Effects of Multi-modal Filler Size Distributions on Thermal Conductivity of Electrically Conductive Adhesives Containing Ag Micro and Nanoparticles

M. Inoue and J. Liu*

The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

*Department of Microtechnology and Nanoscience, Chalmers University of Technology, Kemivägen 9, SE-412 96 Göteborg, Sweden

Key Laboratory of Advanced Display and System Applications and SMIT Center, Shanghai University, Mechatronical Engineering and Automation Building, Box 282, No. 149 Yan Chang Road, Yan Chang Campus, Shanghai University, Shanghai 200072, China

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Abstract

Electrically conductive adhesives composed of a multi-functional epoxy-based matrix containing micro- and nano-fillers with bimodal and trimodal size distributions were prepared in order to investigate their electrical and thermal conductivities. When Ag flakes were used as the filler, anisotropy was clearly observed in the thermal conductivities due to the alignment of the flakes along the in-plane direction. A bimodal adhesive containing Ag flakes and spherical micro-particles exhibited a maximal value for thermal conductivity in the vertical direction when the content of the micro-particles was 50–60 wt% of the total filler loading, although its conductivity in the in-plane direction decreased monotonically with increasing content of micro-particles. With trimodal adhesives containing Ag flakes, micro- and nanoparticles, the Ag nanoparticles could be sintered during the curing process. Adequate dispersion and sufficient sintering of the nanoparticles were found to be essential in order to improve the electrical and thermal conductivities of these adhesives.

Keywords: Thermal Interface Materials, Electrically Conductive Adhesives, Heat-resistant Matrix Resin, Thermal Conductivity, Electrical Resistivity

1. Introduction

Recently, the thermal management of chip-based electronic devices has become a major bottleneck that is hindering attempts to increase chip performance and integration density.[1] Power-electronics applications are also being significantly limited by the inability to transfer heat across interfaces into heat-sinks. Therefore, the development of high-performance thermal interface materials (TIMs), including thermal greases, gels, adhesives and phase-change materials, is essential in order to advance the thermal management of Microsystems such as those mentioned above.[2] Among the various types of TIMs that are available, the present work focuses on the heat-resistant conductive adhesives that are required for high-power die-attach applications.

In order to develop heat-resistant conductive adhesives, there are a number of subjects that must be addressed, including the design of suitable materials for the matrix resin and for the fillers. The present authors have already reported on the effects of the chemistry of the matrix resin on the transport properties (such as the electrical and thermal conductivities) and on the thermo-mechanical properties of heat-resistant epoxy-based adhesives.[3] Therefore the present work focuses on the effects of the size-distribution of the fillers on the electrical and thermal conductivities of heat-resistant adhesives.

Since the electrical and thermal conductivities of conductive adhesives are directly governed by their loading and by geometrical factors (such as shape and size distribution) that are determined by the fillers themselves, different designs of filler materials have been actively studied in order to improve these properties.[4–7] However, optimal design concepts using multi-modal filler-size distributions that will improve the transport properties of conductive adhesives can not always be established. For example, many researchers have tried to prepare close-packed...
structures of fillers with multi-modal size distributions in a matrix resin in order to improve their thermal conductivity.[4] In contrast, other researchers claim that the percolation threshold can be significantly reduced by using micro- and nano-fillers with multi-modal size distributions.[5] Furthermore, previous works suggest that the alignment of the fillers also affects the thermal conductivity of the adhesives when fillers that exhibit geometrical anisotropy (such as flakes and fibers) are used.[3, 8–10]

In addition to the geometry of the packing-structure of the filler materials, the contribution to the thermal conductivity made by conducting electrons should also be taken into account when the electrical resistivity of the adhesives is less than $10^{-4}$ Ω cm.[8] In this case, the thermal conductivity of the adhesives correlates with the electrical conductivity. Therefore, the interface electrical resistances (constriction and tunneling resistances) between the fillers are an essential factor for improving the thermal conductivity of electrically-conductive adhesives.

In the present work, adhesives containing micro- and nano-fillers with bimodal and trimodal size distributions were fabricated in order to experimentally investigate the relationship between the geometrical characteristics of the fillers and the transport properties of the adhesives. Furthermore, the effects of sintering the nanoparticles[7] during the curing process on the electrical and thermal conductivities of the materials are also discussed.

2. Experimental Procedure

A multi-functional epoxy resin[3] was used as the main matrix component of the adhesives. The matrix resin additionally contained appropriate proportions of curing agent and reactive diluent (a mono-epoxide). In addition, Ag fillers, including flakes (3–10 μm), spherical micro-particles (average diameter: 3 μm) and nanoparticles (prepared by a chemical process; average diameter: 5 nm) were mixed into the matrix at up to 85 wt% total loading in order to prepare conductive adhesives with multi-modal filler-size distributions.

The curing behavior of the adhesive pastes was examined using a differential scanning calorimeter (DSC) at a heating rate of $8.33 \times 10^{-2}$ °C s$^{-1}$. The degree of conversion was estimated by interpreting the results of the DSC measurements. Any change in the weight of the specimens during curing was also evaluated using a thermogravimetric analysis (TGA) at a heating rate of $8.33 \times 10^{-2}$ °C s$^{-1}$. When we used Ag nanoparticles as the fillers, variations in the ultraviolet-visible (UV-vis) diffuse reflection spectra (wavelength: 250–800 nm) of the specimens were examined before and after curing.

Two kinds of specimens (i.e. printed and free-standing specimens) were prepared using an isothermal curing process (at 150°C for 0.5 h) in order to evaluate the electrical and thermal conductivities of the adhesives. The adhesive pastes were printed on glass and polytetrafluoroethylene (PTFE) substrates before the curing process. After curing, the adhesives that were formed on the PTFE were peeled away from the substrates in order to obtain free-standing specimens. The electrical resistivities of the specimens (3 mm × 76 mm × 50 μm) that were cured on glass substrates were evaluated in the in-plane direction using the four-point probe method at ambient temperature. The thermal conductivities of the cured adhesives were measured at ambient temperature, both in the in-plane and vertical directions, by the laser-flash method using free-standing specimens with dimensions of 25 mm × 25 mm × 250 μm. The surfaces and cross-sectional microstructures of the cured adhesives were observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Bimodal distributions using flakes and micro-particles

In order to prepare adhesives with bimodal filler-size distributions, Ag flakes and spherical micro-particles were employed as the fillers. Although the total Ag loading was fixed at 85 wt%, the weight-ratio of these fillers was varied, with spherical micro-particles constituting 20–80 wt% of the total filler loading.

Figure 1 shows the DSC curve of an adhesive paste containing flakes and spherical micro-particles (micro-
particles/flakes = 1.125 by weight). An exothermic peak related to the curing reaction of the paste can be clearly observed. The degree of conversion of the specimens cured at 150°C for 0.5 h was analyzed based on the DSC measurement. It was confirmed that the curing condition is sufficient to obtain full conversion for the pastes.

After curing, the electrical resistivity of the specimens was evaluated in the in-plane direction using the four-point probe method. Figure 2 shows the electrical resistivity as a function of the weight fraction of the spherical micro-particles in the total filler loading. The electrical resistivity significantly increases with increasing content of the spherical micro-particles. The significant increase in electrical resistivity due to the spherical micro-particles can be mainly attributed to an increase in the interface resistance between the fillers. The interface electrical resistance can be briefly divided into two components: constriction and tunneling resistances.[11] The constriction resistance is influenced by the geometrical characteristics of the fillers when micro-fillers are used. The contact area between filler particles should be reduced when spherical particles are used as the fillers for the adhesives. Therefore, the constriction resistance at least is believed to increase due to the presence of spherical micro-particles, resulting in an increase in the electrical resistivity of the adhesives. Furthermore, the geometric characteristics of the fillers may affect the tunneling resistance between the fillers in the as-cured adhesives.[12] When spherical fillers are used for the adhesives, the tunneling resistance sometimes becomes much higher than that when flakes are used as the fillers.

Figure 3 shows the thermal conductivity of free-standing specimens in both the in-plane and the vertical directions. In the in-plane direction, the thermal conductivity of the specimens tends to decrease with increasing content of spherical micro-particles. This tendency is considered to correlate with the observed increases in the electrical resistivity in the in-plane direction, as shown in Fig. 2. Because the specimens exhibited a low electrical resistivity of below $10^{-4}$ Ω cm in the in-plane direction, the contribution from the conducting electrons to the thermal conductivity is not considered to be negligible.[8] Hence, the decrease in thermal conductivity due to the spherical micro-particles in the in-plane direction relates to a decrease in the contribution from the conducting electrons in the same direction.

Figure 3 also shows the thermal conductivity of the specimens in the vertical direction. Specimens containing only flakes, and those containing both flakes and spherical micro-particles, always exhibit low thermal conductivities in the vertical direction compared to the in-plane direction.[3, 8, 9] This anisotropy in thermal conductivity is often observed in adhesives that contain fillers which have anisotropic geometries, such as flakes. When the thickness of the adhesive specimens is reduced, fillers with anisotropic geometries tend to align along the in-plane direction. Anisotropy in the transport properties is expected to be induced by the alignment of the fillers.[13]

In fact, the alignment of the Ag flakes along the in-plane direction was observed both in the specimens with only flakes and with bimodal distributions, as shown in Figs. 4 (a) and (b). Since there are more interfaces between the
fillers in the vertical direction than there are in the in-plane direction due to the alignment of the fillers, the specimens exhibit lower thermal conductivities in the vertical direction.

By contrast, those adhesives containing only spherical micro-particles are expected to exhibit isotropic thermal conductivity because the fillers themselves should be dispersed isotropically. In fact, the values of thermal conductivity in the vertical direction of specimens containing only spherical micro-particles are almost equal to those in the in-plane direction, as shown in Fig. 3.

When the weight-fraction of spherical micro-particles in the total filler loading reaches 50–60 wt%, the specimens exhibit a maximal value of thermal conductivity in the vertical direction. The thermal conductivity of the specimens in the vertical direction is considered to be influenced by two factors, i.e., the number of interfaces and the geometry of the spherical micro-particles. The number of interfaces between the fillers in the vertical direction is reduced with increasing content of spherical micro-particles. This reduction in the number of interfaces can contribute to an increase in thermal conductivity in the vertical direction. However, further increases in the content of spherical micro-particles results in an increase in the electrical resistivity of the adhesives due to the increase in the interface electrical resistance between the fillers. Because of the decrease in the contribution from conducting electrons, the thermal conductivity can be decreased by enhancing the electrical resistivity. Due to the effects of these two conflicting factors, adhesives with bimodal filler-size distributions exhibit a maximal value in terms of thermal conductivity in the vertical direction when the content of the spherical micro-particles reaches 50–60 wt% of total filler loading.

3.2 Trimodal distribution using micro- and nanofillers

In the last decade, many researchers have proposed material design concepts for electrically- and thermally-conductive adhesives using nano-fillers such as metal nanoparticles.[5–7, 14] However, very few groups have succeeded in developing adhesives that have excellent electrical- and thermal-conductivities using metal nanoparticles.[7, 14] Most of these studies failed to improve the electrical and thermal conductivities due to the increase in the number of the interfaces between fillers which occurs when using nanoparticles.[15] Some researchers clearly showed that sufficient sintering of the nanoparticles is essential in order to improve the electrical conductivity of these adhesives.[7, 14]

In the case of adhesives that exhibit low electrical resistivities of less than $10^{-4} \ \Omega \cdot \text{cm}$, the contribution from conducting electrons significantly influences the thermal conductivity.[8] Therefore, decreases in electrical resistivity resulting from appropriate sintering of the metal nanoparticles are believed to be an effective way of improving the thermal conductivity of the adhesives. In the present work, we investigated the possibility of improving the electrical and thermal conductivities of heat-resistant adhesives by sintering the Ag nanoparticles.

When we prepared the trimodal adhesives in the present work, the content of the spherical micro-particles for the bimodal adhesive composition that exhibited the highest value of thermal conductivity in the vertical direction (micro-particles flakes = 1.125 by weight; total filler loading = 85 wt%) was partially substituted by the inclusion of nanoparticles.

Because some surfactants were adsorbed on the metal nanoparticles in order to achieve independent dispersion
states, the surfactants should be removed in order to induce sintering of nanoparticles. Therefore, the desorption of surfactants during the curing process is the key for sintering metal nanoparticles. Figure 5 (a) shows the DSC curve of an adhesive paste with a trimodal filler distribution (content of nanoparticles = 8.24 wt% of the total filler loading). The onset temperature of the exothermic reaction of the trimodal paste is clearly lower than that of the bimodal paste. Furthermore, the trimodal paste exhibits a larger heat of reaction than the bimodal paste during the curing of the matrix resin, since exothermic reactions are induced when surfactants on the nanoparticles are desorbed from the surface.

Figure 6 shows the TGA curves of the bimodal and trimodal pastes. The magnitude of weight loss during the curing process of the trimodal paste is much larger than that of the bimodal paste. With the trimodal paste, a decrease in the weight of the specimen due to the desorption of surfactants occurs in the temperature range of 100–140°C. This temperature range agrees well with the onset of the exothermic reaction in the DSC curve shown in Fig. 5 (a). Because the desorption behavior was quite different from the paste containing only the Ag nanoparticles (without any matrix resins), the desorption of surfactants was affected by the matrix resin. Therefore, the selection of surfactants from the viewpoint of chemical interactions with the matrix resin will be an important point for designing the adhesives containing metal nanoparticles.

Although the DSC and TGA curves suggest that sintering of the Ag nanoparticles can be started during the curing process, the curing reaction rate of the matrix resin seems to decrease due to the desorption of surfactants because the exothermic peak shifted slightly higher. However, the trimodal pastes could be also fully cured by heating at 150°C for 0.5 h.

In order to confirm sintering of the Ag nanoparticles during an isothermal curing process, the UV-vis diffuse reflection spectra of the trimodal specimens printed on a glass substrate were measured before and after curing. Figures 7 (a) and (b) respectively show the UV-vis diffuse reflection spectra of a trimodal specimen before and after curing at 150°C for 0.5 h. Absorption bands due to the surface plasmon resonance of Ag nanoparticles[16] apparently coexist with that caused by the volume plasmon resonance of Ag[17] before curing. By contrast, the absorption bands due to the surface plasmon resonance of the nanoparticles have completely disappeared after curing. The disappearance of the surface plasmon resonance suggests that the Ag nanoparticles were sintered during the curing process.

After curing at 150°C for 0.5 h, the electrical and thermal conductivities of the specimens were evaluated. Figure 8 shows the electrical resistivity of the trimodal specimens as a function of the content of nanoparticles in the total filler loading. The specimens exhibited a minimal value of electrical resistivity when the content of the nanoparticles was 3.53 wt% of the total filler loading. Figure 9 shows the thermal conductivity in both the in-plane and the vertical directions of the trimodal adhesives cured at 150°C for 0.5 h. The thermal conductivities of the trimodal adhesives
containing 3.53 wt% of nanoparticles are slightly higher than the bimodal adhesives in both the in-plane and the vertical directions. These experimental results suggest that sintering of the nanoparticles possibly contributes to a reduction in the electrical and thermal resistances between the micro-fillers.

However, above ~5 wt%, the electrical resistivity increases with higher nanoparticle content. This increase in electrical resistivity is considered to be caused by poor dispersion of the nanoparticles in the adhesive specimens. In fact, many agglomerates of particles were observed in the specimens containing above ~5 wt% of nanoparticles by a cross-sectional SEM observation (Fig. 10). Figure 11 shows the SEM micrograph of an agglomerate of Ag nanoparticles. Although sintering of the Ag nanoparticles seems to be started in the agglomerate, grain growth was limited to below 100 nm. Since there are many grain boundaries in the agglomerates, these regions are likely to

Fig. 7 UV-vis diffuse reflection spectra of a trimodal adhesive (composition of nanoparticles = 8.24 wt% of the total filler loading; (micro-particles + nanoparticles)/flakes = 1.125 by weight) (a) before and (b) after curing at 150°C for 0.5 h.

Fig. 8 Electrical resistivity of the trimodal adhesives cured at 150°C for 0.5 h, as a function of the weight fraction of nanoparticles in the total filler loading.

Fig. 9 Thermal conductivities in the in-plane and the vertical directions of the trimodal adhesives cured at 150°C for 0.5 h, as a function of the weight fraction of nanoparticles in the total filler loading.

Fig. 10 Cross-sectional SEM micrograph of a trimodal adhesive (composition of nanoparticles = 8.24 wt% of the total filler loading; (micro-particles + nanoparticles)/flakes = 1.125 by weight). Arrows indicate the agglomerates of Ag nanoparticles.
exhibit high electrical resistances. Therefore, the selection of a suitable surfactant for improving the dispersion of the nanoparticles is also important to consider when preparing adhesives containing nanoparticles.

The present work suggests that there are two problems to solve when developing adhesives containing metal nanoparticles. The first is the problem of dispersion of nanoparticles in the matrix resin. In order to improve the dispersion of the nanoparticles in the matrix resin, appropriate surfactants should be used for the nanoparticles, depending on the particular matrix resins in question. When a sufficient dispersion of nanoparticles is achieved, we can investigate the optimum composition of the nanoparticles for improving electrical and thermal conductivities. The second problem is that of sintering of the nanoparticles. Because the surfactants should be desorbed from the surface in order to induce the sintering process, the selection of appropriate surfactants is also important from the viewpoint of sintering of the nanoparticles. In addition, the degree of sintering should be taken into account when investigating the sintering of the nanoparticles. If the sintering process were to terminate in the initial stages, the addition of nanoparticles would not always be effective in improving the electrical and thermal conductivities of the adhesives.

3.3 Curing temperature dependence of transport properties of the adhesives

The electrical and thermal conductivities of electrically conductive adhesives frequently vary depending on the curing temperature.[3, 18, 19] In this section, the curing temperature dependence of the transport properties of the bimodal and trimodal adhesives is discussed.

Figure 12 shows the electrical resistivity (in the in-plane direction) and thermal conductivities (in the in-plane and vertical directions) of the bimodal (micro-particles flakes = 1.125 by weight) and trimodal adhesives cured at 200°C for 0.5 h. These adhesive specimens exhibit higher electrical and thermal conductivities than those cured at 150°C. Although the anisotropy in thermal conductivity is also observed in the adhesives cured at 200°C, they exhibited relatively high thermal conductivities (9–10 Wm⁻¹K⁻¹) even in the vertical direction.

Here, variations in the electrical and thermal conductivities in the in-plane direction depending on the curing temperature are analyzed. If the assumption of quasi-elastic scattering[8, 20, 21] is valid for the conducting electrons during the intra-particle and inter-particle (constriction and tunneling) conductions in electrically conductive adhesives, we can estimate the partial thermal conductivity from the contributions of the conducting electrons (λₑₑ) using the Wiedemann-Franz (W-F) law without any modeling for the structure of the percolation network of the fillers.[8]

In this case, the differences in λₑₑ due to the variation in curing temperature (Δλₑₑ) were almost equal to the differences in (total) thermal conductivity. Therefore, the increases in thermal conductivity due to the variation in curing temperature from 150 to 200°C are mainly attributable to increased contributions from the conducting electrons. The thermal conductivity of the adhesives appears to be sensitively affected by contributions from the conducting electrons.
4. Conclusions

The present work investigates the electrical and thermal conductivities of various adhesives composed of a multifunctional epoxy binder containing Ag fillers with bimodal and trimodal particle size distributions. The main results of this work are summarized below:

(1) Adhesives containing flakes exhibit anisotropy in terms of thermal conductivity due to the alignment of flakes along the in-plane direction. The thermal conductivity in the in-plane direction is always higher than that in the vertical direction when the flakes are aligned along the in-plane direction.

(2) Bimodal adhesives containing an appropriate composition of flakes and spherical micro-particles exhibit a maximal value of thermal conductivity in the vertical direction.

(3) In the case of trimodal adhesives containing Ag nanoparticles, the electrical and thermal conductivities are possibly improved by the effects of sintering the nanoparticles. Important points for the further development of trimodal adhesives are the dispersion and the sintering of the nanoparticles.

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References


