Characterization of a Hybrid Cu Paste as an Isotropic Conductive Adhesive

Yong-Sung Eom, Kwang-Seong Choi, Seok-Hwan Moon, Jun-Hee Park, Jong-Hyun Lee, and Jong-Tae Moon

As an isotropic conductive adhesive, that is, a hybrid Cu paste composed of Cu powder, solder powder, and a fluxing resin system, has been quantitatively characterized. The mechanism of an electrical connection based on a novel concept of electrical conduction is experimentally characterized using an analysis of a differential scanning calorimeter and scanning electron microscope energy-dispersive X-ray spectroscopy. The oxide on the metal surface is sufficiently removed with an increase in temperature, and intermetallic compounds between the Cu and melted solder are simultaneously generated, leading to an electrical connection. The reliability of the hybrid Cu paste is experimentally identified and compared with existing Ag paste. As an example of a practical application, the hybrid Cu paste is used for LED packaging, and its electrical and thermal performances are compared with the commercialized Ag paste. In the present research, it is proved that, except the optical function, the electrical and thermal performances are similar to pre-existing Ag paste. The hybrid Cu paste could be used as an isotropic conductive adhesive due to its low production cost.

Keywords: Hybrid Cu paste, fluxing resin, isotropic conductive adhesive, solder wetting.

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I. Introduction

Ever since an Ag filled conductive paste was first introduced in U.S. Patent [1], isotropic conductive adhesives (ICAs) have continuously been developed for electrical interconnections in semiconductor packaging. In general, a conductive paste as a composite material is composed of polymeric resins and metallic filler. For a high electrical conductivity, flaked Ag powder is widely used by many researchers [2], [3]. Lu and others reported that the conductivity of Ag paste was achieved by a mechanical contact between Ag particles due to the shrinkage of the polymer matrix during the cure processing [2]. Also, Jiang and others attempted to use nano-sized Ag particles and micro-sized Ag flakes mixed with an epoxy resin for an increase in electrical conductivity [3]. The high conductivity was achieved using a dramatic reduction of interfaces between conductive fillers due to a low temperature sintering of the nano Ag particles. However, it is well known that Ag powder is still too expensive as a raw material for the production of conductive paste.

In the present research, a novel concept of a conductive mechanism for an isotropic conductive paste is proposed. The isotropic conductive paste, called hybrid Cu paste, is formulated by the mixing of three components: Cu flakes, solder powder, and fluxing resin. The fluxing resin has an ability to remove the oxide layer in the Cu and solder powder during the curing process. It is well known that the price of raw Cu material is approximately 100 times cheaper than that of raw silver material.

1. Mechanisms of an Electrical Interconnection

Figure 1 shows a schematic of an electrical interconnection

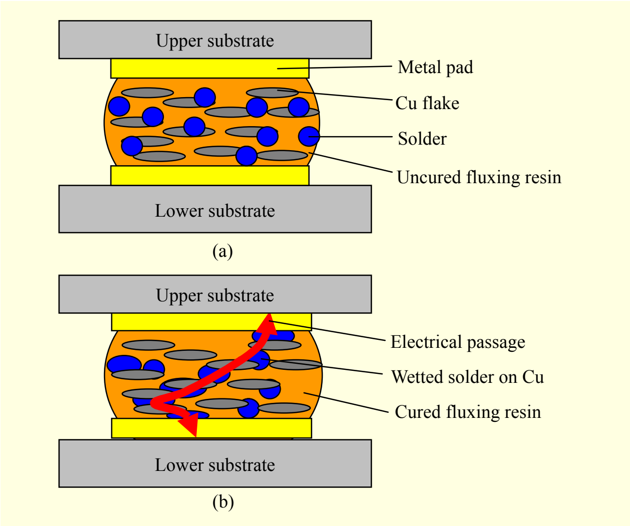

Fig. 1. Schematic of electrical interconnection mechanism with hybrid Cu paste: (a) before curing process and (b) after curing process.

mechanism using the hybrid Cu paste. Before the curing process shown in Fig. 1(a), the hybrid Cu paste composed of Cu flakes, solder powder, and uncured fluxing resin is placed between the upper and lower metal pads. With an increase of processing temperature, the oxide layer preformed on the surfaces of the solder and Cu flakes is continuously removed by the fluxing function of the fluxing resin, while the viscosity of the uncured fluxing resin is decreased. When the processing temperature reaches the melting temperature of solder, the solder particles placed between the Cu flakes are suddenly melted and wetted with adjacent Cu flakes in the liquid state of the fluxing resin. At this time, the electrical passage shown in Fig. 1(b) is dramatically performed between the upper and lower metal pads. Then, the liquid state of the fluxing resin matrix is continuously changed to a solid state through a chemical reaction at the given curing temperature. When the liquid state of the solder is wetted on the surface of the Cu flakes, an intermetallic compound can be created due to the metallic reaction between solder and Cu with a diffusion effect.

II. Materials and Experimental

1. Materials

Figure 2 shows SEM photographs of Cu flakes and Sn/58Bi solder with a melting temperature of 138ºC. The average diameters of the Cu flakes and Sn/58Bi are about 5 μm and less than 5 μm, respectively. A fluxing resin matrix with the ability to remove the oxide layer preformed on the surface of the metal particles was formulated based on an epoxy resin without the use of volatile materials. In previous research [4]-

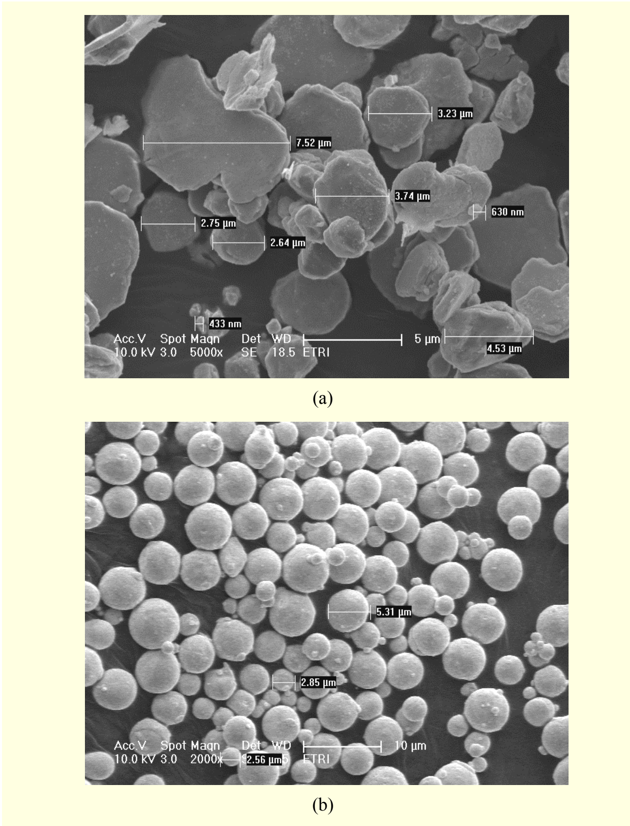

Fig. 2. SEM photographs of metal powder used for hybrid Cu paste: (a) Cu flakes and (b) Sn/58Bi solder powder.

[9], the chemo-rheological mechanism of a fluxing resin with Cu and solder powders were investigated and reported. Those three materials are mixed at room temperature at several volume ratios. For a stable state of electrical conduction, two metal materials should be homogeneously mixed with the fluxing resin matrix. The viscosity of the hybrid Cu paste is strongly dependent on the volume ratio between the metal powder and the fluxing resin, as well as the diameter of metal particles. For a comparison of the electrical performance between a commercial conductive paste and the hybrid Cu paste, an Ag paste with the model of Hi-BOND CCD-1B produced by Protavic Ltd. was selected. The glass transition temperature of the commercial Ag paste is 111ºC, as reported in its catalog.

2. Experiment

To understand the chemical reaction mechanism between solder and Cu powders, as well as the fluxing resin and metals, a dynamic differential scanning calorimeter (DSC, Q20, TA Instruments) was used in a temperature range of 0ºC to 300ºC at a heating rate of 10ºC/min under the nitrogen atmosphere. All samples are enclosed by the hermetic aluminium pan. To

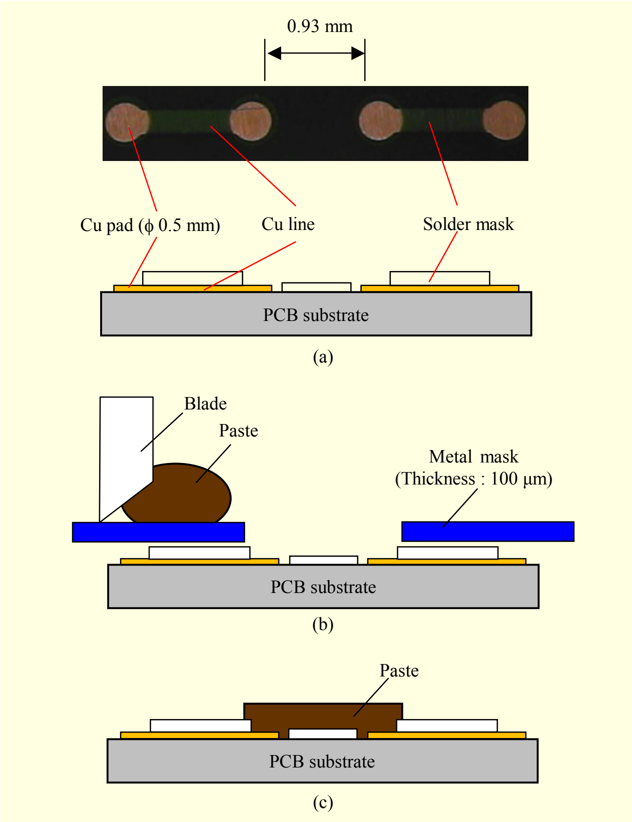

Fig. 3. Schematics of screen-printing process on PCB substrate: (a) photo and cross-sectional view before process began, (b) screen printing process using doctor blade method, and (c) cross-sectional view of sample after process was finished.

identify the wetting mechanism between Cu flakes and solder particles performing the electrical passage shown in Fig. 1(b), scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDX) analysis was conducted after the curing process. Figure 3 shows schematics of a screen printing process on a PCB substrate. Four Cu pads with a diameter of 0.5 mm are exposed in air as shown in Fig. 3(a) while the Cu line is completely covered by the solder mask. In the center area of the PCB substrate, the two Cu pads with a distance of 0.93 mm are not connected by a Cu line. Using a screen-printing process with a thickness of 0.1 mm for the metal mask, two inner Cu pads were connected by a conductive paste, shown in Figs. 3(b) and 3(c). After the screen-printing process, the hybrid Cu paste and a commercial Ag paste were cured at 180ºC for 5 min and 140ºC for 20 min, respectively. To measure the electrical resistance of both conductive pastes, a 4-point probe method was used to obtain the pure electrical resistance without a contact resistance of the probes [6]. For a precise measurement of both conductive pastes, the electrical resistance of the Cu lines shown in Fig. 3(a) was mathematically eliminated.

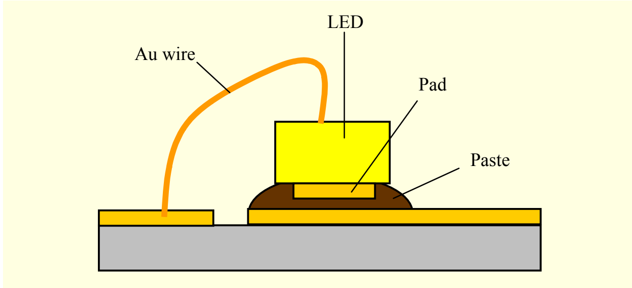

Fig. 4. Cross-sectional view of LED bonding package with both conductive pastes.

For a reliability test of both conductive pastes after the curing process, the samples were soaked in an environment of 85ºC and 85% relative humidity. Changes in electrical resistance were measured for 6 weeks (1,008 h). For an evaluation of the electrical and thermal performances, an LED with a 1.2 W grade produced by CREE Ltd. was bonded onto the metal PCB (Al) substrate with both conductive pastes as shown in Fig. 4. A current of 400 mA was applied to both LED packages. After 10 min, the stabilized voltage and temperature of the metal PCB substrate were measured. The backside temperatures of the PCB substrates were measured using a thermal video camera (ThermaCAM A40M).

III. Results and Discussion

Figure 5 shows dynamic DSC thermograms with a heating rate of 10ºC/min for the hybrid Cu paste and its material components. The melting of solder was clearly detected at around 140ºC as an endothermic peak shown in Fig. 5(b), while that of Cu was not observed in the temperature range of 0^o to 300ºC, shown in Fig. 5(a). In the mixture of the Cu and solder powder with the volumetric mixing ratio of 1:1 in Fig. 5(c), an endothermic peak caused by the melting of solder is only observed without any exothermic reaction peaks between the Cu and solder powders. Based on the dynamic DSC thermogram of the fluxing resin, shown in Fig. 5(d), it can be seen that the initial, peak, and end temperatures of the chemical reaction are around 105ºC, 159ºC, and 201ºC, respectively. Figure 5(e) shows the result of the dynamic DSC with the hybrid Cu paste with the volumetric mixing ratio of 20% Cu, 25% solder, and 70% fluxing resin. With an increase of temperature, a chemical reaction begins at around 105ºC, and is then rapidly increased up to the melting temperature of Sn/58Bi solder, after which an endothermic peak is suddenly detected at around 140ºC. Then, another intense endothermic reaction peak is observed at 143ºC. The entire exothermic peak is completely finished at 180ºC as shown in Fig. 5(e). In Fig. 5(e), other endothermic peaks are particularly detected at 201ºC and 271ºC, but are not observed in the other DSC results

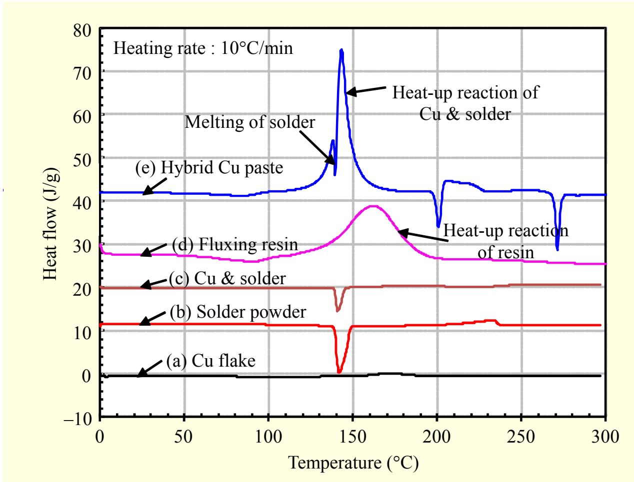

Fig. 5. Comparison of DSC thermograms: (a) Cu flake, (b) solder powder, (c) Cu flake and solder powder, (d) fluxing resin, and (e) hybrid Cu paste.

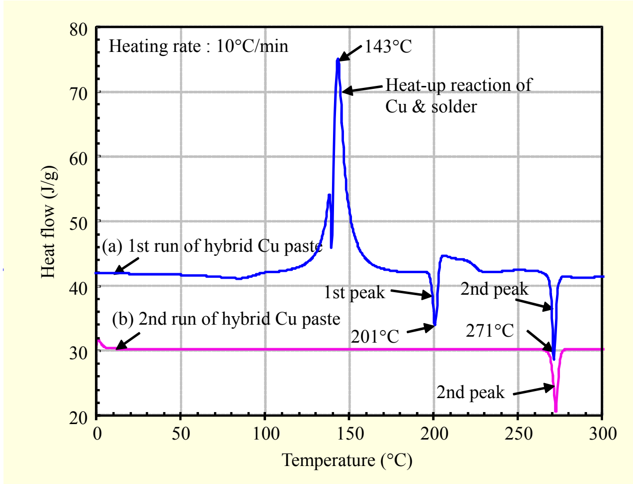

Fig. 6. Comparison of DSC thermograms: (a) first and (b) second runs of hybrid Cu paste.

shown in Fig. 5. From a comparison of Figs. 5(d) and 5(e), it is clear that the chemical reaction peak of the fluxing resin matrix is moved from 159ºC to 143ºC. In previous research [8], it was clearly proved that this phenomenon is caused by a catalytic effect due to the presence of the solder powder.

The measured heat-up energy from the chemical reaction of the fluxing resin in Fig. 5(d) and the hybrid Cu paste in Fig. 5(e) were 282 J/g and 420 J/g, respectively. It is inferred that the heat-up energy of 420 J/g with the hybrid Cu paste was generated for the following two reasons: the chemical reaction from the fluxing resin and exothermic heat from the metallic reaction between Cu and Sn/58Bi. Therefore, it is believed that these two endothermic peaks observed in the high temperature range in Fig. 5(e) are strongly dependent on the generation of new intermetallic compounds.

Figure 6 shows a comparison of the DSC thermograms of 6(a) first and 6(b) second runs with the hybrid Cu paste. In Fig. 6(b), the melting of Sn/58Bi solder is not observed at around 140ºC because Sn in the Sn/58Bi solder was completely transformed into an intermetallic compound during the first run. In particular, the first peak at 201ºC in Fig. 6(a) is not detected in Fig. 6(b), while the second peak is repetitively observed at 271ºC in both Figs. 6(a) and 6(b). It is assumed that the endothermic first peak detected at around 201°C is the melting phenomenon of Sn-bearing Bi phases. The Sn solubility in a Bi phase is extremely low; however, the solidus temperature of a Sn-bearing Bi phase is strongly dependent on the Sn content in the Bi phase [10]. The melting of a Sn-bearing Bi phase might induce a continuous exothermic reaction between Sn and Cu, which is observed in the temperature range of 200ºC to 230ºC in Fig. 6(a). Finally, the endothermic second peak observed at around 271ºC was analyzed as the melting of pure Bi, because the metallic reaction between Sn in solder and Cu leaves pure Bi phases. It is clearly confirmed that the second peak coincides with the melting temperature of pure Bi at 271.4ºC [10].

In general, it is known that the initial metallic reaction between the Cu and Sn in Sn/58Bi solder generates an intermetallic compound of Cu_6Sn_5 with a melting temperature of 415ºC [11]. Therefore, it is understood that the Cu_6Sn_5 intermetallic compound is formed by the reaction between solid Cu powders and Sn in molten solder during an exothermic reaction at around 143ºC, as shown in Fig. 6(a). From the small exothermic reaction peak observed in the temperature range of 200ºC to 230ºC in Fig. 6(a), it can be assumed that the Sn ingredient in the remaining Sn-bearing Bi phases continuously reacts with the Cu until the Sn component is completely exhausted. Then, pure Bi is finally educed from Sn/58Bi. This assumption corresponds exactly with the results of the second run in Fig. 6(b).

To check the electrical passage introduced in Fig. 1(b), a cross-section of the hybrid Cu paste after processing was analyzed using an SEM-EDX as shown in Fig. 7. Figure 7(a) shows a photograph of the Cu particles wetted and reacted by the solder, while Figs. 7(b) and 7(c) show the material composition measured by the EDX. From Figs. 7(b) and 7(c), it can be seen that the light gray color of Area A is a pure Bi phase, while the heavy gray color of Area B is a Cu_6Sn_5 intermetallic compound. From Fig. 7(a), it is clearly seen that the Cu particles are completely wetted and reacted by the solder to form an electrical passage, which was previously assumed from Fig. 1. Therefore, it is concluded that the three kinds of endothermic peaks indicating a Sn-bearing Bi phase at 201ºC, a pure Bi at 271ºC, and Cu_6Sn_5 at 415ºC (not shown in Fig. 6(a)) are caused by the exothermic reaction at around

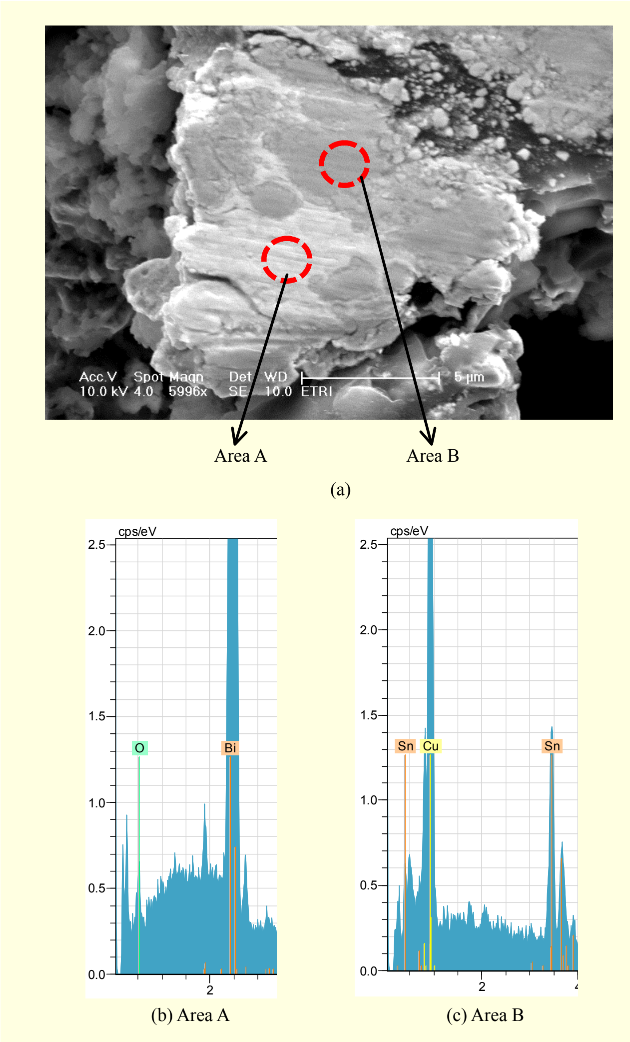

Fig. 7. Measurement results of SEM-EDX with hybrid Cu paste after curing process: (a) SEM photograph, (b) EDX of Area A, and (c) EDX of Area B.

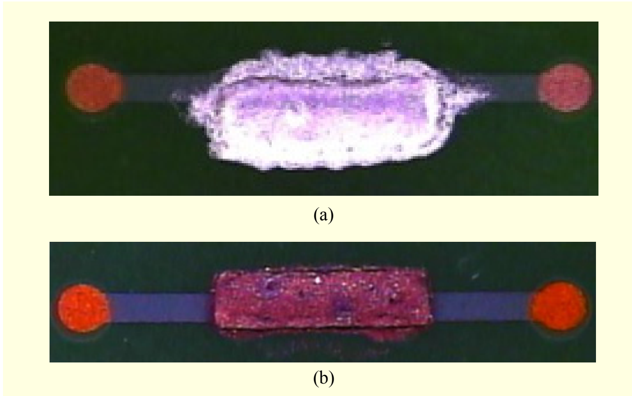

Fig. 8. Photographs of conductive pastes after curing process: (a) commercial Ag paste and (b) hybrid Cu paste.

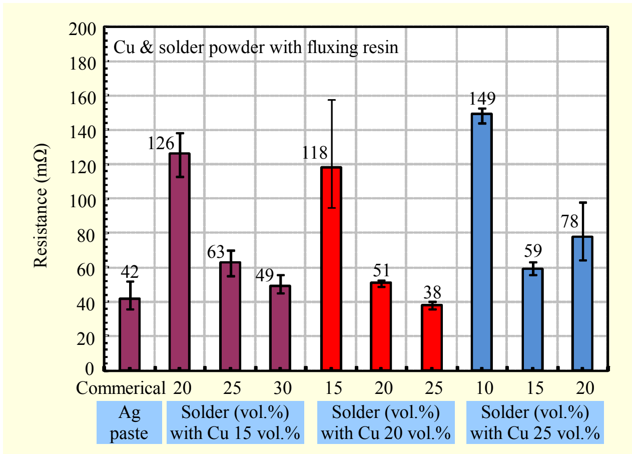

Fig. 9. Comparison of measured electrical resistance according to different compositions of hybrid Cu paste.

143ºC shown in Fig. 6(a). However, a further in-depth study concerning the intermetallic compound will not be conducted because the accurate identification of the intermetallic composition is out of the scope of the present research.

Figure 8 shows photographs of screen printed samples with a metal mask on the PCB substrate shown in Fig. 3(a), where Fig. 8(a) is commercial Ag paste and 8(b) hybrid Cu paste. The same volume of each conductive paste was applied on PCB substrates. However, the area of the Ag paste is larger than the hybrid Cu paste because the viscosity of the commercial Ag paste is relatively lower than the hybrid Cu paste at room temperature. The electrical resistance is compared in Fig. 9 based on the 4-point probe method used to measure the electrical resistance without the contact resistance of probes. To determine the optimum volumetric mixing ratio of Cu, solder, and fluxing resin under a maintained appropriate viscosity allowing its processing, the volume percentages of the Cu flakes were first decided as 15%, 20%, and 25%, while that of the solder was changed from 10% to 25%. The average electrical resistance of the commercial Ag paste and hybrid Cu paste with 20 vol.% of Cu, 25 vol.% of solder, and 55 vol.% of fluxing resin are 42 mΩ and 38 mΩ, respectively. The average value of electrical resistance was obtained from 30 samples each for a high reliability of the measured data.

For verification of the material reliability, the electrical resistances of the 30 samples made from the two types of conductive paste were measured under 85ºC and 85% relative humidity for 6 weeks, as shown in Fig. 10. Before the reliability test, the electrical resistances were 42 mΩ for the commercial Ag paste and 41 mΩ for the hybrid Cu paste with the volumetric mixing ratio of 20% Cu, 25% solder, and 70% the fluxing resin. After 1 week (168 h), which means a reliability condition of JEDEC level 1, the electrical resistance of the commercial Ag paste and hybrid Cu paste were increased up to 45 mΩ (7%) and 46 mΩ (12%), respectively.

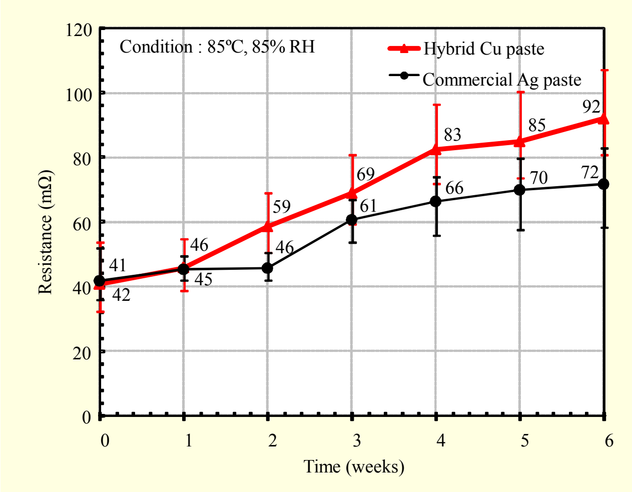

Fig. 10. Comparison of the electrical resistance with conductive pastes under reliability condition of 85ºC and 85% relative humidity for 6 weeks.

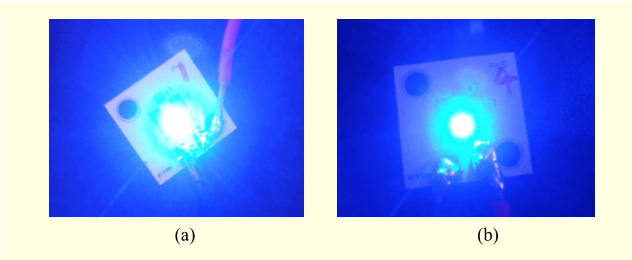

Fig. 11. Photographs of LED package with applied current of 400 mA: (a) with the commercial Ag paste and (b) hybrid Cu paste.

During the 6 weeks, the electrical resistances were continuously increased to 72 mΩ (71%) for the commercial Ag paste and 92 mΩ (124%) for the hybrid Cu paste. However, it is believed that the electrical performances of both conductive pastes are excellent for industrial application even though that of the hybrid Cu paste is lower than commercial Ag paste.

For an evaluation of the novel type of conductive paste, the commercial Ag paste and hybrid Cu paste were applied to the packaging of an LED as shown in Fig. 11. When a current of 400 mA was applied to both LED packages, the measured voltage of the LED packages with the commercial Ag paste and hybrid Cu paste were 3.36 V and 3.32 V, respectively. As shown in Fig. 11, the white area in Fig. 11(a) is larger than that in Fig. 11(b) because the color of the commercial Ag paste is bright silver, while that of the hybrid Cu paste is dark brown. To check the thermal conductivity of both materials, the temperature on the backside surface of the LED package was measured as 68ºC for the commercial Ag paste and 66ºC for the hybrid Cu paste. Therefore, it is believed that the hybrid Cu paste shows a compatible performance from the view point of electrical and thermal conductivity, while the characteristics of the light reflection were relatively low. In particular, the cost of raw material using Cu and solder is about 100 times cheaper than that of silver.

In conclusion, the hybrid Cu paste using a novel concept for a conductive mechanism may be widely used instead of the commercial Ag paste in the near future because its physical and economical competitiveness, with the exception of its optical performance, are almost compatible with existing Ag paste.

IV. Conclusion

To substitute Ag paste as an isotropic conductive adhesive, a hybrid Cu paste composed of Cu, solder powders, and fluxing resin was developed and characterized using a novel concept of electrical conductivity. In previous research [4]-[9], the fluxing resin system was investigated to have a function to remove the oxide layer formed on the surface of Cu and solder particles. The mechanism of electrical conductivity was carefully characterized through an analysis using DSC and SEM-EDX. It was clearly proved that the electrical and thermal performances are almost similar with the existing Ag paste. Therefore, the hybrid Cu paste may be used instead of Ag paste because the material costs of hybrid Cu paste are almost 100 times cheaper.

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