



Full Length Article

Enhancement in electrical conductivity of pastes containing submicron Ag-coated Cu filler with palmitic acid surface modification



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ABSTRACT

The fabrication and applied use of submicron Ag-coated Cu (Cu@Ag) particles as a filler material for epoxy-based conductive pastes having the advantages of a lower material cost and antioxidation behavior were studied. Submicron Cu@Ag particles were successfully prepared and surface-modified using palmitic acid. Diffuse reflectance infrared Fourier transform spectroscopy and thermogravimetric differential scanning calorimetry results indicated the formation of an organic layer by the chemical interaction between the Cu@Ag surface and palmitic acid and the survival of the organic layer after treatment at 160 °C for 3 h in air. The printed pastes containing both commercial micron Cu@Ag flakes and the fabricated submicron Cu@Ag particles showed a greatly reduced electrical resistivity ($4.68 \times 10^{-4} \Omega \text{ cm}$) after surface modification compared to an initial value of $1.85 \times 10^{-3} \Omega \text{ cm}$ when cured.

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1. Introduction

In recent years, Ag-coated Cu (Cu@Ag) particles have been studied as an alternative to pure Ag fillers for resin-based interconnection pastes in the electronics industry owing to high material costs. Cu is a promising candidate owing to its low cost and similar electrical resistivity compared to Ag. As such, Cu can be used as a core material with an Ag coating on the Cu surface to prevent Cu oxidation [1–6].

Because submicron-sized filler particles can fill the vacant spaces formed between the micron-sized fillers in a conductive paste, these particles can be used as additional filler materials to improve the electrical conductivity of the paste without increasing the paste's viscosity when adding an optimal amount of filler [7,8]. However, the excessive addition of submicron conductive filler particles can decrease the electrical conductivity of the paste owing to the increased physical contact within the microstructure of the cured paste [9]. Moreover, techniques for increasing the electrical conductivity are required when using conductive filler particles to obtain a higher quality paste. To this end, diverse methods such as low-temperature sintering using nanoparticles

[10,11], an increase in the shrinkage rate of the resin during curing [12], and a reduction in the metal oxide [13,14] have been examined. Among them, surface modification of the fillers may be an effective method to increase the electrical conductivity with only minor changes [1,15–17]. For example, Zhang et al. formulated a paste with a bulk resistivity of $1.3 \times 10^{-3} \Omega \text{ cm}$ using Cu@Ag flakes and decreased the resistivity to $2.4 \times 10^{-4} \Omega \text{ cm}$ by modifying the flakes with an amine-based silane coupling agent [1]. This study examines the electrical conductivity of a paste containing submicron-sized Cu@Ag particles with and without surface modification using palmitic acid. Palmitic acid is a fatty acid whose surface modification characteristics have not yet been reported. The Cu@Ag filler used here was a mixture of two types of micron-size flakes and submicron-sized spheres.

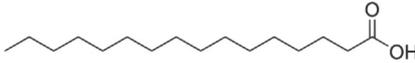
2. Materials and methods

Submicron-sized core Cu particles were synthesized in-house using a polyol solution. A mass of 635 g of synthesized Cu particles was dispersed in 3 L of propylene glycol ($\text{C}_3\text{H}_8\text{O}_2$, 99.9%, SKC) by stirring. The Ag plating solution was fabricated by completely dissolving 1.178 mol of silver nitrate (AgNO_3 , 99.8%, Samchun Pure Chemical Co., Ltd.) in 100 mL ammonium hydroxide (NH_4OH , 28%, Junsei Chemical Co., Ltd.). As a reducing agent, 2 mmol of L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, reagent grade, Aldrich Chemical Co.) was dissolved

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Table 1
Chemical and physical properties of palmitic acid.

Surface-modifying agent	Chemical formula	Chemical Structure	Melting point (°C)	Boiling point (°C)
Palmitic acid	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$		62.9	351

in the Cu solution; then, the Ag plating solution was injected drop-wise (injection rate: 3.3 mL/min) into the Cu solution with continuous stirring at room temperature (RT). The Ag plating process was repeated three times in order to fabricate Cu@Ag particles containing ~15 wt% Ag. After the final plating, the mixed solution was stirred for 1 h, and submicron Cu@Ag particles were obtained after washing with ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, 95%, Korea Alcohol Industrial Co., Ltd.) and drying at RT.

Palmitic acid (95%, Daejung Chemicals and Metals Co., Ltd.) was used as a surface-modifying agent for the fabricated submicron Cu@Ag particles. Table 1 summarizes the chemical structure and physical properties of palmitic acid. After 50 mmol of palmitic acid was completely dissolved in 100 mL of ethyl alcohol, 5 g of submicron Cu@Ag powder was dispersed in the surface treatment

solution for 24 h with continuous stirring at 200 rpm. After that, the powder in the mixed solution was washed using ethyl alcohol in two centrifugation steps at 7000 rpm for 3 min and once again using methyl alcohol (CH_3OH , 99.9%, Shell Chemical Co.). The surface-treated Cu@Ag powder was dried in vacuum at RT.

The morphology and size of the surface-treated Cu@Ag particles were observed using field-emission scanning electron microscopy (FE-SEM, JSM-7500F, JEOL Ltd.). Fourier transform infrared spectroscopy (FT-IR, IR670, Agilent Technologies) was performed to characterize the chemical bonding of the organic molecules on the particle surfaces. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS, Praying Mantis, Harrick) was used to determine the extent of organic bonding on the surface. To evaluate the weight change and heat flow behavior of the surface-

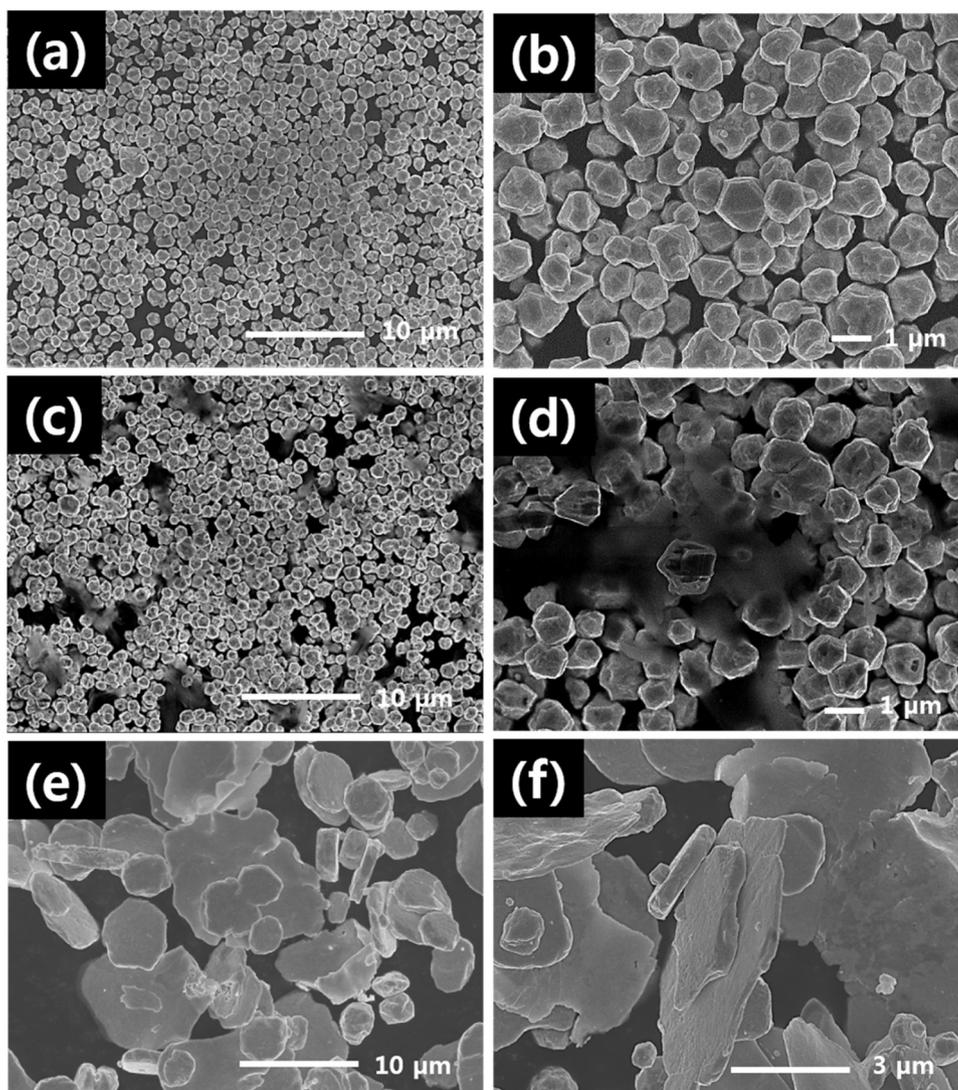


Fig. 1. (a) Low- and (b) high-magnification SEM images of submicron-sized initial Cu@Ag particles, (c, d) Cu@Ag particles surface-treated using palmitic acid, and (e, f) micron-sized Cu@Ag flakes used as a conductive filler.

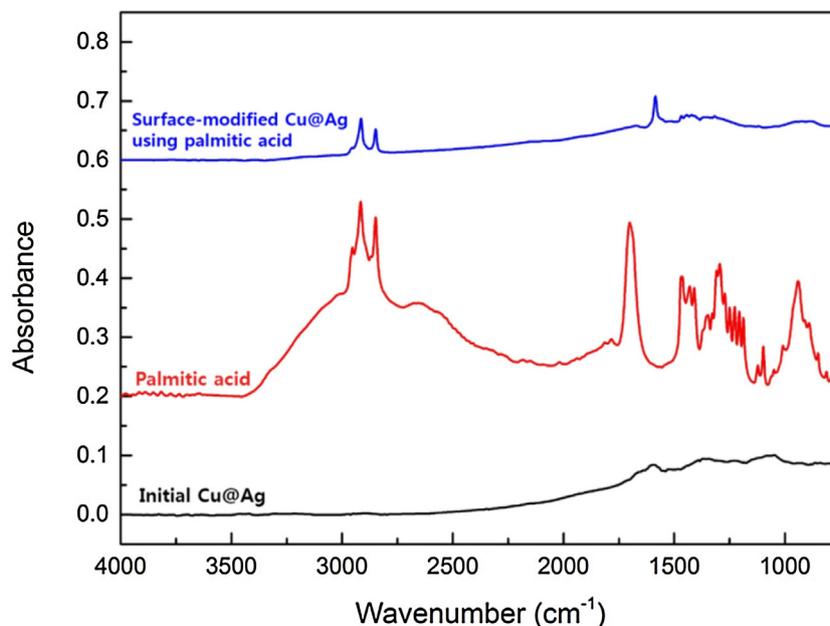


Fig. 2. DRIFT spectra of the initial Cu@Ag particles, palmitic acid, and Cu@Ag particles surface-modified with palmitic acid.

modified Cu@Ag particles during heating in air, thermogravimetric differential scanning calorimetry (TG-DSC, Q600, TA Instruments, in KBSI PH407 Pusan) was also conducted in both the dynamic and isothermal heating modes. During dynamic heating, 20 mg of surface-modified Cu@Ag powder was continuously heated to 400 °C at a heating rate of 10 °C/min under an air purge. During isothermal heating, the same amount of powder was rapidly heated to 160 °C at a heating rate of 20 °C/min and maintained for 3 h at 160 °C under an air purge.

To measure the electrical properties of the surface-modified Cu@Ag particles, pastes were created by mixing with an epoxy resin (bisphenol-A-type liquid epoxy resin diluted with aliphatic glycidyl ether, YD-114, epoxide equivalent weight: 190–210, Kukdo Chemical Co., Ltd.), a curing agent (imidazole, Curezol 2E4MZ, Shikoku Chemicals Co.), and the Cu@Ag powder at a resin formulation concentration of 20 wt%, a concentration of 40 wt% for the commercial micron-sized Cu@Ag flakes (CFL07S, Join M) with/without surface modification, and a concentration of 40 wt% for the submicron-sized Cu@Ag particles with surface modification. The paste was printed on a glass slide through a $10 \times 10 \times 0.1$ mm³ slit volume using a stencil mask. The printed paste was cured at 160 °C for 2 h in air. The electrical resistance was measured by a four-point probe linked to a source meter (2400, Keithley) ten times, and the average values and standard deviations were calculated from these data.

3. Results and discussion

Fig. 1 shows SEM images of the submicron-sized Cu@Ag particles with and without the surface treatment and the commercial micron-sized Cu@Ag flakes. The fabricated Cu@Ag particles have polygonal shapes with an average diameter of 0.975 ($\sigma = 0.195$) μm (Fig. 1(a, b)). The detailed characterization of the particles including the coverage of the Ag shell and the antioxidation properties has been reported in a previous study [18]. Compared to the initial Cu@Ag particles, some aggregation between the particles was observed after the palmitic acid surface treatment, and some regions of the Cu@Ag particles were not clearly observed owing to existence of excessive organic matter (Fig. 1(c, d)). In addition, some electron charging occurred in these regions, as organic matter is typically nonconductive [19]. Further, the SEM images of the

commercial micron Cu@Ag flakes (Fig. 1(e, f)) indicated irregularly shaped particles with a size of 6.5–7.2 μm .

The DRIFT spectra of the submicron Cu@Ag particles before and after the surface treatment as well as pure palmitic acid are displayed in Fig. 2. Although there were no strong peaks for the initial Cu@Ag particles, C–H stretching peaks in $-\text{CH}_2-$ were observed at 2900–2800 cm^{-1} in the surface-treated particles arising from the long C–H chain in palmitic acid (Table 1) [20]. For pure palmitic acid, the sharp and strong peak at 1700 cm^{-1} indicates C=O double bond stretching in the carboxyl ($-\text{COOH}$) groups, and the peaks at 1560–1410 cm^{-1} indicate carboxyl ($-\text{COO}^-$) groups [21–24]. By comparison, the stretching peak at 1700 cm^{-1} disappeared, and a new peak at 1585 cm^{-1} appeared in the spectrum for the Cu@Ag particles surface-treated with palmitic acid, and the same stretching peaks at 1560–1410 cm^{-1} were also observed in the sample. The peak at 1585 cm^{-1} likely indicates a C=O bond, and this shift from 1700 cm^{-1} to 1585 cm^{-1} suggests a chemical interaction between the Ag coating shell and the C=O bonding in the carboxyl group of palmitic acid [25,26]. The peaks at 1560–1410 cm^{-1} in the surface-treated Cu@Ag particles indicate this chemical interaction as well. Therefore, these results imply the presence of an organic layer bonded to the Cu@Ag particle surface.

Fig. 3 shows the TG and DSC curves of the surface-modified submicron Cu@Ag particles during dynamic heating. The total weight of the initial Cu@Ag particles slightly decreased up to a maximum value of 0.16% at 246 °C because of the elimination of the residue remaining on the Cu@Ag particles after fabrication. This weight then increased around 246 °C (determined at the point of 0.1% weight gain from the minimum weight), indicating oxidation of the Cu@Ag particles. Previously, the oxidation of Cu@Ag particles has occurred during air heating at temperatures >200 °C owing to the dewetting of the Ag shell primarily due to the unstable interfacial energy, thereby exposing the core Cu to hot air [27,28]. In the surface-modified Cu@Ag particles, a greater weight loss was observed. The total weight loss reached 1.09% at 257 °C, which is ascribed to the decomposition of the organic layer on the Cu@Ag surface. After that, the particles were oxidized with similar behavior to that of the initial particles.

The heat flow results during dynamic heating in air are shown in Fig. 3(b). Both Cu@Ag particles displayed two exothermic peaks

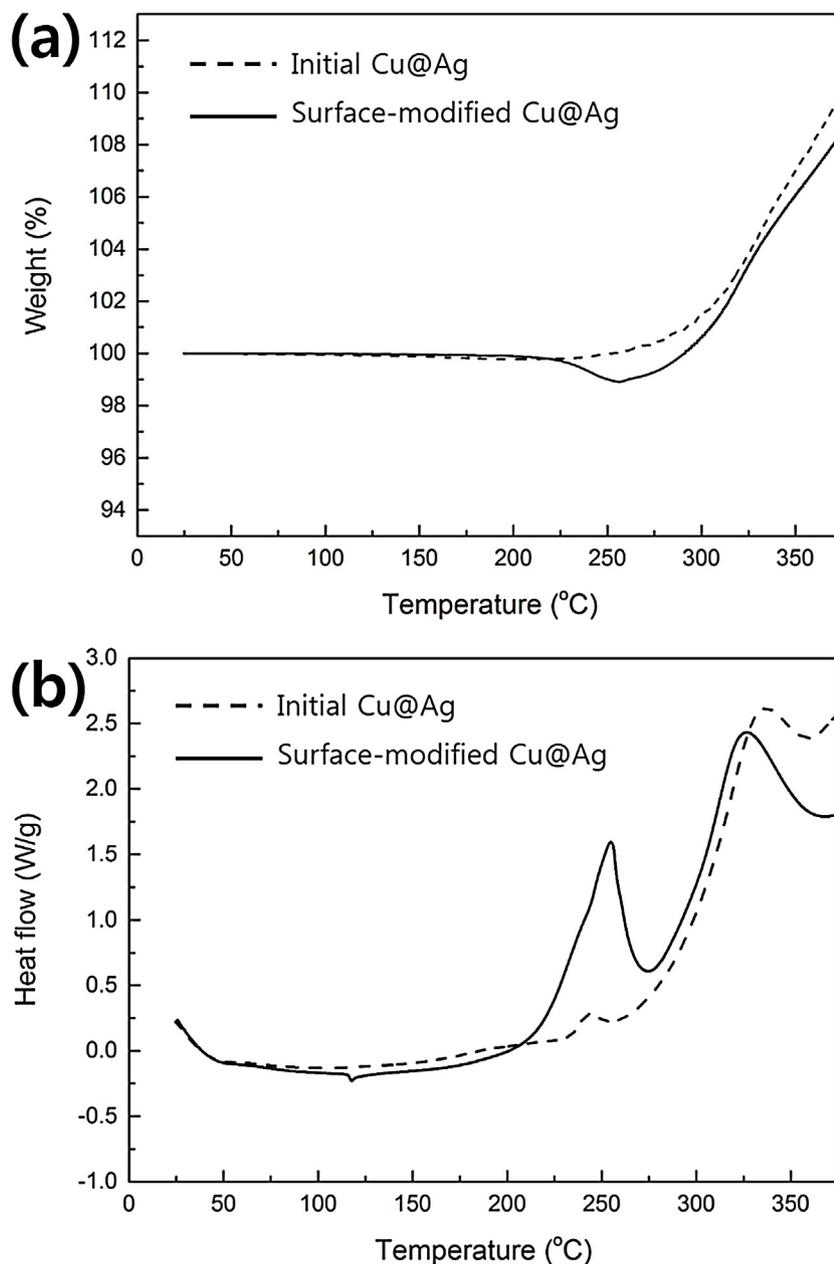


Fig. 3. (a) TG and (b) DSC curves of surface-modified submicron Cu@Ag particles during dynamic heating.

during heating up to 350 °C. The first exothermic peak for the initial Cu@Ag particles was weak at 244 °C, while the second was strong. The first exothermic peak corresponded well with the oxidation initiation temperature of 246 °C in Fig. 3(a), while the second was well-fitted to the dramatically increasing weight in Fig. 3(a). In the case of surface-modified Cu@Ag particles, however, both exothermic peaks at 255 °C were strong. Therefore, the appearance of the first peak can be attributed to the oxidation of an organic layer on the Cu@Ag surface. The C and H atoms in palmitic acid can easily react with O in air to form CO₂ and H₂O, simultaneously creating an exothermic peak and causing weight loss due to the decomposition of the organic layer.

The TG and DSC graphs of the surface-modified Cu@Ag particles during isothermal heating are presented in Fig. 4. In the case of the initial Cu@Ag particles, 0.15% weight loss was observed at 160 °C (heating rate: 20 °C/min). This is similar to the maximum

weight loss of the initial Cu@Ag particles during dynamic heating in Fig. 3(a), implying that this 0.15% weight loss occurs by the elimination of surface residue. On the other hand, the weight of the surface-modified Cu@Ag particles continuously decreased up to 0.51% after 3 h, indicating the decomposition of the organic layers. The amount of weight lost was lower than that of the surface-modified Cu@Ag particles in Fig. 3(a), as the temperature was lower than that in Fig. 3. Moreover, the heat flow curves during isothermal heating did not reveal any striking exothermic results akin to those in Fig. 3(b), indicating that the oxidation of Cu@Ag particles is relatively minor at 160 °C. Moreover, no exothermic peaks due to organic layer decomposition were present for the surface-modified Cu@Ag particles. Consequentially, the submicron sized Cu@Ag particles have antioxidation behavior for 3 h at 160 °C in air, and the palmitic acid layer on the Cu@Ag surface was not entirely decomposed under these conditions.

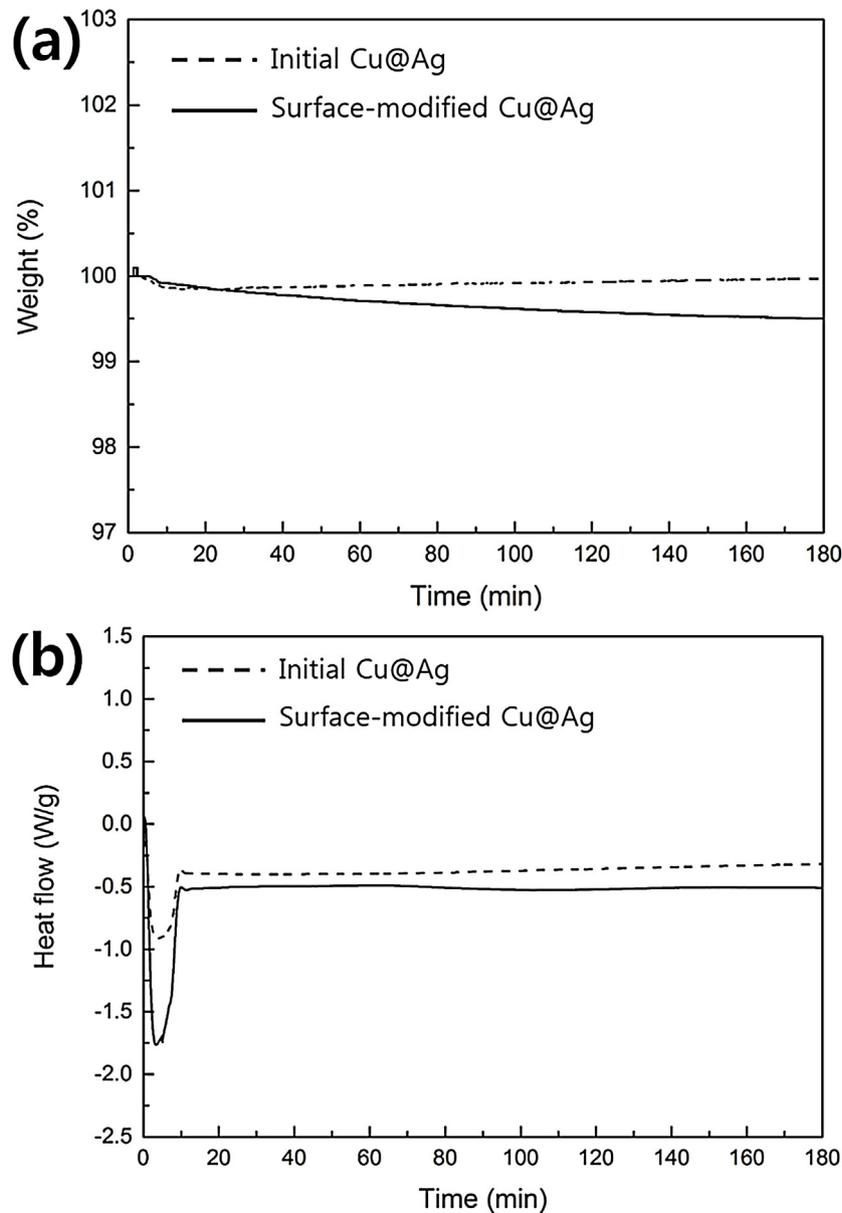


Fig. 4. (a) TG and (b) DSC curves of surface-modified submicron Cu@Ag particles during isothermal heating at 160 °C.

Fig. 5 shows the electrical resistivity of the cured films of pastes containing both submicron Cu@Ag particles and micron Cu@Ag flakes with surface modification. In the paste containing two types of initial fillers without surface modification, the average electrical resistivity was 1.85×10^{-3} ($\sigma = 3.12 \times 10^{-4}$) Ω cm. When only the submicron Cu@Ag particles were surface-modified, the sample exhibited a lower electrical resistivity of 7.28×10^{-4} ($\sigma = 1.01 \times 10^{-4}$) Ω cm. The minimum value of 4.68×10^{-4} ($\sigma = 3.14 \times 10^{-5}$) Ω cm was obtained when both Cu@Ag fillers were simultaneously surface-modified. In addition, the standard deviations of the electrical resistivity also decreased with increased surface modification. These results indicate that the surface modification of Cu@Ag fillers using palmitic acid is effective for enhancing the electrical conductivity of these pastes. Therefore, the results presented here describe the fabrication of a low-cost submicron-sized filler material with enhanced electrical conductivity by surface modification using palmitic acid.

The organic layer that forms on the particle surface using palmitic acid can play an important role in the construction of conducting paths during curing, which affects the electrical conductivity, as depicted in Figs. 6 and 7. First of all, the organic layer on the surface-modified particles may provide superior dispersion behavior by suppressing the aggregation between particles during mixing for the preparation of the paste [17,24]. In particular, the improvement is more effective for the submicron particles. The superior dispersion permits each submicron particle to settle to the vacant spaces between particles separately, which mainly increases the number of contacts between the micron flakes and broadens the contact area (Figs. 6 (c, d) and 7 (b)). Hence, the increase in the number of contact points per unit area is clearly beneficial for enhancing the electrical conductivity of the cured paste. Moreover, the nontreated submicron particles take their place instead of the micron flakes, increasing the number of contact points per unit length because of their behavior as a cluster due to the aggregation between particles (Figs. 6 (a, b) and 7 (a)). The increased number of

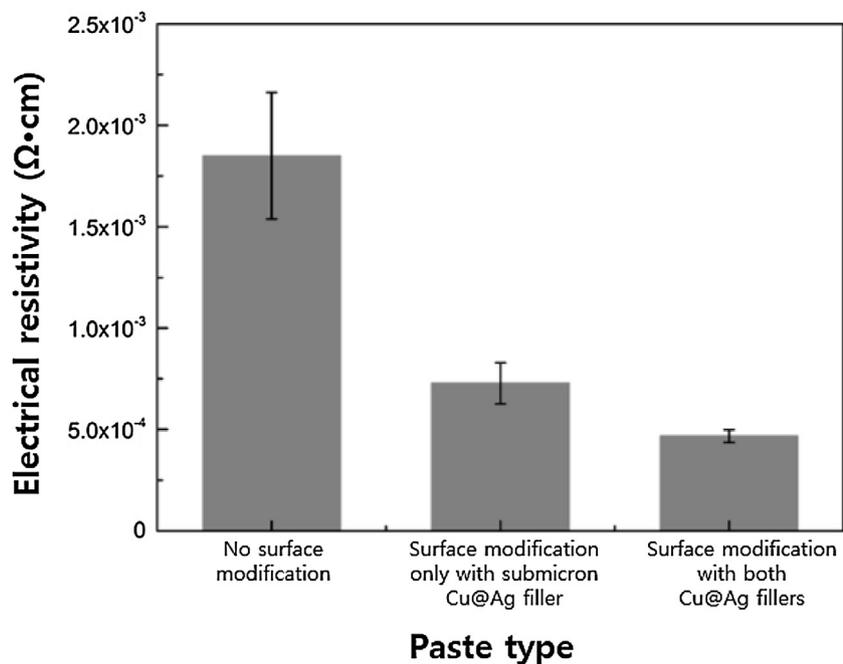


Fig. 5. Electrical resistivities of paste samples containing both submicron Cu@Ag particles and micron Cu@Ag flakes for various surface modifications using palmitic acid.

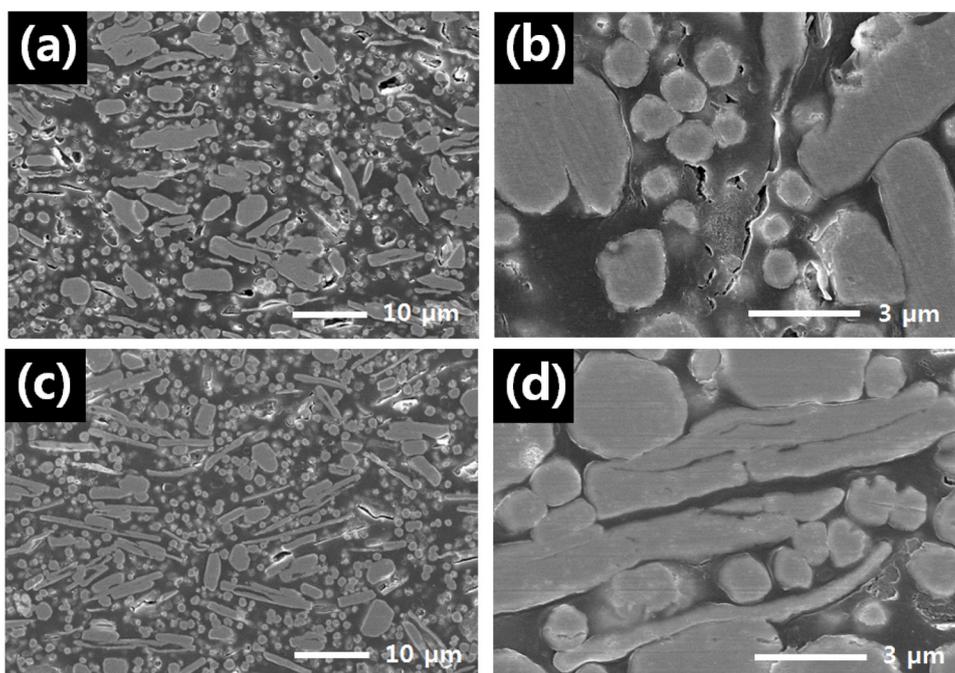


Fig. 6. Low- and high-magnification SEM images showing the cross-sectional microstructures after curing the pastes containing (a, b) normal Cu@Ag particles and (c, d) surface-modified Cu@Ag particles.

contact points per unit length becomes detrimental to the electrical conductivity of the cured paste.

4. Conclusions

Submicron Cu@Ag particles were successfully fabricated and surface-modified using palmitic acid. The DRIFTS data of these particles clearly indicated the formation of chemical bonding between

the Cu@Ag surface and the C=O bonds in the carboxyl group of palmitic acid. Moreover, TG and DSC results confirmed the existence of an organic layer by chemical interaction and indicated that the organic layer was not entirely decomposed after 3 h of heating at 160 °C in air. The printed pastes containing both commercial micron Cu@Ag flakes and the fabricated submicron Cu@Ag particles exhibited a greatly reduced electrical resistivity of $4.68 \times 10^{-4} \Omega \text{ cm}$ after surface modification compared to the initial

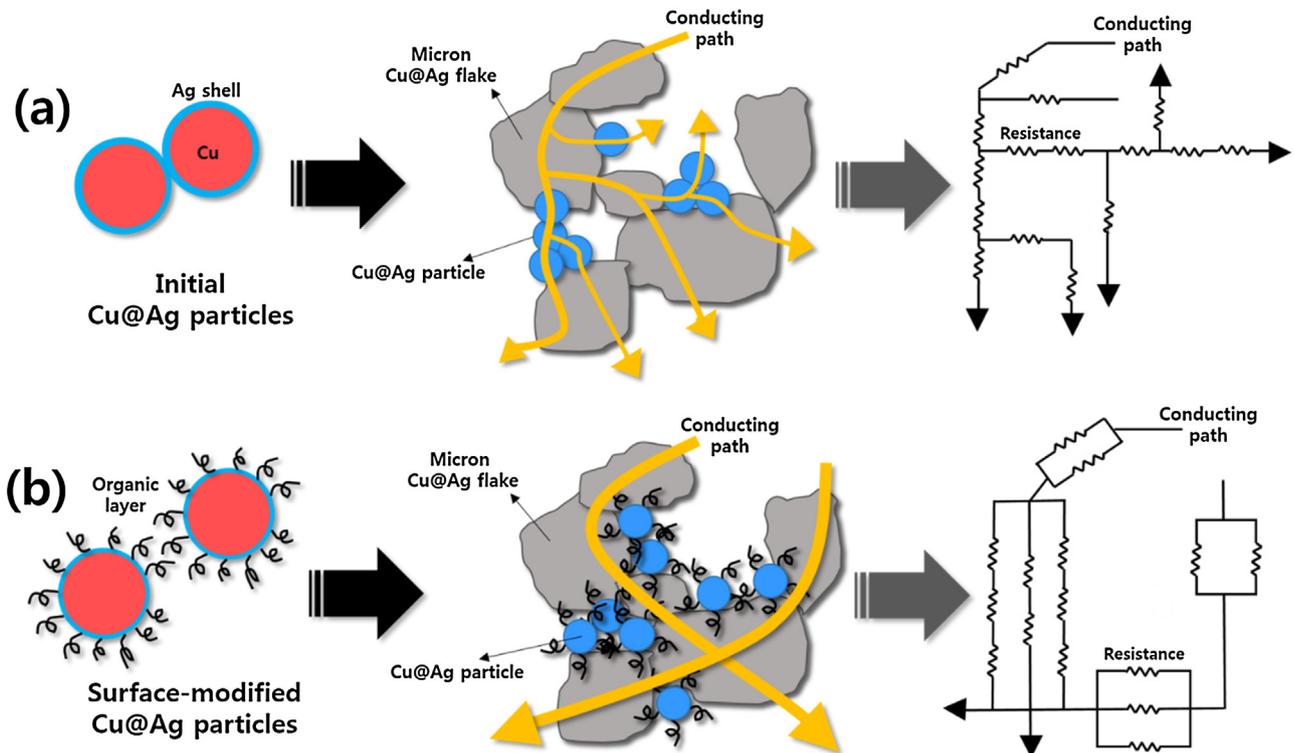


Fig. 7. Schematics showing the formation of conducting paths during paste curing containing (a) normal Cu@Ag particles and (b) surface-modified Cu@Ag particles.

value of $1.85 \times 10^{-3} \Omega \text{ cm}$ upon curing. These improved electrical properties were attributed to the superior dispersion behavior by suppressing the aggregation between particles and the consequent increase in the number of contact points per unit area.

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