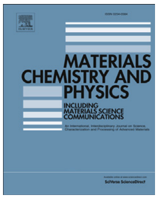
Materials Chemistry and Physics xxx (2016) 1–7

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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



Preparation and characterization of sub-20 nm $Cu_X@Ag_1$ core-shell nanoparticles by changing concentration of silver precursor

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HIGHLIGHTS

- Ultrafine Ag-coated Cu nanoparticles less than 20 nm in diameter were fabricated.
- Different Ag precursor concentrations influenced thickness and density of Ag shell.
- Excessive Ag precursor concentrations induced formation of surplus fine pure NPs.
- Ag dewetting behavior and Cu oxidation in $Cu_4@Ag_1$ nanoparticles were observed.
- Electrical resistivities of sintered $Cu_4@Ag_1$ films were 2.70–4.96 × 10^{-3} Ω cm.

ARTICLE INFO

Article history:
Received 24 August 2015
Received in revised form
17 September 2016
Accepted 15 October 2016
Available online xxx

Keywords:
Nanostructures
Chemical synthesis
Electron microscopy
Electrical conductivity

ABSTRACT

Ultrafine Ag-coated Cu (Cu@Ag) nanoparticles (NPs) less than 20 nm in diameter were prepared. After synthesizing ultrafine Cu NPs using a solvothermal method to serve as the core particles, Cu@Ag NPs were fabricated with different initial Ag precursor concentrations, resulting in different thicknesses, densities, and uniformities of Ag shells. The average thickness and density of the Ag shell increased with increasing initial Ag precursor concentration in a Cu:Ag atomic ratio from 6:1 to 1:1. However, excessive Ag precursor concentrations induced homogeneous nucleation and growth of surplus fine pure NPs. Ag dewetting behavior and Cu oxidation in the $Cu_4@Ag_1$ NPs were observed, they occurred during heating at 200 and 250 °C, respectively. The electrical resistivities of sintered $Cu_4@Ag_1$ films decreased with increasing temperature from 200 to 240 °C. The resistivity after washing the OA and sintering for 60 min at 240 °C in air was measured to be 4.96 × 10^{-3} Ω cm. The film was sintered in nitrogen using the ink containing non-washed $Cu_4@Ag_1$ NPs indicated the lower resistivity of 2.70 × 10^{-3} Ω cm owing to the non-oxidation atmosphere, although the chemically capped oleylamine in the core-shell NPs hindered the sintering behavior.

1. Introduction

Ag nanoparticles (NPs) have been extensively used as conductive inkjet printing inks because of inherently lower resistance and nature of their conductive oxide as compared to other metal NPs [1–6]. Nevertheless, Ag is cost-ineffective and thus still causes bottlenecks in the inkjet printing technology market. In this regard, Cu NPs are excellent alternative materials to Ag because their resistance is similar to that of Ag and they are very inexpensive. However, Cu NPs are vulnerable to surface oxidation in air [7–9]. Hence, methods of fabricating Ag-coated Cu (Cu@Ag) NPs have been recently studied by many researchers in order to reduce the material cost while preventing Cu oxidation [9–13]. Also, it was recently reported that Ag agglomerates form on Cu surface through Ag dewetting during heating as a result of the unstable interfacial energy, which induces oxidation of exposed pure Cu [12–14]. Consequently, it is important to determine the optimum thickness of a Ag shell and anneal the ink under optimal sintering conditions in order to suppress the Ag dewetting behavior and the conductivity degradation in the Cu@Ag film sintered in air [15–17].

In this study, ultrafine Cu@Ag NPs several tens of nanometers in size, which can be applied to ink-jet printing, were prepared with different Ag shell thicknesses using a solvothermal method for the synthesis of core Cu NPs and an immersion-coating process to prepare thicker and more uniform Ag coatings on the Cu NPs. Then, the Ag dewetting behavior and Cu oxidation were analyzed using

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http://dx.doi.org/10.1016/j.matchemphys.2016.10.020
0254-0584/

Please cite this article in press as: S.-S. Chee, J.-H. Lee, Preparation and characterization of sub-20 nm $Cu_X@Ag_1$ core-shell nanoparticles by changing concentration of silver precursor, Materials Chemistry and Physics (2016), http://dx.doi.org/10.1016/j.matchemphys.2016.10.020

the samples with the thickest and most uniform Ag shell, and the electrical resistivities of sintered Cu@Ag films were measured with respect to different sintering conditions.

2. Experimental procedures

For synthesizing core Cu NPs, a solvothermal method using oleylamine (OA, 70%, Aldrich Co.) was employed for 3 h at 240 °C in a nitrogen atmosphere. The detailed synthesis conditions were reported in a previous paper [17]. The synthesis of Cu@Ag core–-shell NPs was carried out using a Ag immersion-coating process conducted at 150 °C using varying Ag precursor (silver nitrate, $AgNO_3$, 99.9%, Kojima Chemicals) concentrations. The Ag precursor was added to 30 mL of OA and allowed to dissolve for 1 h at 60 °C. The added amount of Ag precursor was determined based on Cu:Ag atomic ratios of 6:1–1:1. The completely dissolved solution was then poured into another 100 mL OA solution containing 0.23 g of pure Cu NPs. This mixed solution was heated for 2 h at 150 °C under N_2 bubbling and stirring. Eventually, the color of the solution changed from reddish-brown to yellowish-red. This solution was cooled down for 1 h at room temperature with continual stirring. After the Ag coating, the OA was repetitively exchanged with ethanol (99.9%, Ducksan Chemical Co.) via centrifugation at 10,000 rpm (167 s^{-1}) for 10 min several times in order to remove unnecessary ionic impurities and excess OA in the final NPs. After drying of the Cu@Ag NPs, X-ray diffraction (XRD, X'pert PRO-MPD, PANalytical) analysis was applied to confirm qualitatively the experimental amount ratios between Cu and Ag in the Cu@Ag NPs synthesized with different Cu:Ag atomic ratios. The XRD measurement was carried out in the 2θ range of 20–80° using Cu Kα radiation.

In order to examine the sizes and morphologies of the Cu@Ag NPs, transmission electron microscopy (TEM, Tecnai G^2 F30ST, FEI Company) was conducted at 300 kV. Formation of fine pure Ag NPs in the Cu@Ag samples was preferentially identified by analyzing the TEM image and using energy dispersive x-ray spectroscopy (EDS) equipped on a TEM. Fast Fourier transformation (FFT) analyses of TEM images were also carried out to determine the phases existed. In addition, scanning transmission electron microscopy (STEM) was performed to analyze the elemental distribution of Cu and Ag according to the same conditions that were used in TEM. The TEM and STEM samples were prepared by adding and drying a droplet of the ethanol solution containing Cu@Ag NPs on a molybdenum grid. The TEM and STEM samples were heated up to 250 °C under air to analyzethe metallurgical reactions between the Cu@Ag NPs occurring on a nanoscale with respect to the increase in temperature. In order to observe the sintered properties of the Cu@Ag NPs, moreover, the microstructures of the sintered films were observed using field-emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL Ltd.).

The films were fabricated via thermal sintering at specific temperature after dropping 1 mL of an ethanol ink containing the 10 wt% Cu@Ag NPs on a 10 × 10 mm silicon wafer. The sintering was performed under air or N_2 atmosphere. Some Cu@Ag NPs were used for the ink material after washing with acetic acid in order to remove chemically capped OA on the NPs. The electrical resistivities of the films with respect to the sintering parameters were measured using a four-point probe (Model 2400, Keithley Instruments Inc.) method.

3. Results and discussion

Fig. 1 shows the TEM images and a selected area electron diffraction (SAED) pattern of Cu@Ag NPs synthesized for 2 h at 150 °C with Cu:Ag atomic ratio of 4:1. The size of the spherical Cu@Ag NPs ranged from 11.0 to 17.8 nm, and the average diameter and standard deviation were 14.5 and 1.9 nm, respectively. The average diameter of the core Cu NPs was 11.6 nm and the standard deviation was within 2.0 nm [17]. Thus, 2.9 nm, the difference between 14.5 and 11.6 nm, can be considered double the coated Ag-shell thickness. When the size of the spherical Cu NP was 11.6 nm, it was estimated that the size of Cu@Ag NP synthesized with Cu:Ag atomic ratio of 4:1 was 12.9 nm, indicating that the average Ag-shell thickness was just 0.63 nm. Hence, the measured average size of Cu@Ag NPs showed a discrepancy. Given that the actual shapes of the core Cu and Cu@Ag particles were not perfect spherical, the resultant average sizes of the Cu@Ag NPs were slightly higher because the average Ag-shell thickness increased according to the decrease in the surface area. In addition, this discrepancy was attributed to the agglomeration between fabricated Cu@Ag NPs which caused the decrease in the surface area to be plated, as shown in the TEM image of Fig. 1. However, the nearly identical standard deviation value indicates uniformity of the Ag coating. In the high-magnified image of Fig. 1(b), organic capping layers which may be judged as OA were observed. The SAED pattern did not indicate any oxide phases other than pure Cu and Ag, which confirms that Cu was not oxidized during the Cu synthesis and Ag coating under N_2 bubbling.

In order to confirm formation of the core-shell NPs, STEM elemental line profile analysis was carried out and two results are shown in Fig. 2. The ratios between the Ag and Cu counts were the highest at the edges of the profiles and the profiles showed nearly bilateral symmetry. These results confirm the presence of a Ag coating layer on a Cu core NP and the uniformity of the Ag coating.

Fig. 3 shows the TEM and STEM elemental mapping images of Cu@Ag NPs synthesized for 2 h at 150 °C with a Cu:Ag atomic ratio of 2:1. With increasing Ag precursor amount, fine pure Ag NPs several nanometers in diameter were observed in addition to the Cu@Ag NPs, as shown in the TEM image of Fig. 3(a). It can be inferred that the NPs were synthesized through homogeneous nucleation and growth from the excessive amount of initial Ag precursor. It can be easily observed by the elemental mapping images of Fig. 3(b) that the fine NPs are a pure Ag phase. The fine NPs observed in the STEM image indicated detection of the highest Ag intensity, whereas Cu was scarcely detected. The elemental line profiles of another particle in this sample (Fig. 4) also confirm the formation of fine pure Ag NPs. The Ag profile did not show bilateral symmetry, unlike the results shown in Fig. 2, and an intensive Ag count was observed at one edge of the particle. Along with the existence of a fine NP observed in the high-magnified STEM image of Fig. 4(a), the result confirmed the formation of fine Ag NPs.

Fig. 5 presents the elemental mapping images of Cu@Ag NPs synthesized for 2 h at 150 °C with different Cu:Ag atomic ratios. With decreasing Cu:Ag atomic ratio from 6:1 to 1:1, achieved by increasing the initial amount of Ag precursor ($AgNO_3$), the Ag shell generally became gradually thicker and denser. In the case where the Cu:Ag atomic ratio was 6:1 [Fig. 5(a)], some Ag shells did not cover the Cu surfaces completely, implying a deficiency of Ag atoms. However, thicker and denser Ag shells covered the Cu surfaces and the shell uniformity was also fair in the cases where the Cu:Ag atomic ratio was 5:1 [Fig. 5(b)] or 4:1 [Fig. 5(c)]. In the Cu@Ag NPs synthesized with Cu:Ag atomic ratio of 5:1, the average Ag-shell thickness was calculated as 0.51 nm. In the cases where the Cu:Ag atomic ratio was 3:1 [Fig. 5(d)], 2:1 [Fig. 5(e)], or 1:1 [Fig. 5(f)], meanwhile, Ag mapping in the Ag shell regions became gradually nonuniform. In the cases where the Cu:Ag atomic ratio was 2:1 [Fig. 5(e)] or 1:1 [Fig. 5(f)], moreover, Ag mapping was clearly detected, even when Cu mapping indicated an absence of Cu, indicating that fine pure Ag NPs were synthesized. Therefore, the aim of preparing the thickest and most uniform Ag shells could

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