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Effects of Silane Coupling Agents on the Properties of Copper Filled Electrically Conductive Adhesive

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Abstract. Effects of silane coupling agents with different functional groups such as epoxy, isocyanate and ureide on the electrical and mechanical properties of copper filled electrical conductive adhesives (ECAs) were studied. Copper (Cu) fillers were used as conductive fillers and polyurethane resin was applied as the adhesive material in this study. Significant differences could be observed on the as cured electrical resistivity and shear strength of the Cu filled ECAs prepared with different silane coupling agents. Silane coupling agents functionalized with epoxy groups showed the lowest electrical resistivity and highest shear strength among the ECAs in this study. Besides, effect of post-curing at 170 ℃ for 1 h on the ECAs was also investigated. Results showed that ECAs after post-curing exhibited enhanced electrical conductivity compared to the as cured ECAs. Besides, improved shear strength could be observed for all the ECAs after post-curing.

Keywords: Conductive adhesive, Copper, Shear strength, Electrical resistivity, Polyurethane

2. Introduction

As electronic packaging requirements are driven towards smaller size, higher density, and lower cost solutions, using electrically conductive adhesives (ECAs) for interconnections between surface mount device components and a substrate are well positioned to meet these challenges. ECAs composed of conductive metallic fillers that provide electrical conduction and polymeric resin for mechanical adhesion. Compared to conventional soldering-based interconnection technology, ECAs have more advantages in terms of: being environmentally benign, having lower processing temperature requirements, thus lesser energy consumption; finer pitch capability; higher flexibility; and facilitating easier disassembly for repair and recycling [1]. Silver (Ag) is the most widely used conductive filler in ECA owing to its high electrical conductivity and chemical stability. However, the drawback of Ag is being relatively expensive. Hence, alternative conductive fillers such as copper, nickel, and graphite powder have been applied as conductive fillers to manufacture low cost ECAs. Copper can be a promising candidate for conductive metallic filler because of its low resistivity, low cost and improved electro-migration performance compared to the commonly used Ag.

In our previous study [2-4], Cu particles prepared by different methods were applied as conductive fillers in the ECA with phenolic resin as the adhesive binder. However, the shear strength of the phenolic resin was not as good as the commercially used epoxy based ECA. Hence, development of an environmental friendly adhesive material with improved mechanical strength is of great interest. Polyurethane based ECA exhibits

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long shelf-life and stable, and moderate viscosity which is suitable for general screen-printing process in terms of the electrical and mechanical properties affected by the silane coupling agents and post-curing process.

3. Experimental

3.1. Materials and Methods

Cu fillers (1400Y) used in this study were purchased from Mitsui Mining & Smelting Co. Ltd., Tokyo, Japan. Morphology of Cu fillers was observed using FE-SEM from Hitachi (Model: SV-700). Polyurethane resin (Desmodur BL3175SN) was provided by Sumika Bayer Urethane Co. Ltd., Osaka, Japan. Silane coupling agents with different functional groups as shown in Table 1 were provided by Shin-Etsu Chemical Co. Ltd., Osaka, Japan. Diethyl carbitol (TCI, Japan) was used as solvent during mixing of the ECA paste. Cu fillers of 80 mass % were mixed with polyurethane resin and diethyl carbitol in an agate mortar. Simultaneously, silane coupling agent was added respectively during mixing of each ECA paste. It was then mixed and defoamed in a hybrid planetary centrifugal mixer (Model: ARE 250, Thinky Corp., Japan).

Table 1: Silane coupling agents used to prepare ECAs in this study.

Name	Chemical structure	Functional group	ECAs
KBM-402	$(CH_3O)_2SiC_3H_6OCH_2CH\text{-}CH_2$ (with CH_3 on Si, O on CH)	epoxy	ECA 1
KBE-9007	$(C_2H_5O)_3SiC_3H_6N=C=O$	isocyanate	ECA 2
KBE-585	$(C_2H_5O)_3SiC_3H_6NHCNH_2$ (O on C)	ureide	ECA 3

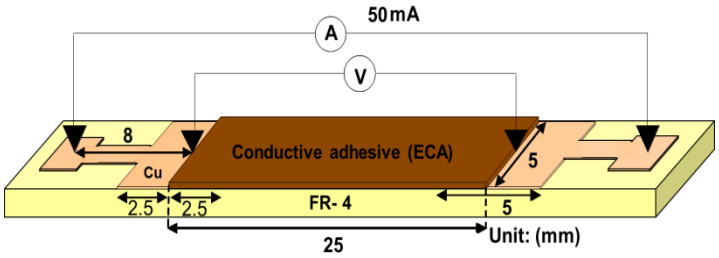

Fig. 1: Schematic diagram of FR-4 for measurement of electrical resistance of ECA.

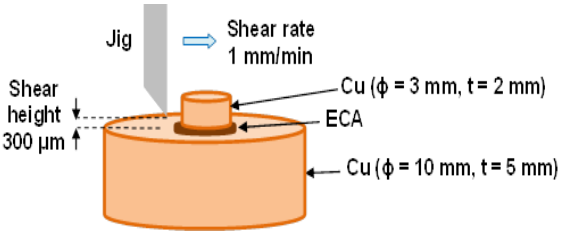

Fig. 2: Schematic diagram of Cu/Cu joint specimens for shear test.

A standard size of 50 x 95 mm FR-4 board with copper pads at both ends was used to measure the electrical resistivity of ECA. Two parallel strips of cellophane tape were placed apart along the length of 95 mm of the FR-4 board. Then, another two strips of the tape were placed perpendicular to the parallel strips in order to create a test specimen opening with 25 mm length and 5 mm width. The ECA paste was then spread on the specimen opening to create a uniform thin film of ECA. A total of 5 specimens were prepared on a single FR-4 board for each ECA sample (Fig. 1). Then, it was placed into a convection oven to cure at 140 ℃ for 30 mins. After curing, it was allowed to cool to room temperature before the as cured electrical resistivity was measured. In addition, ECA samples cured at 140 ℃ for 30 mins and further post-cured at 170 ℃ for 1 h were also prepared to evaluate the changes of the electrical and mechanical properties of the ECA. The bulk resistance of the ECAs was measured from ends of the pattern using Nanovoltmeter (Model: 2182A) and Precision Current Source (Model: 6220) from Keithley, with a four-point probe method. The thickness of the cured ECA samples on the FR-4 board was measured by using a charge-coupled device (CCD) laser displacement sensor (Model: LK-G Series) from Keyence together with software MAP-3D from COMS. Besides, shear strength of the ECA samples was evaluated by using Cu/Cu joint specimens as shown in Fig. 2. The shear speed and shear height of the jig was set at 1 mm/min and 300 μm, respectively. The shear tester

instrument used was from Rhesca (Model: STR-1001). Both as cured and post-cured condition of the ECAs were similar to that in the case of electrical property evaluation as mentioned above.

4. Results and Discussions

Fig. 3 presents the SEM image of the Cu fillers in this study. The morphology of the Cu fillers showed uniform crystallite structure with median particle size about 5.5 μm. Effect of different silane coupling agents and post-curing on the electrical resistivity of ECAs was shown in Fig. 4. In order to show the effect of coupling agent in the ECA, ECA free of coupling agent was prepared for comparison. The as cured resistivity of this ECA was 1.36 $x10^{-2}$ Ω.cm whereas the as cured resistivity of all the ECAs prepared with coupling agents was at the order range of 10^{-3} Ω.cm. This could be due to the coupling agent plays an important role in bridging the polyurethane resin and the surface of the Cu filler by having two different functional groups. Coupling agents are usually used for inorganic fillers-contained plastics to improve the adhesion between fillers and polymer, and their use improves the performance of composite materials [5]. When mixed with the adhesive, the coupling agents are capable of migrating to the interface and reacting with the substrate surface as the adhesive cures [5]. It seems that silane act as molecular bridges between the polyurethane and Cu filler, resulting in the formation of covalent chemical bonds across the interface, that improve the electrical properties of the ECAs. Among the ECAs prepared in this study, ECA 1 showed the lowest electrical resistivity whereas ECA 3 showed the highest electrical resistivity. Besides, all the ECAs showed enhanced electrical conductivity after post-curing at 170 ℃ for 1 h. It was reported that post-curing process promotes additional cross-linking reactions and making possible the completion of the curing process [6]. This enhanced the shrinkage of the polymeric matrix, which reduced the electrical resistivity of the ECA by increasing the network of Cu fillers in terms of the percolation concentration.

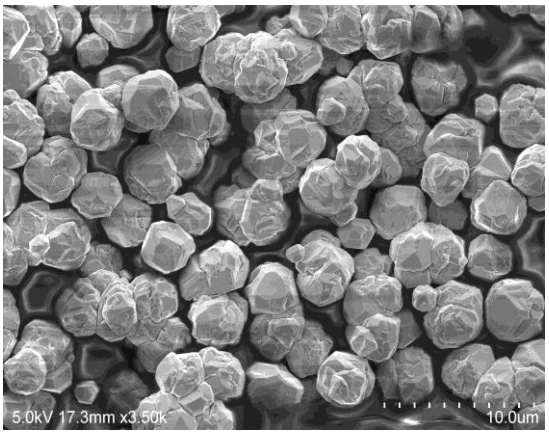

Fig. 3: SEM image of Cu fillers in this study.

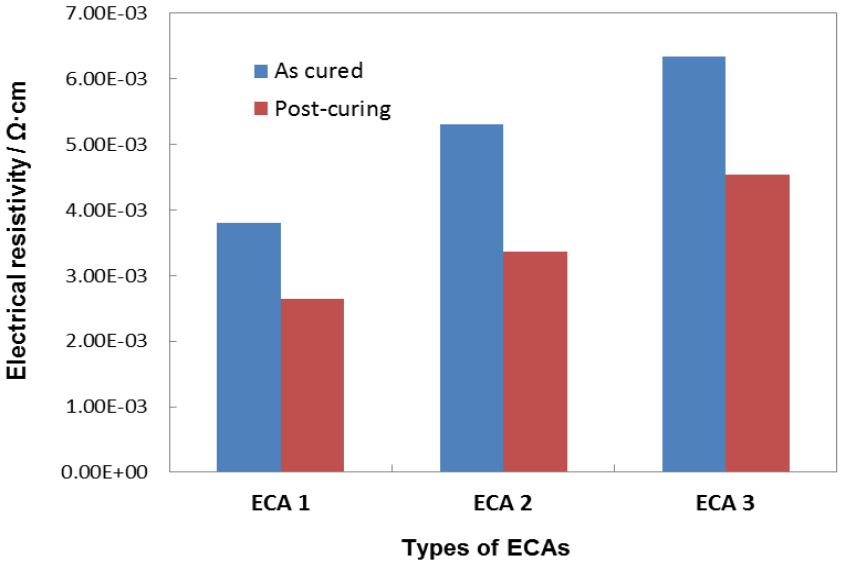

Fig. 4: Electrical resistivity of the as cured and post-cured ECAs.

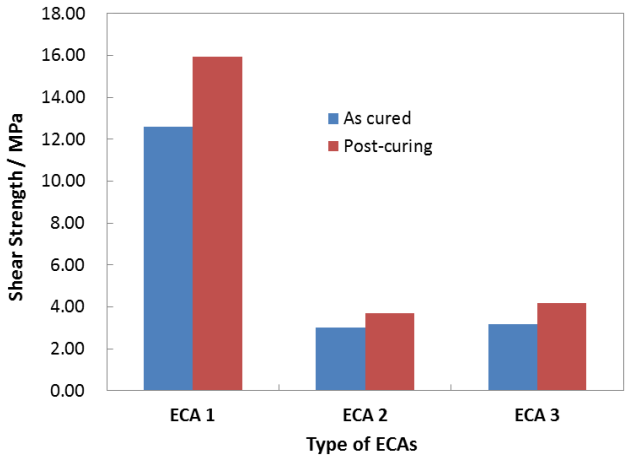

Fig. 5: Shear strength of the as cured and post-cured ECAs.

Mechanical strength of the ECAs in this study was investigated by using shear test method. Effect of different silane coupling agents and post-curing on the shear strength of ECAs was shown in Fig. 5. The as cured ECA prepared free of coupling agent exhibited shear strength about 10.73 MPa which was relatively lower than ECA 1 but higher than ECA 2 and ECA 3. Among the ECA samples in this study, ECA 1 exhibited the highest shear strength, whereas ECA 2 and ECA 3 showed low and comparable shear strength in both as cured and post-cured samples. Apparently, it was found that coupling agents with different functional groups yielded different effects in shear strength. Epoxy functionalized silane coupling agent improved the shear strength of the ECA, but deteriorated shear strength was found with addition of isocyanate and ureide functionalized silane coupling agents. Besides, it could be observed that the shear strength of the ECAs increased after post-curing. The shear strength increased about 27, 24 and 32 % in ECA 1, ECA 2 and ECA 3, respectively after post-curing. As mentioned in the case of the decrease of electrical resistivity after post-curing, similar reason could be applied in the enhanced shear strength after post-curing. Additional cross-linking reactions and completion of the curing process promotes better adhesion of the ECA to the surface of the Cu specimens. This would strengthen the joint of the ECA between the Cu/Cu specimens that lead to improved shear strength.

5. Conclusions

In summary, we could conclude that both silane coupling agents and post-curing played important roles in the electrical resistivity and shear strength of the ECAs in this study. Epoxy functionalized silane coupling agent yielded the best performance in ECA in terms of electrical and mechanical properties. Overall, additional of silane coupling agents had improved the electrical conductivity of the ECAs, but only epoxy functionalized silane coupling agent enhanced the shear strength of the ECA. Post-curing at 170 ℃ for 1 h had improved both electrical conductivity and shear strength of the ECAs in this study.

6. Acknowledgements

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