CHARACTERISTICS OF CONDUCTIVE INK USING OCTANETHIOLATED COPPER NANOPARTICLES PRODUCED VIA INERT-GAS CONDENSATION

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1. Introduction

In recent years, nanotechnology has attracted lots of attentions in various fields due to the special characteristics of nanomaterials or nanostructures. [1] These metal nanoparticles have large surface area which absorb heat easily, so that sintering at low temperature is possible and these metal patterns can be used on flexible substrates. [2]

Most of relevant recent studies have focused on novel metals such as silver and gold nanoparticles, because of their high conductivity and high antioxidation properties. [3] However these materials are too expensive to be used in mass production, thus many researcher have been trying to find less expensive materials which can be fabricated easily into a nanoparticle shape. Copper is considered to be a good alternative material because of its lower cost and less electromigration effect. One problem to be concerned is that nano sized copper is easily oxidized. In order to overcome this issue, coating with organic materials, e.g., octanethiol was applied to polyol process. [4] These have been numerous studies on octanethiol coating layer which is one of the self-assembled multi layers (SAMs) on copper nanoparticles. Seong et al. have researched using the dry method to coat SAMs on copper nanoparticles produced by polyol process. [5, 6] Vaporized self-assembled monolayer (VSAMs) method is effective in forming the coating layer. However, this method can be exposed to air while as prepared particles are transferred to the VSAM equipment.

In this study, the inert-gas condensation (IGC), which is one of the dry processes was used to fabricate pure copper nanoparticles and these were *in-situ* stabilized by octanethiol in a chamber. Chemical bonding was occurred by octanethiol, and the –SH group at the end of alkanethiol ($CH_3(CH_2)_nSH$) can easily bond with metal surface. [7] In this way, stabilized Cu nanoparticles stably coated with octanethiol were successfully fabricated. In addition, conductive ink was synthesized using the stabilized copper particles.

2. Experimental details

2.1 Fabrication of octanethiolated copper nano particles

Copper (shot, 2~8mm, 99.9995%, sigma-aldrich), 1-octanethiol (98.5%, sigma-aldrich) and high purity argon (99.999%) were used for fabrication. Octanethiolated copper nanoparticles were fabricated via IGC technology. The process for the IGC consists of the evaporation of the metal inside the chamber that is evacuated to a very high vacuum of about 10^{-6}torr. Then the chamber was backfilled with argon to 0.5torr. At this atmosphere, copper vapor which was vaporized by heat resistance was condensed on the cold finger. In addition, octanethiol was introduced at the chamber. Finally pure copper nanoparticles were combined with octanethiol vapor at the surface of particles.

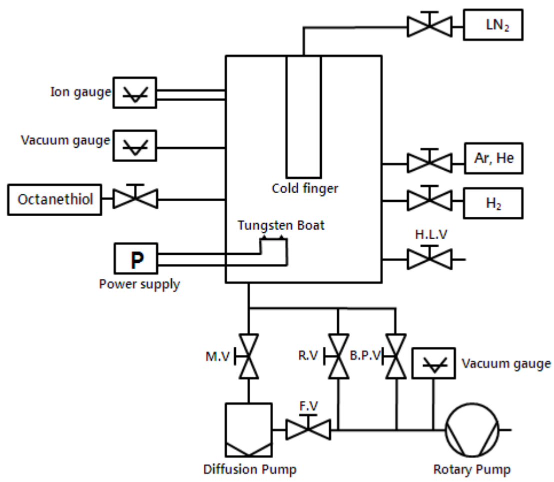


Fig.1. Schematic of the experimental set-up to produce nanoparticles via IGC method.

2.2 Synthesis of copper ink

Octanethiolated copper nanoparticle ink was prepared using a mixed solvent of ethylene glycol, isopropyl alcohol. In addition, additives and surfactants were added to solution for dispersion. Mixed materials were exposed to ultra sonication for dispersion. The formulated ink was filtered through 5μm nylon mesh prior to use. The solid loading of ink was 20wt%.

2.3 Sintering and resistivity measurements

Octanethiolated copper ink was printed as an electrode pattern on the glass using copper suspension at 20wt% and pattern was heat-treated in a reduction atmosphere using nitrogen and hydrogen at various temperatures. Then the printed glass was naturally cooled in the oven until the temperature was ambient air. Schmidt and coworkers confirmed that the small particles can be easily sintered in low temperature because nanoparticles have a higher proportion of surface area than large particles do.[8] The surface morphology of the glass was observed via field emission scanning electron microscope (FESEM) and the resistivity was estimated via the four-probe method.

3. Results and discussion

In this study, copper nanoparticles for conductive ink was evaluated by a scanning electron microscope (SEM) and transmission electron microscope (TEM) to determine the particle size, and distribution of the each particle. We confirmed ingredients in the manufactured particles via Fourier transform infrared spectroscopy (FTIR) and energy dispersive X-ray (EDX).

Fig. 2 shows the FESEM images of octanethiolated copper nanoparticles. From the figure, it could be confirmed that the mean size of the clusters was about 30nm and they were well distributed. Although some particles were aggregated, there is spherical morphology without neck among particles. It helps the good dispersion for the synthesis of ink.

XRD analysis of the *in-situ* coated copper nanoparticles produced via IGC was conducted using Cu Kα radiation. A diffraction pattern of nanoparticles was shown in Fig. 3. Pattern was analyzed to determine the intensities, positions, and widths of the diffraction peaks. The diffraction peaks of octanethiolated copper nanoparticles synchronize into the characteristic face-centered cubic (FCC) bulk copper. No other peak was found in the copper particles. This is because octanethiol layer is formed on the surface of the copper nanoparticles.

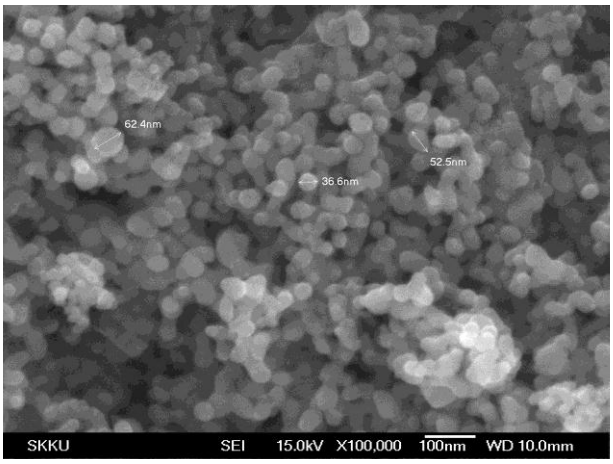


Fig.2. FESEM image of octanethiolated copper nanoparticles produced via IGC. The sample was prepared from an ethanol dispersion drop cast and dried into a thin film on a glass, followed by sputter coating a thin layer of platinum for added contrast.

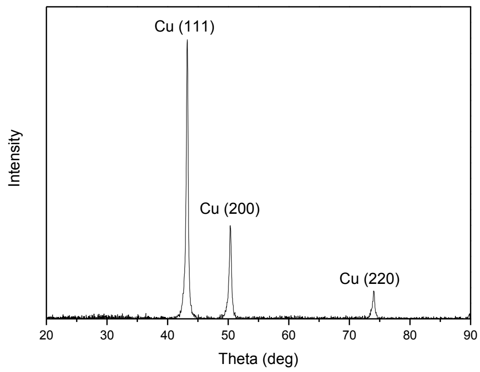


Fig.3. XRD analysis of octanethiolated copper nanoparticles produced via IGC.

To confirm the existence of the SAMs, *in-situ* coated copper nanoparticles were analyzed via TEM. Fig.4 shows the TEM image of the copper nano particles surrounded by octanethiol to form the SAMs.

The thickness of the SAMs was measured to be up to 7nm. Although thickness of the SAMs is not uniform, coating layer is completely surrounded. This means that copper could be prevented from oxygen. In a previous study by Whitesides et al. it was reported that a single monolayer of octanethiol was expected to be 1-2 nm thick. [9]

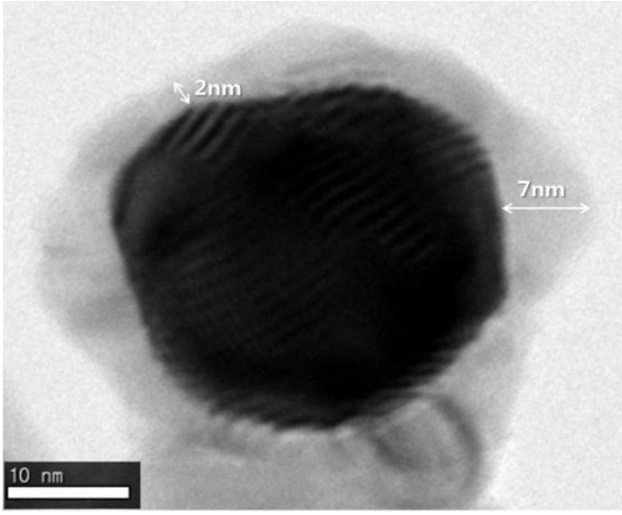
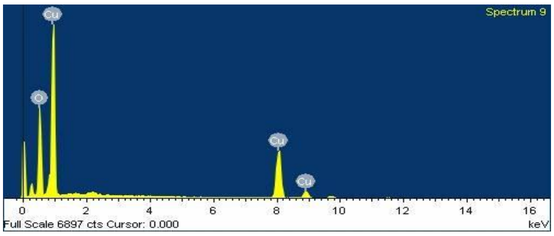
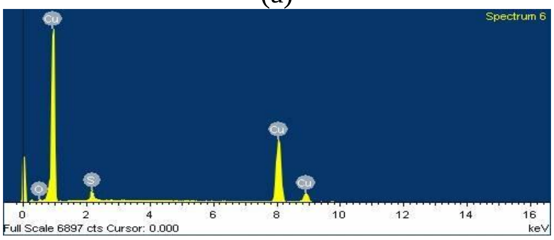


Fig.4. Octanethiol layer is evident in this TEM of coated copper nanoparticles.



(a)



(b)

Element	(a)		(b)	
	Weight %	Atomic %	Weight %	Atomic %
O	37.58	70.51	1.61	6.10
Cu	62.42	29.49	96.24	89.60
S	0.00	0.00	2.15	4.30

Fig.5. EDX microanalyses of uncoated copper nanoparticles (a) and copper nanoparticles coated with octanethiol (b). Copper nanoparticles were exposed in the air for 10 days.

We confirmed ingredients in the manufactured particles by energy dispersive X-ray (EDX). As shown in Fig.5 (a), Sulfur, which was component of octanethiol, was absent in uncoated copper nanoparticles and most of the uncoated particles were oxidized by exposure in the air for 10 days. In addition, coated copper particles were not oxidized even after 10 days because there were the SAMs consisting of sulfur on surface of the copper nanoparticles.

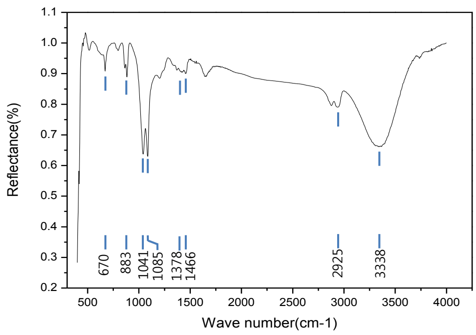


Fig.6. FTIR spectra of octanethiolated copper nano ink 20wt%.

Fig.6. shows FTIR spectra of conductive ink using octanethiolated copper nanoparticles. The presence of octanethiol is confirmed by characteristic peaks in the FTIR spectrum at 722.7, 1275.3, 1378.0, 1466.2 and 2925.8cm^{-1}. [10] Except octanethiol peak and other peaks were solvent for conductive ink such as ethylene glycol, isopropyl alcohol and BYK series.

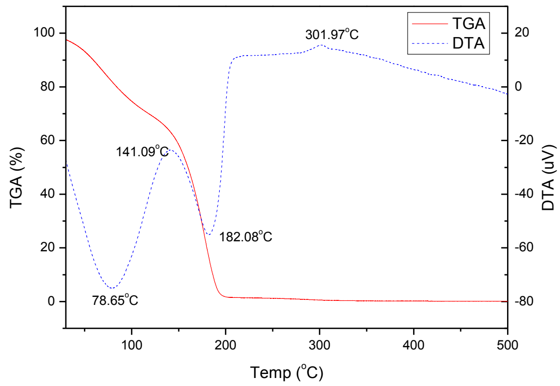


Fig.7. DT-TGA image of octanethiolated copper ink.

DT-TGA results of the prepared copper ink obtained under argon atmosphere are shown in Fig. 7. Under inert-gas atmosphere, a sharp loss of weight occurs from around 182℃. This is highly related with the decomposition of octanethiol on copper surface. In addition, the minimum sintering temperature was confirmed via DT-TGA analysis. Based on these results, all solvents of ink were evaporated at least 182℃ and copper nanoparticles begin to melt at a temperature of almost 300℃ above.

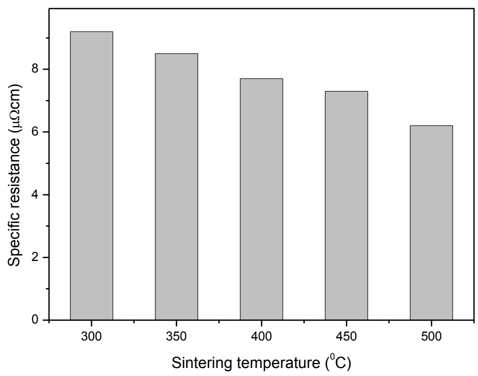


Fig.8. The specific electrical resistance of the conductive ink pattern using octanethiolated copper nanoparticles with sintering temperatures at 300, 350, 400, 450 and 500℃.

After heat treatment at temperatures between 300 and 500℃ with an interval of 50℃, Fig. 8 shows the specific resistance of the copper ink printed on a glass was measured to between 6.2 μΩcm and 9.2 μΩcm depending on the sintering temperature. Resistance of the patterns was higher than that of bulk copper (1.78×10^{-8} Ωcm), but it seems that this value is sufficiently low for an electrical conductor.

4. Conclusions

Octanethiolated copper nanoparticles were *in-situ* prepared via IGC method, which is one of the dry processes. Particles prepared in this study have shown the diameter of about 30nm and good distribution. The composition of particles coating layer were analyzed via EDX and FTIR and confirmed the presence of the SAMs. Coated copper nanoparticles were not oxidized even after 10 days because there were the SAMs consisting of sulfur on copper surface. Octanethiolated copper nanoparticles ink took place at the sintering temperature of 300℃. It was found that the specific electrical resistivity of 6.2μΩcm. Conductivity of the copper pattern printed on a glass seems to be compatible for various electrical conductors.

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