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Submicron Ag-coated Cu particles and characterization methods to evaluate their quality

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ABSTRACT

Three different types of submicron particles, pure Cu, Cu@Ag prepared without a reductant, and Cu@Ag prepared with a reductant (L-ascorbic acid), were fabricated, and two characterization methods, direct pelletization and curing of paste containing the particles, were used to evaluate the average quality of the submicron particles for use as a conductive filler. The fabricated Cu particles exhibited a polygonal shape and a smooth surface; the Cu@Ag particles prepared without a reductant showed tiny bumps lightly formed on the surfaces; and the Cu@Ag particles fabricated with an L-ascorbic acid indicated very rough surfaces. The Ag shell in the particles fabricated without a reductant was thinner than that in the particles fabricated with the reductant. In the as-pelletized samples, the sample containing the particles fabricated with the reductant exhibited a slightly high electrical resistivity; the slight change in the resistivity was interpreted in terms of difference in the contact area between the particles after pelletization. The as-pelletized samples after oxidation showed a striking difference in the resistivities of pure Cu particles and the Cu@Ag particles fabricated without a reductant. However, the Cu@Ag particles fabricated with the reductant presented a nearly consistent resistivity with a superior antioxidation property. When the resistivities of the films was measured after curing the paste co-containing micronsized Cu@Ag flakes and submicron particles, it was confirmed that the pure Cu particles and Cu@Ag particles prepared without a reductant are oxidized in the paste during curing. In contrast, the paste containing Cu@Ag particles fabricated with the reductant presented the lowest resistivities, which were 2.85×10^{-3} and $8.90 \times 10^{-4} \,\Omega$ cm in air and nitrogen, respectively, indicating the strongest antioxidation behavior than the other pastes.

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1. Introduction

Ag powder has been extensively used as a filler material in various conductive pastes owing to its low bulk/contact electrical resistivity and excellent resistance to oxidation [1-5]. However, high price of Ag is a significant impediment to their industrial application as an electronic material. This has led to Cu being considered as an alternative to Ag, as it offers similar resistivity to that of Ag at a much lower cost. However, pure Cu is vulnerable to surface oxidation in air even at room temperature, and this oxidation becomes more severe with increasing temperature [6-8]. To overcome this problem while still reducing the material cost, the fabrication and application of Ag-coated Cu (Cu@Ag)

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The use of novel hybrid pastes, a recent trend in conductive paste technology, can be considered. For example, Eom et al. prepared a hybrid paste containing both solder powder and Cu particles as the filler and confirmed the processibility and superior thermal conductivity of the hybrid paste when used as a chip bonding material [14]. In the paste, the Cu particles can be exchanged with Cu@Ag particles in order to enhance the processibility and property [15]. Moreover, if tiny Cu@Ag particles that can be settled in the vacant space between the existing particles of the solder and micron-sized Cu@Ag are additionally added, the thermal conductivity would be enhanced with a slight change in the paste viscosity [16]. Thus, we believe that Cu@Ag filler particles in the submicron size range can be used in the conductive pastes.

The average quality of Cu@Ag particles has been checked by using an indirect evaluating method such as by measuring electrical conductivity in the cured film prepared by using the paste filled





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with Cu@Ag particles. For example, R Zhang et al. formulated the paste with bulk resistivity of $1.3 \times 10^{-3} \Omega$ cm using Cu@Ag flakes, and the resistivity decreased down to $2.4 \times 10^{-4} \Omega$ cm after the flakes modified by an amine-based silane coupling agent [10]. However, a paste containing only tiny conductive particles such submicrometer-scale Cu@Ag might not present electrical conductance or present outstandingly high electrical resistivity in the quality evaluation [17]. Therefore, two characterization methods to evaluate the average quality of submicron Cu@Ag were explored in this study: direct pelletization and curing of paste containing Cu@Ag particles. Three different types of submicron particles were prepared depending on whether the particles were coated with Ag and whether a reductant was used during the Ag coating, and the quality of each type was evaluated by using the characterization methods mentioned above.

2. Experimental

The submicron Cu particles, whose surface would be coated with Ag, were synthesized in-house by a polyol method using propylene glycol ($C_3H_8O_2$, 99.9%, SKC) and a surfactant. After the synthesis, about 1 M pure Cu particles were suspended in 300 mL of the solution. A Ag precursor solution was prepared by completely dissolving 1.178 M of silver nitrate (AgNO₃, 99.8%, Sooshin Chemical Co., Ltd.) in 30 mL ammonium hydroxide (NH₄OH, 25%, OCI Company Ltd.).

The Ag coating was made by using two methods depending on whether a reductant was used. When the reductant was not used, the Ag precursor solution was simply injected dropwise (at an injection rate of 3 mL/min) into the Cu solution under continuous stirring (300 rpm). After conducting the reaction for 1 h under continuous stirring, the mixed solution was centrifuged at 7000 rpm for 3 min. Then, the supernatant was decanted and the slurry was refilled with ethyl alcohol (C_2H_5OH , 95%, Samchun Pure Chemicals Co.). Additional medium-exchanging steps were performed by using ethyl alcohol and centrifugation process, and the solution was condensed by removal of supernatant after the last cycle. The final dried Cu@Ag Cu particles were obtained after drying them at room temperature in a low-vacuum chamber.

When L-ascorbic acid ($C_6H_3O_6$, reagent grade, Aldrich Chemical Co.) was used as the reductant, the Ag precursor solution was prepared by dissolving 1.178 M of silver nitrate in 10 mL of ammonium hydroxide, and the Ag precursor solution was injected at the same rate into the Cu solution prepared by dissolving 2 mM of L-ascorbic acid. The holding time after the injection was 10 min, and another 10 mL Ag precursor solution was re-added after the interval; this addition was repeated three times to form 15 wt% Ag shell. The final mixed solution was maintained for 1 h under 300 rpm stirring. Subsequent medium-exchanging and drying steps were identical to those used in the abovementioned procedures.

The size and morphology of Cu or Cu@Ag Cu filler were investigated by field emission-scanning electron microscopy (FE-SEM, JSM-7500F, JEOL Ltd.), and the weight of silver used in the filler and the line intensity profile of the major elements in the cross-section of the filler were measured by energy dispersive spectroscopy (EDS, 4502A-3UES-SN, Thermo). In addition, thermogravimetricdifferential scanning calorimetry (TG-DSC, Q600, TA Instrument, KBSI PH407 Pusan) analysis was conducted to evaluate the oxidation behavior of Cu and Cu@Ag powders. In a dynamic heating mode, 5 mg of the powder was consistently heated up to 500 °C at a heating rate of 10 °C/min. In the isothermal heating mode, the powder was quickly heated to 160 °C and maintained at that temperature for 3 h.

The electrical property of the synthesized submicron particles

was evaluated using two methods: direct pelletization and curing of paste containing the particles. For the pelletization method, 0.5 g of particles was poured into a mold cavity over a stainless bottom punch of 15 mm diameter and a force of 4900 N was exerted through the upper punch for 1 min. The samples containing the three types of particles, pure Cu, Cu@Ag prepared without a reductant, and Cu@Ag prepared with a reductant (L-ascorbic acid), were prepared by using as-fabricated or oxidized powders. Some pellets were oxidized after pelletization. The oxidation conditions used for the samples were identical to the curing conditions used for the paste, i.e., oxidation medium: air; temperature: 160 °C; and duration: 2 h.

Another method to evaluate the electrical property of submicron particles involves measuring the electrical resistance of a film pattern after curing the paste containing the particles. The resistivity values of the pastes were calculated from the bulk resistance of the cured film pattern. The paste, i.e., the mixture of epoxy (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 a conductive filler, was printed on a glass slide through a stencil mask with the slit volume $10 \times 10 \times 0.1 \text{ mm}^3$ by using a squeegee. Because the electrical conductivity of the paste was not measured by using submicron-sized particles only, 40 wt% of submicron Cu or Cu@Ag particles were mixed again with 20 wt% of the resin formulation after mixing with 40 wt% of commercial micron-sized Cu@Ag flakes (CFL07S, Join M). For the comparison, a paste was prepared by mixing 75 wt% of the micron-sized Cu@Ag flakes and 25 wt% of the resin formulation. The paste pattern filled with the filler was completed by curing the mixture in air or nitrogen (99.999%) at 160 °C for 2 h. The flow rate of nitrogen gas was 100 ml/min. Resistance (R) of the cured pattern was measured with a four-point probe linked to a source meter (2400, Keithley). The total distance between the probes set at an interval of 1 mm was 3 mm. Resistivity, ρ , was calculated from the following equation: $\rho = (Rtw)/l$, where t, w, and l are the thickness, width, and length of the pattern, respectively.

3. Results and discussion

Fig. 1 shows the SEM images and TG-DSC result of micron-sized Cu@Ag flakes used as a basic filler material in this study. The d50 size was $6.5-7.2 \mu m$, and it was found that their surfaces were slightly nonuniform because some surfaces were stained or rough. The TG-DSC result of the flakes measured under dynamic heating in air show progressive increase of weight and formation of an exothermal peak from around 220 °C on increasing temperature, which indicates that the flakes abruptly oxidize owing to the dewetting of Ag shell at the temperature exceeding 200 °C [11–13]. It has been reported that the phenomenon is due to phase separation caused by the positive enthalpy of mixing (104 meV/atom at 50 at.% of Cu) [18], a small difference (0.03) in electronegativity [19], a large lattice mismatch (12%) [20,21], and the instability of the Ag/Cu interface [21]. During the dynamic heating to 200 °C, however, notable oxidation was not observed by stable Ag shells.

The electrical resistivities of the films after curing the paste containing 75 wt% micron-sized Cu@Ag Cu flakes at 160 °C for 2 h were 8.53 \times 10⁻⁴ and 3.39 \times 10⁻⁴ Ω cm for air and nitrogen atmospheres, respectively. As expected from the above TG-DSC result, the resistivities were different each other; the resistivity of the paste cured in nitrogen was lower than that of the paste cured in air. This result confirmed that the micron-sized Cu@Ag Cu flakes slightly oxidize under the actual curing condition when they are used as a filler material.

The SEM images of the submicron Cu particles and submicron



Fig. 1. (a) Low- and (b) high-magnified SEM images of micron-sized Cu@Ag flakes used in this study and (c) their TG-DSC result under dynamic heating to 500 °C.

Cu@Ag particles used in this study are presented in Fig. 2. The submicron Cu@Ag particles were fabricated by using two methods (without or with the addition of a reductant). The Cu particles (Fig. 2(a) and (b)) fabricated in-house exhibited a polygonal shape, indicating an average size of 0.862 ($\sigma = 0.166$) µm and a smooth surface. In addition, the aggregation between the particles was extremely suppressed. The particles (Fig. 2(c) and (d)) coated with Ag without using a reductant on the Cu particles showed tiny bumps formed lightly on the surfaces. The amount of Ag present in the particles was measured as 20.19 wt% in the EDS measurement, because the measurement detects more intensive X-ray signals from the surface region of a particle. Meanwhile, the Cu@Ag particles (Fig. 2(e) and (f)) fabricated using an L-ascorbic acid reductant indicated very rough surfaces. Nevertheless, there was barely any aggregation between Cu@Ag particles. In the EDS measurement, the Ag content was 23.06 wt% in such Cu@Ag particles, which is higher than the previous one.

Although the results shown in Fig. 2 also provide indirect information about the thickness of the Ag shell, EDS line profiling on the cross-section of the particles was conducted to confirm changes in the thickness of the Ag shell as a function of the addition of a reductant (Fig. 3). In contrast to the result obtained with Cu@Ag particles fabricated without a reductant, that obtained with the particles fabricated by adding a reductant showed a significantly high intensity of Ag at the edge of a particle. This means that the Ag shell in the particles fabricated without a reductant is thinner than that in the particles fabricated with a reductant.

Fig. 4 shows the electrical conductivities of the as-pelletized samples, samples oxidized after pelletization, and as-pelletized samples after oxidation as a function of powder type. The following oxidation conditions were used: oxidation medium, air; duration, 2 h; temperature, 160 °C. In the as-pelletized samples, pure Cu, Cu@Ag Cu prepared without a reductant, and Cu@Ag Cu prepared with a reductant presented resistivities of 2.92×10^{-4} , 3.05×10^{-4} , $3.80 \times 10^{-4} \Omega$ cm, respectively. The electrical resistivity

of bulk pure Cu has been reported to be $1.58 \times 10^{-6} \Omega$ cm [22]. The discrepancy in resistivity values could be attributed to the presence of voids in microstructure and the high contact resistance by the physical contact between particles. Although the contact metal in pure Cu and Cu@Ag particles is different from each other, the slight change in the electrical conductivity is interpreted as owing to the difference in the initial contact area between the particles after pelletization because the electrical conductivity in Cu is slightly higher than that in Ag. During pelletization, the number of contact points between the particles changes with the degree of surface roughness; the number would increase with an increase in roughness. The increase in the number of contact points would reduce the plastic deformation of particles in proportion to the increase, with the decrease in initial stress by the increase in initial contact area during the pelletization under the same force of 4900 N (Fig. 5). In contrast, the interparticle region having only one contact point would be severely deformed, thereby tremendously increasing the final contact area in the region. Therefore, the final contact area between pure Cu particles having the smoothest surface after pelletization would be highest and the area would decrease with increasing surface roughness. Thus, the Cu@Ag particles prepared with an L-ascorbic acid reductant might induce a decrease in the final contact area, resulting in a slight increase in electrical resistivity.

In the samples oxidized after pelletization, the slight increase in resistivity was observed in all powder types. It means that the core contact regions between particles are not oxidized even after oxidation, although the contact regions are slightly oxidized under the oxidation condition used. The measured electrical resistivities with pure Cu, Cu@Ag Cu prepared without a reductant, and Cu@Ag prepared with a reductant were 3.47×10^{-4} , 3.36×10^{-4} , and $4.01 \times 10^{-4} \Omega$ cm, respectively. Hence, the degree of oxidation was the highest with pure Cu powder and the lowest with the Cu@Ag powder prepared with the reductant.

A striking difference in the resistivity was observed in the as-



Fig. 2. (a) Low- and (b) high-magnified SEM images of submicron Cu particles and (c, e) low- and (d, f) high-magnified SEM images of submicron Cu@Ag particles using Ag plating without (c, d) or with (e, f) a reductant.



Fig. 3. EDS line profiling on the cross-section of Cu@Ag particle fabricated without (a) or (b) with a reductant.

pelletized samples after oxidation. With the pure Cu powder, the resistivity was very high (8294 Ω cm). The oxidation property of pure Cu is clearly detected from the TG-DSC result (Fig. 6). Even though the measurement was conducted with the dynamic heating mode, the oxidation occurred at around 146 °C. The resistivity value of 17.8 \times 10⁻⁴ Ω cm was measured with the Cu@Ag Cu powder prepared without a reductant, indicating that the powder was considerably oxidized. However, in the Cu@Ag Cu powder prepared

with the reductant, the value was $3.94 \times 10^{-4} \Omega$ cm, which is slightly higher than that of the as-pelletized sample, which implies a suppressed oxidation of the Cu@Ag powder.

Fig. 7 shows the electrical resistivities of the films measured after curing the paste co-containing 40 wt% micron-sized Cu@Ag flakes and 40 wt% submicron particles for 2 h in different atmospheres at 160 °C. Although the resistivity of a film cured in nitrogen was lower than that of a film cured in air in all types of





Fig. 6. TG-DSC result of submicron Cu powder used in this study with a dynamic heating mode.

Fig. 4. Electrical conductivities of as-pelletized samples, samples oxidized after pelletization, and as-pelletized samples after oxidation with different powder types.



Fig. 5. Schematics showing change in the number of contact point and total contact area between particles as a function of surface roughness.

sample, the sample containing pure Cu particles presented an outstandingly high value (1.32 Ω cm) even though it was cured in nitrogen. This indicates that the high-purity (5 N) nitrogen cannot prevent the oxidation of pure Cu particles [23]. The paste containing Cu@Ag prepared without a reductant showed resistivity values of 9.29 × 10⁻³ and 7.92 × 10⁻³ Ω cm in air and nitrogen, respectively, which are between those of pure Cu and Cu@Ag Cu

prepared with a reductant. Thus, it is inferred that the Cu@Ag powders prepared without a reductant was oxidized more than those prepared with a reductant because the imperfect regions in Ag coating might increase owing to the thin Ag shells. Meanwhile, the paste containing Cu@Ag powder prepared with a reductant presented the lowest resistivity values, which were 2.85×10^{-3} and $8.90 \times 10^{-4} \Omega$ cm in air and nitrogen, respectively. This striking



Fig. 7. Electrical conductivities measured as a function of powder type and atmosphere after curing the paste with the powder.

difference between the values implies that the particles (mainly in micron-sized Cu@Ag flakes) in a sample cured in air were oxidized more than those in a sample cured in nitrogen. Consequently, when the paste containing Cu@Ag powder prepared with a reductant is cured in nitrogen, the powder shows the strongest antioxidation behavior and the lowest electrical resistivity than the other powders. However, the resistivity of the Cu@Ag paste cured in nitrogen was higher than that of the as-pelletized Cu@Ag samples after the oxidation treatment. The result is estimated from the strong contact and enlarged contact area between particles by the external pressure during the pelletization.

To compare more closely the antioxidation property between the used commercial micron-sized Cu@Ag flakes and synthesized submicron Cu@Ag particles, TG-DSC analysis was performed under isothermal heating in air at 160 °C, and the results are displayed in Fig. 8. Although striking increase of weight or an exothermal peak was not observed, the isothermal heating made the weight gain keep progressing very slowly. As a result, the times required to obtain 0.1% weight gain were 108.9 and 158.1 min for the used micron-sized Cu@Ag flakes and submicron Cu@Ag particles, respectively. This means that the antioxidation property of submicron Cu@Ag particles is superior to that of micron-sized Cu@Ag flakes, though the results indicate that both flakes and particles gradually oxidize on increasing the exposure time. It is estimated that the oxidation is caused from an incomplete coating of Ag in the flakes.

The comparison of antioxidation property between micronsized Cu@Ag flakes and submicron Cu@Ag particles was also performed using pellet samples (Table 1). In the as-pelletized sample and sample oxidized after pelletization, the electrical resistivities of samples prepared using micron-sized Cu@Ag flakes was lower than those of samples prepared using 100% submicron Cu@Ag particles because the number of contacts between filler per unit length reduces. However, the resistivity trend was opposite in the samples pelletized after oxidation; the resistivity (4.35 × 10⁻⁴ Ω cm) of samples prepared using micron-sized Cu@Ag flakes was distinctly higher than that (3.94 × 10⁻⁴ Ω cm) of samples prepared using submicron Cu@Ag particles. This result indicates again that the antioxidation property of submicron Cu@Ag particles is superior to that of micron-sized Cu@Ag flakes. Because the submicron Cu@Ag particles prepared in this study were successively fabricated using



Fig. 8. TG-DSC result under isothermal heating in air at 160 °C: (a) micron-sized Cu@Ag flakes and (b) submicron Cu@Ag particles.

as-synthesized Cu particles, ammonium hydroxide as a pretreatment agent for removing the surface oxide was not used [24–26]. It has been reported that the pretreatment method using ammonium hydroxide creates defects such as a hole on the surface of Cu particles, finally forming the Cu surface uncoated with Ag or the Cu surface very slightly coated with Ag. Hence, more excellent electrical property of submicron Cu@Ag particles in the samples pelletized after oxidation resistivity is estimated from the enhanced coverage result of Ag coating layer.

4. Conclusions

Submicron Cu particles fabricated in-house exhibited a polygonal shape and a smooth surface; submicron Cu@Ag particles prepared without a reductant showed tiny bumps formed lightly on the surfaces; and submicron Cu@Ag particles fabricated with an Lascorbic acid reductant showed very rough surfaces. Moreover, the Ag shell in the particles fabricated without a reductant was thinner than that in the particles fabricated with the reductant. In the as-

Table 1Electrical resistivities of pellet samples.

Electrical resistivity ($\Omega \cdot cm$)	Micron-sized Cu@Ag flakes	Submicron Cu@Ag particles
As-pelletized Oxidized after pelletization Pelletized after oxidation	$\begin{array}{l} 3.51\times 10^{-4} \\ 3.73\times 10^{-4} \\ 4.35\times 10^{-4} \end{array}$	$\begin{array}{l} 3.80 \times 10^{-4} \\ 4.01 \times 10^{-4} \\ 3.94 \times 10^{-4} \end{array}$

pelletized samples, the sample containing the particles fabricated with the reductant exhibited the highest electrical resistivity and slight changes in the electrical conductivity were interpreted in terms of the difference in the contact area between the particles during the pelletization. In the samples oxidized after pelletization, the slight increase in resistivity was detected in all powder types. However, except the Cu@Ag particles fabricated with the reductant, a striking difference was observed in the resistivities of the pure Cu and Cu@Ag particles fabricated without a reductant in the aspelletized samples after oxidation. With the electrical resistivities of the films measured after curing the paste co-containing micronsized Cu@Ag flakes and submicron particles, the paste containing pure Cu particles showed an outstandingly high value and it was also confirmed that the Cu@Ag particles prepared without a reductant are oxidized in the paste during the curing process. Meanwhile, the paste containing the Cu@Ag powder prepared with the reductant presented the lowest resistivity values, which were 2.85×10^{-3} and $8.90 \times 10^{-4} \Omega$ cm in air and nitrogen, respectively, indicating the strongest antioxidation property than the other powders.

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