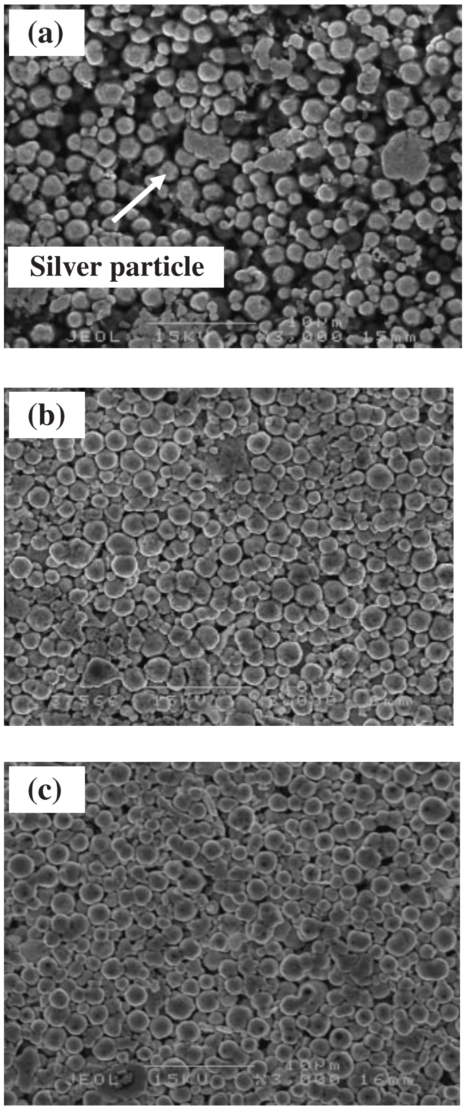

Fig. 5 Surface morphology of conventional conductive adhesive for silver particle content (a) CCA1 (88 mass%), (b) CCA3 (92 mass%), (c) CCA4 (94 mass%).

(c). At the margin of 92 to 94 mass%, distribution of silver particles in CCA is very similar. From these results (Figs. 3 and 5), it can be inferred that the possibility of forming an electrical path in conventional conductive adhesives improves with the silver content. That is, at low volume fraction of silver particles, the possibility of generating continuous contacts is relatively small because the silver particles are distributed randomly throughout the epoxy matrix. At high volume fraction of silver particles, the conductivity becomes high due to the larger continuous contacts produced among the silver particles.[2,13,19] However, at the range of high volume fraction (92 to 94 mass% in this study), it also inevitably increases the contact resistance, thus resulting in a much smaller decrease of electrical resistance.[24] Therefore, the most suitable silver content in CCA is determined to be around 92 mass% (CCA3) in this study. When the filler metal content reaches a certain value (92 mass% in this study), the variation of electrical resistance becomes stable; thus, no further decrement of electrical resistance is obtained even above this critical content (*e.g.* 94 mass% in this study). This phenomenon revealed that a limitation for decreasing electrical resistance exists for the CCA (with micro-sized particles only).

For this reason, a HCA was explored to overcome the limitation of the CCA and obtain lower electrical resistance of conductive adhesives. Total silver content of HCA is fixed at 92 mass% (most suitable content for electrical resistance in this study), and changes content of nano-particles and micro-particles. DSC analysis was performed to determine the curing temperature of HCA. Table 3 displays the DSC results of HCA1 to 3. The curing reaction peak of three conductive adhesives occurred at about 453 K. The curing reaction peak of HCA is different from that of CCA as shown in Fig. 4. Apparently, the difference of chemical composition between CCA and HCA is attributed to the presence of dispersing agent. Therefore, it could be inferred that the dispersing agent

Table 3 DSC results of three hybrid conductive adhesives.

Class of conductive adhesives	Curing reaction peak temperature, T/K
HCA1	455.8
HCA2	452.8
HCA3	453.5

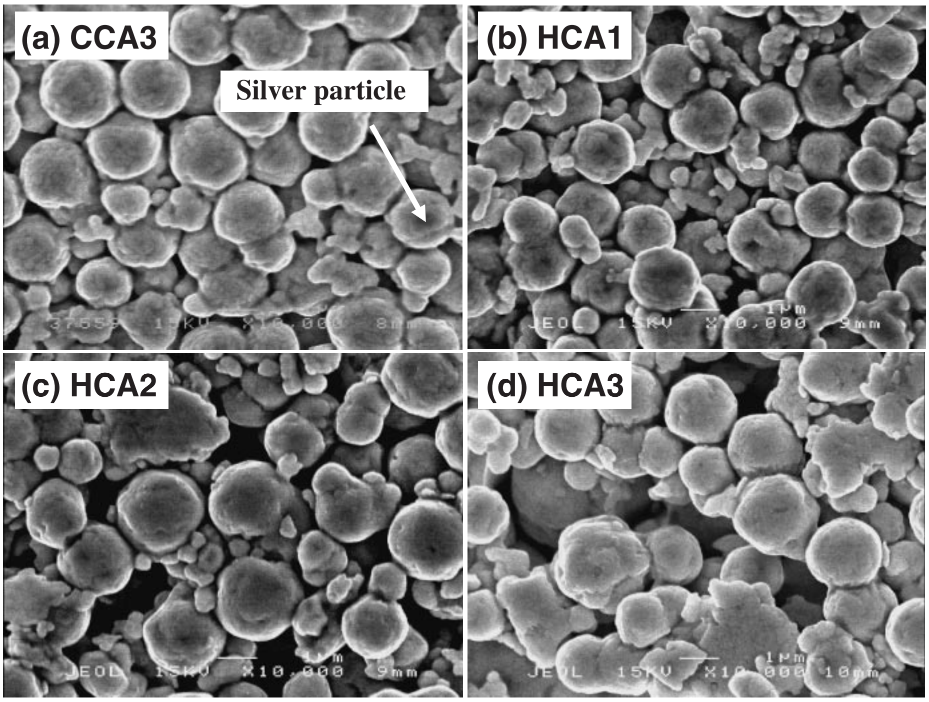

Fig. 6 Surface morphology of CCA3 and hybrid conductive adhesives.

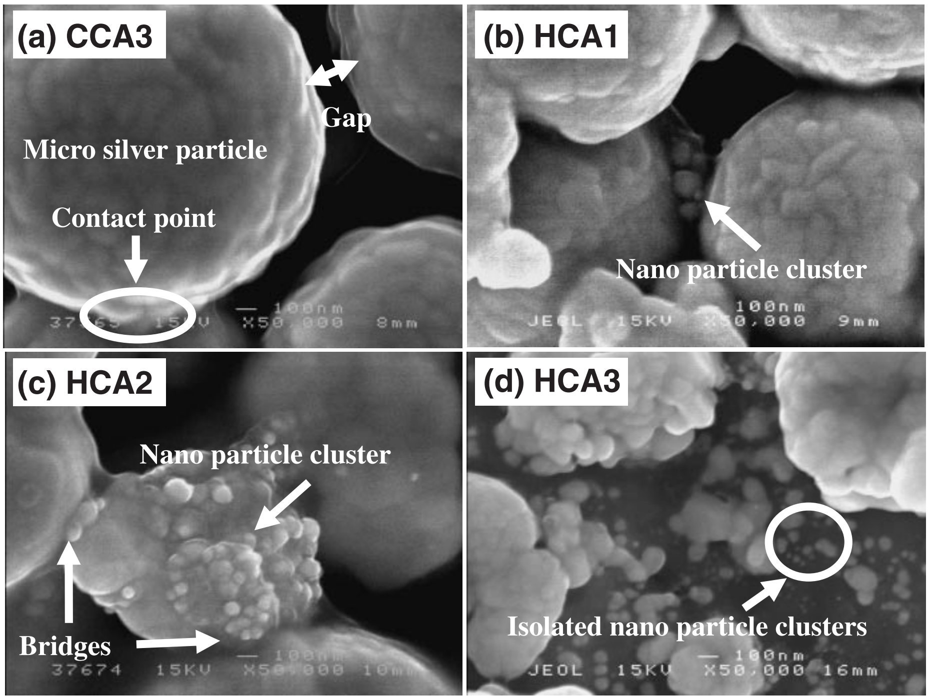

Fig. 7 Enlarged morphology of CCA3 and hybrid conductive adhesives.

in HCA reacts with epoxy during DSC process, which definitely altered the curing reaction peak. Consequently, the curing temperature was set at 473 K, which was higher than the curing reaction peak to improve electrical conductivity for conductive adhesives. The curing time was fixed at 1 h.

Figure 6 illustrates the surface morphology of CCA3 and HCA for different silver nano-particle content; 0 (CCA3), 2, 4 and 8 mass%. As nano-particle content increased, the gaps distributed in the conductive adhesive increased due to the decrement of micro-particle content, namely, the decrement of the vehicle that serves as a bridge in hybrid conductive adhesives.

To investigate the configuration for nano-particles and micro-particles, an enlarged micro structure of CCA3 and HCA was observed (Fig. 7). With only micro-particles in epoxy (CCA3), the micro structure revealed the micro-particles are close to each other, leading to the formation of a continuous linkage at low magnification (Fig. 6). However, gaps still exists among the micro-particles, which can be clearly seen in Fig. 7(a). Therefore, the electrical current

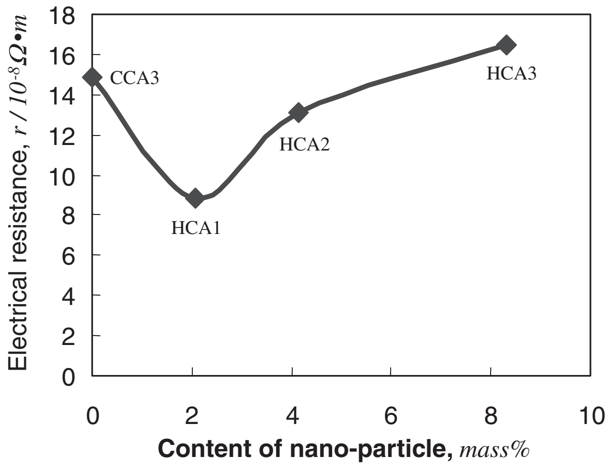

Fig. 8 Relation of electrical resistance and silver nano-particle content (total silver content: 92 mass%, curing condition: 473 K, 1 h).

flows through the combination of tunneling effect and contact point in the CCA. In cases of 2 and 4 mass% of nano-particle content, the nano-particle clusters were adsorbed on the surface of the micro-particles. Some of them acted as bridges to connect the micro-particles, as shown in Fig. 7. However, in the case of 8 mass% of nano-particles, some isolated nano-particle clusters away from other micro-particles were generated due to low micro-particle content.

The relationship between electrical resistances and nano-particle content is presented in Fig. 8. At the margin of 0 to 2 mass% of nano-particle content, the electrical resistance decreases. In the case of 4 mass% nano-particle content, the electrical resistance increased and became comparable to the result for CCA3 in epoxy. For higher nano-particle content, namely 8 mass%, the electrical resistance in conductive adhesives continues to increase and reaches a higher value than the one for CCA3.

To investigate the effect of nano-particles in detail, the variation of electrical resistance of HCA was examined and compared with CCA (90 to 92 mass%), as shown in Fig. 9. For CCA, with the increase of silver particle content from 90 to 92 mass%, the reduction of electrical resistance is about 16.3%. However, for HCA (90 to 92 mass%), a larger decrement of electrical resistance is obtained than with CCA,

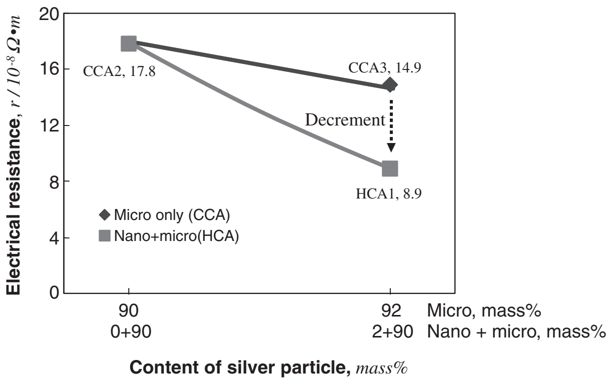

Fig. 9 Comparison of reduction rate of electrical resistance between conventional conductive adhesive and hybrid conductive adhesive (curing condition: 473 K, 1 h).

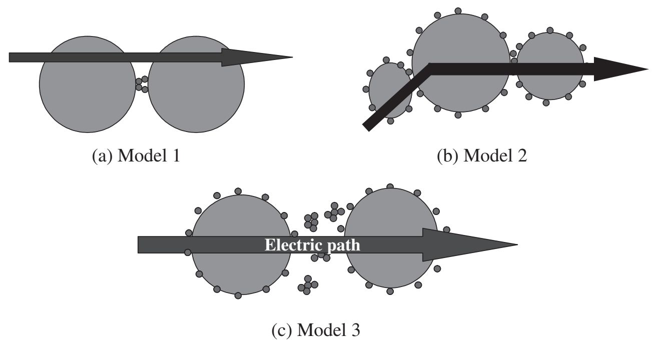

Fig. 10 Scheme of role of nano-particle among the micro-particles in epoxy (a) Model 1: nano-particles enter gap among the micro-particles (b) Model 2: forming "bridges" among the micro-particles (c) Model 3: forming "isolated clusters" among the micro-particles.

and the reduction of the electrical resistance is about 50%.

This behavior can be explained by Models 1, 2 and 3 exhibited in Fig. 10. Models 1 and 2 illustrate the cases with a small amount of nano-particles, *i.e.*, a larger percentage of micro-particles. Some of the nano-particle clusters act as bridges to connect micro-particles. Others enter the gaps among the micro-particles to increase the contact area and electrical paths. In Model 3 with larger nano-particle content, the electrical paths among the micro particles are reduced due to the larger gaps among the micro-particles. Model 3 indicates that the isolated nano-particle cluster might form easier among the micro-particles. Accordingly, this paper suggests that HCA1 behaviors following Models 1 and 2, as the result, the electrical resistance decrease. The electrical resistance of HCA2 is similar to CCA3 because as nano-particle content increases and micro-particle content decreases, the bridges and isolated nano-particle clusters among the micro-particles are formed simultaneously. For the hybrid conductive adhesive HCA3, the gaps among the micro-particles become larger due to the smaller content of micro-particles that serves as vehicles. Thus, the isolated nano-particle cluster of nano-particles is more easily formed than the bridges between micro-particles, which cause higher electrical resistance compared to CCA3.

4. Conclusion

Four conventional conductive adhesives (micro-particle only, CCA1 to 4) and three hybrid conductive adhesives (nano- and micro-particle, HCA1 to 3) were investigated and compared for electrical resistance. Moreover, for HCA, the proper ratio of nano/micro particles for conductivity was investigated.

In CCA, the electrical resistance decreased with the increase of silver content and curing temperature. However, when the silver content increased from 92 to 94 mass%, the variation of electrical resistance was not remarkable. This means that CCA has a limitation for reducing electrical resistance. From this result, the most suitable silver content in CCA is determined to be around 92 mass% (CCA3).

To decrease the electrical resistance of conductive adhesives, a new class of conductive adhesive, Hybrid Conductive Adhesive (HCA), was studied. When 2 mass% of nano-particle content was added into micro-particle, some of nano-particle cluster acted as bridges, others entered the gaps among the micro-particles resulting in increased contact point and electrical path and the electrical resistance eventually decreased. For 4 mass% of nano-particles, the electrical resistance was increased and became comparable to the result for CCA3. However, at 8 mass% of nano-particle content, the isolated nano-particle cluster was formed among micro-particles, creating a decrease of contact points and reduced electrical path. Therefore, the electrical resistance increased. The addition of a small amount of nano-particles helps to build the electrical path and lowers the electrical resistance of conductive adhesives. On the other hand, with the addition of larger nano-particle content, the electrical paths are reduced due to the larger gaps among the micro-particles because isolated nano-particle clusters form easier among the micro-particles, increasing electrical resistance as a result.

Therefore, the ratio of nano/micro particle content was confirmed to affect electrical resistance for conductive adhesives using the same total content of metal filler in conductive adhesives studied in this paper.

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