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Surface modification of Cu metal particles by the chemical reaction between the surface oxide layer and a halogen surfactant

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ABSTRACT

Surface oxides on small (2–5 μm) copper metal particles can be removed by chemical reaction with tris (2,3-dibromopropyl) isocyanurate (TIC) in diethylene glycol mono-n-hexyl ether (DGHE) solution under mild conditions where metal particles are not damaged. Surface oxides convert to copper bromide species and subsequently dissolve into the solvent. It was found that resultant surface species are resistant to re-oxidation due to remaining surface bromides. This finding opens up a possibility to create microclines based on cheap copper nanoparticles.

1. Introduction

Recently, there have been many efforts to reduce the size of metallic particles to the nanoscale since nano-sized metallic particles have various advantages including low melting temperatures, quantum size effects and extremely active surfaces. For example, gold nanoparticles can exhibit surface plasmon resonance by controlling their size and shape [1,2]. The surface plasmon depends on the size, shape, and dispersion state of the metal colloids in liquids [3]. Decreasing the size to nanoscale level causes changes in the physical properties, such as lowering of the melting point from 960 °C (Ag, bulk) to ca. 150 °C (Ag nanoparticles with diameter of 20 nm) [4]. Au and Ag nanoparticles are effective for the fabrication of conductive patterns because of their high conductivity, low melting point and stability against oxidation. Therefore, much attention has been paid to synthesizing metallic nanoparticle pastes in the field of micro-wiring research and industrial development [5–9].

Au and Ag nanoparticles paste have been successfully explored to utilize its high conductivity and stability, though its high cost is a demerit [6,10]. On the other hand, application of Cu nanoparticles for paste materials has not been successfully accomplished so far, even though the cost of Cu is low and electronic properties of Cu are similar to those of Au and Ag. The reason why Cu nanoparticles have not been successfully developed is that Cu surface easily oxidizes. There are many reports on the synthesis of Cu nanoparticles. However, in every case, an oxide layer inevitably forms on the Cu nanoparticles surface due to its thermodynamic stability [11–14]. The surface oxide layer decrease electrical conductivity since the oxide layer is not good electrical conductors. Surface oxidation of Cu nanoparticles occurs more easily with decreasing metal particle size since the surface energy increases remarkably. In order to avoid surface oxidation on Cu particles, surface modification methods using inert materials have been recently explored [15–20]. On the other hand, there are techniques to remove the oxide layer from Cu metal particle surfaces [21–24]. The simplest technique is to dissolve the oxide layer using an acid or a complex reagent, although the metal particles themselves may dissolve and disappear. Recently Takahashi et al. reported that a halogen surfactant reacts with the surface oxide on Sn–Ag–Cu alloy particle and the surface oxide is removed [25,26]. In addition, our previous work indicates that the chemical reaction has a great potential for removing surface oxide on Cu metal [27]. This chemical reaction can remove only the surface oxide on Cu particles if Cu metal is not oxidized or attacked by this reaction.

In order to develop the new method of removing surface oxide, this study examines the variety of chemical species on Cu particles and the ability of the halogen surfactant to remove the surface oxide.

2. Experimental

Cu particles with diameters of 2–5 μm (DOWA Electronics Materials) were used. Tris(2,3-dibromopropyl) isocyanurate (TIC, $C_{12}H_{15}Br_6N_3O_3$; TOKYO CHEMICAL INDUSTRY; purity: $\geq 97.0\%$) and diethylene glycol mono-n-hexyl ether (DGHE, $C_{10}H_{22}O_3$; Alfa

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Aesar; purity: 97.0%) were used as the halogen surfactant and solvent, respectively. 500 mg of TIC was completely dissolved into 50 ml of DGHE. This mixture and 5 g of Cu particles were added into a 100 ml-reaction vessel, and the dispersion was sonicated in an ultrasonic bath for 10 min. Subsequently, the dispersion was heated up to each reaction temperature between 30 and 100 °C using a water bath or an oil bath, and each reaction condition was maintained for 3 days. Treated Cu particles were rinsed with toluene and then dried for 12 h under vacuum. The surface morphology of the treated Cu particles was analyzed by HR-SEM (Hitachi, S-4200 Field Emission SEM). Cross-sections of the Cu particles with and without surface treatment were evaluated by TEM using samples sliced by a focused ion beam (FIB, Hitachi, FB-2000A system). The particle surface was coated with carbon using a carbon coater (Vacuum Device, VC-100) to prevent damage from particle processing by FIB. Surface morphology and surface elemental analyses of the processed Cu particles were performed by HR-TEM (Hitachi, HF-2000 Field Emission TEM) and EDS (Thermo Fisher Scientific, Noran Vantage). The chemical state of each Cu particle was analyzed by XPS (Shimazu, Japan; ESCA-3400).

3. Results and discussion

Surface species of Cu, Cu_2O and CuO can be distinguished from the combined results of XPS (Cu 2p) and Auger spectroscopy (Cu LMM). The peak positions of Cu and Cu_2O are close to each other in the Cu 2p region in XPS, while those of Cu and CuO are near the Cu LMM region in the Auger spectra [28–32]. Fig. 1(a) and (b) shows the XPS (Cu 2p) and Auger profiles (Cu LMM) of original Cu particles in this system. Ar etching was performed under a pressure of 2.0×10^{-2} Pa in order to analyze the depth profile from the surface (upper spectrum) to the inside (etching 1–6) of the particle. The relative concentration of Cu, Cu_2O and CuO was determined on Cu particles surface by using curve fitting. The Shirley background subtraction method was employed throughout this fitting procedure [33,34]. In the case of non-etched original Cu particles, the peaks correspond to Cu (932.6 eV) and/or Cu_2O (932.5 eV) in the Cu 2p region and Cu_2O (916.6 eV) in the Cu LMM region, are clearly observed. Surface species were calculated to be CuO:Cu_2O:Cu = 52.3%:46.1%:1.6% as shown in Table 1. Copper oxide is the dominant material on the surface of the original Cu particles. The peak intensity corresponding to Cu (918.6 eV) increased in the Cu LMM region with increasing exposure time of Ar etching. The ratio changed from 52.3% to non-detected for CuO, from 46.1% to 43.9% for Cu_2O and from 1.6% to 56.1% for Cu before and after the 6th Ar etching. Cu_2O remained on the Cu particle surface while CuO completely disappeared after the 6th Ar etching. This result indicates that CuO was present on top of the oxide layer on the Cu particle surface before the Ar etching.

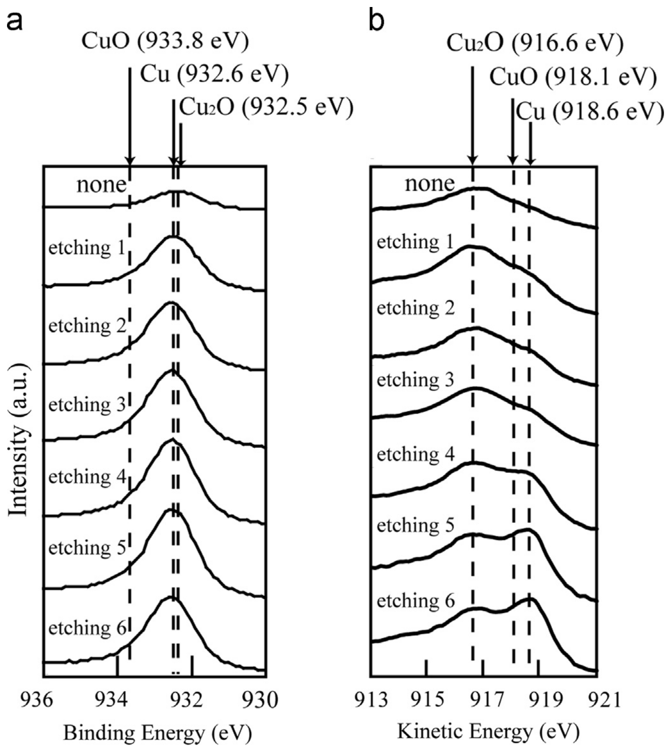

Fig. 1. Depth profiles on the original Cu particle surface obtained by XPS and Auger spectroscopy combined with Ar etching. (A) Cu 2p region and (B) Cu LMM region.

Fig. 2 shows a cross-sectional TEM micrograph of the original Cu particle. It is clearly observed that Cu particle surface have a phase with the thickness of ca. 30 nm. Taking the results of XPS measurements mentioned above into consideration, the original Cu particles have a surface oxide layer composed of Cu_2O and CuO. These Cu particles were used as the sample in the following investigations.

Figs. 3 and 4 show SEM and TEM micrographs of Cu particles treated using the TIC/DGHE solution at various temperatures between 30 and 100 °C. It can be seen from Fig. 3 that the Cu particle surface treated at 30 °C is rough, the same as the original Cu particles surface, while the surface become smoother with increasing treatment temperature. From the TEM micrographs shown in Fig. 4, a 20-nm-thick oxide layer on the Cu particles is clearly observed at 30 °C, similar to the original Cu particles, while the thickness of the oxide layer decreases with increasing reaction

Table 1
Surface species of Cu, Cu_2O and CuO on the Cu particle surface from Auger profiles as a function of the number of etching treatment.

Number of etching	Percentages of CuO, Cu_2O and Cu		
	CuO (%)	Cu_2O (%)	Cu (%)
None	52.3	46.1	1.6
1 Etching	44.6	45.8	9.6
2 Etching	34.0	49.4	16.6
3 Etching	14.5	59.6	25.9
4 Etching	3.7	53.1	43.2
5 Etching	Not detected	45.5	54.5
6 Etching	Not detected	43.9	56.1

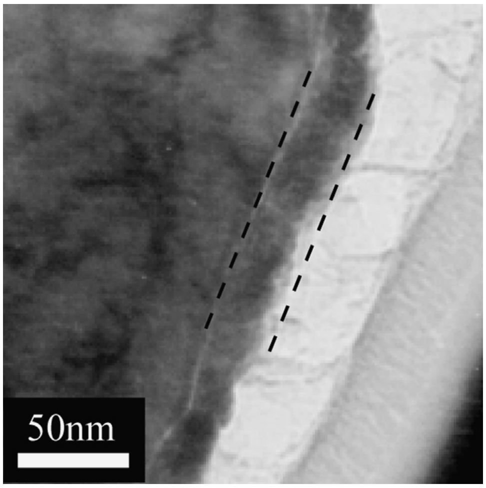

Fig. 2. Cross sectional TEM micrograph of the original Cu particle. The dotted lines indicate the borders of the oxide layer.