Applied Surface Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

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

Eun Byeol Choi, Jong-Hyun Lee*

Department of Materials Science and Engineering, Seoul National University of Science and Technology, 232 Gongneung-ro, Nowon-gu, Seoul 139-743, Republic of Korea

ARTICLE INFO

Article history:
Received 21 August 2016
Received in revised form
31 December 2016
Accepted 2 January 2017
Available online xxx

Keywords:
Ag-coated Cu
Submicron particle
Surface modification
Palmitic acid
Electrical resistivity

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 ($4.68 \times 10^{-4}\ \Omega\,\mathrm{cm}$) after surface modification compared to an initial value of $1.85 \times 10^{-3}\ \Omega\,\mathrm{cm}$ when cured.

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 $1.3 \times 10^{-3}\ \Omega\,\mathrm{cm}$ using Cu@Ag flakes and decreased the resistivity to $2.4 \times 10^{-4}\ \Omega\,\mathrm{cm}$ 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 ($C_3H_8O_2$, 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 ($C_6H_3O_6$, reagent grade, Aldrich Chemical Co.) was dissolved

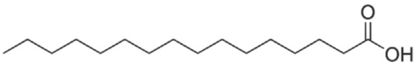
---

* Corresponding author.
E-mail address: pljh@snut.ac.kr (J.-H. Lee).

http://dx.doi.org/10.1016/j.apsusc.2017.01.006
0169-4332/

Please cite this article in press as: E.B. Choi, J.-H. Lee, Enhancement in electrical conductivity of pastes containing submicron Ag-coated Cu filler with palmitic acid surface modification, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2017.01.006

Table 1
Chemical and physical properties of palmitic acid.

Surface-modifying agent	Chemical formula	Chemical Structure	Melting point (°C)	Boiling point (°C)
Palmitic acid	$CH_3(CH_2)_{14}COOH$		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 (C_2H_5OH, 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-

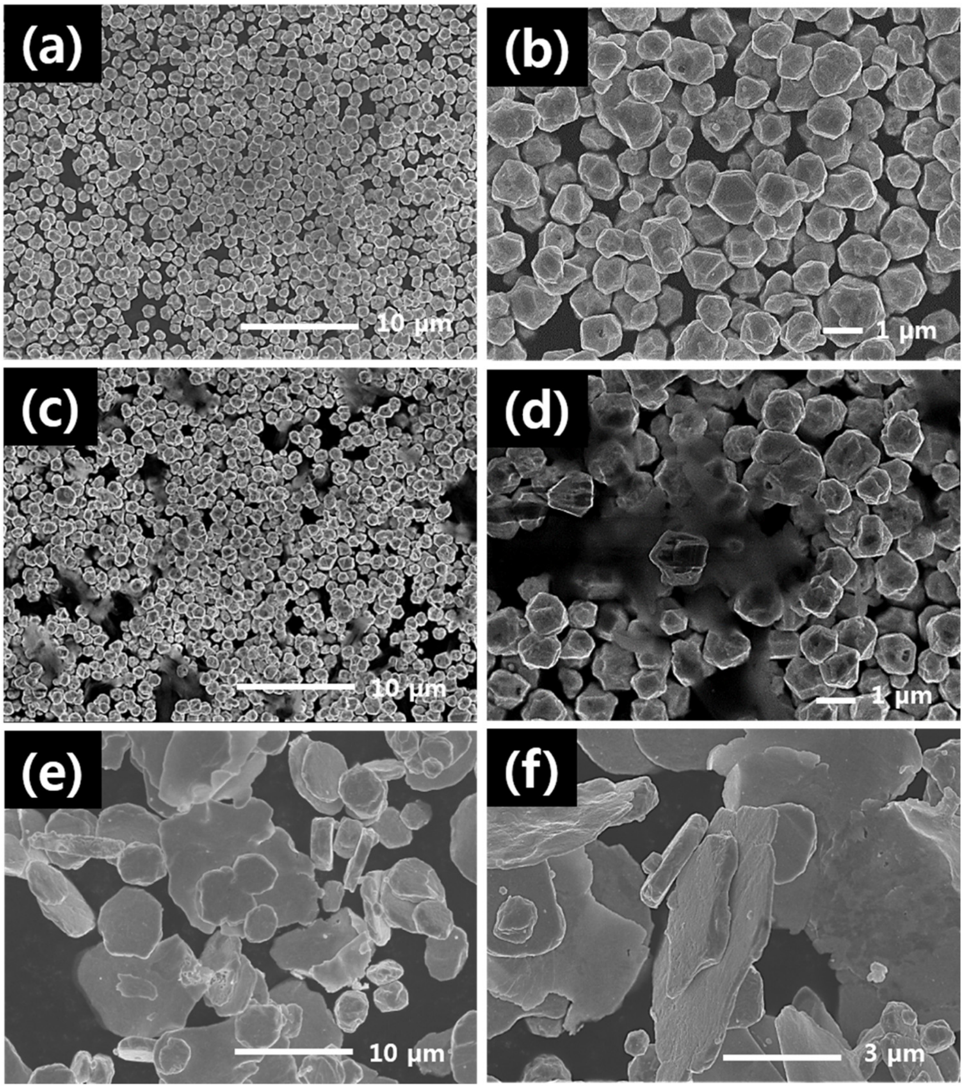


Fig. 1. (a) Low- and (b) high-magnification SEM images of submicron-sized initial Cu@Ag particles, (c, d) Cu@Ag particles surface-treated using palmitic acid, and (e, f) micron-sized Cu@Ag flakes used as a conductive filler.

Please cite this article in press as: E.B. Choi, J.-H. Lee, Enhancement in electrical conductivity of pastes containing submicron Ag-coated Cu filler with palmitic acid surface modification, Appl. Surf. Sci. (2016), http://dx.doi.org/10.1016/j.apsusc.2017.01.006