Oxidation Stability of Conductive Copper Paste Prepared through Electron Beam Irradiation

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ABSTRACT

For producing printed electronics, Cu is an effective material as it overcomes the limitations of traditional noble metals in terms of cost and availability. Hence, this work involved developing a synthesis method for conductive pastes used in printed electronics with electron beam (e-beam) irradiation. Cu nanoparticles with high oxidation stability were prepared by adjusting the absorbed dose of e-beam irradiation. The high stable Cu nanoparticles, even though exposure to air for 75 days, were used for preparing conductive ink pastes. The electrical conductivity of the Cu conductive pastes was studied under different sintering conditions. Among the conductive pastes coated on glass substrates under various heat treatment conditions, the paste prepared under the formic acid atmosphere formed a porous, thin film with well-connected particles. Further, we observed that sheet resistance increased as the Cu₂O volume fraction and crystalline domain size increased. Thus, e-beam irradiation is a suitable process for mass production of conductive nanoparticles owing to its simplicity and fast reaction time.

Keywords: Electron beam irradiation, Metal conductive paste, Printed electronics

1. Introduction

Methods for fabricating printed electronics have attracted considerable research attention because of their ability to produce flexible electronic devices [1-3]. Traditional electronic devices have been prepared using a broad range of substrates to induce electrical functionalities [4,5]. Methods for fabricating electronic devices on bendable and flexible substrates are extremely important owing to their advantages over traditional methods for fabricating electronics [6]. Conventional approaches such as electroless plating, vacuum deposition, and lithography require expensive equipment and harsh processing conditions, and these processes emit toxic wastes owing to the use of highly reactive chemicals [7]. Compared to conventional approaches, printed electronics fabrication methods enable faster production, and they are economical and environmentally friendly. These advantages make such fabrication methods feasible for producing electronic components used in displays, photovoltaics, smart packaging, and sensors.

As a practically employed fabrication method for producing printed electronics, inkjet printing requires a conductive paste with an organic-inorganic composition, including metals, metal oxides, and metal-organic complexes. Inkjet printing allows for roll-2-roll fabrication [6,8]. Conductive pastes are generally composed of resins to achieve mechanical and adhesive strength and conductive fillers for providing an electrical path [7,9]. Typically, conductive nanoparticles are dispersed in organometallic compounds with conductive polymers. Physico-chemical properties of the printed patterns should be measured for determining their conductivity, optical transparency, stability against

bending, and adhesion to the substrates [6,10]. In particular, the combinations of metals, metal oxides, and resins are important for interconnecting materials in electrically conductive pastes [6]. Because the electrical properties of conductive pastes depend on the amount of solid metallic filler, increasing the metallic filler content results in higher conductivity; however, the other properties of the pastes, such as rheological properties, deteriorate.

Considering the abovementioned requirements, mixtures of micrometer- and nanometer-sized Ag flakes have been widely used as conducting fillers for establishing effective electrical contact among the components of conductive pastes [6,7]. Currently, highly conductive Ag ($\sigma = 6.3 \times 10^7 \Omega^{-1} \cdot \text{m}^{-1}$) particles are the best candidates for conductive inks in industrial applications [10]. Ag nanoparticles fill the pores between Ag microparticles and establish effective electrical connections [10]. Noble metals such as Ag and Au have been studied as conductive fillers in for paste formulation because they show high conductivity and oxidative stability. However, these materials are not suitable for practical applications because of their intrinsically high cost. Therefore, recent studies have evaluated conductive fillers based on non-noble metal alloys for producing conductive pastes. Practically feasible alternative materials that are inexpensive, highly conductive, and exhibit stability during air exposure must be developed.

In current printed electronics, Cu is an effective conductive material for overcoming the shortcomings of noble metals including cost and availability [11]. From the viewpoint of industrial production, Cu ($\sigma = 5.96 \times 10^7 \Omega^{-1} \cdot \text{m}^{-1}$) is recognized as one of the most promising candidates for conductive fillers because its electrical properties

including electrical resistivity and thermal conductivity are equivalent to noble metals; moreover, it is inexpensive and suitable for the printed electronics industry [12]. Therefore, various methods for producing Cu nanomaterials with tailored morphologies and properties have been reported, including photo- and electrodeposition, physiochemical treatments, and wet chemical approaches. Considering the disadvantages and advantages of these methods, a solution-based approach is widely used for ensuring mild synthetic conditions, facile size control, and mass production with low cost. However, when exposed to air, Cu nanoparticles are easily oxidized, resulting in poor conductivity. In one of the important studies aimed at producing oxidation-resistant Cu nanoparticles, P. Zhang *et al.* prepared Cu nanoparticles with high stability using bis(2-ethylhexyl)amine as the surfactant in the presence of carbon disulfide [13]. J. Li *et al.* investigated Cu nanoparticles formed using a water/oleic acid mixed solvent [14]. The morphology of the Cu nanoparticles was controlled during nucleation, using sodium hypophosphite and oleic acid as the reductant and surfactant, respectively. Spherical Cu nanoparticles with a size of approximately 30 nm were obtained. Further, M.P. Pileni *et al.* [15] used an aqueous dodecyl sulfate solution for reducing Cu ions. The shapes and sizes of the final products were influenced by the critical micellar concentration.

In the current work, we aimed to fabricate air-stable Cu nanoparticles for use as conductive metallic fillers through oxidation using electron beam (e-beam) irradiation, without employing any chemical reducing agent. Through controlling the absorbed e-beam dose [16], air-stable Cu nanoparticles with high stability were prepared for producing conductive ink pastes. The electrical conductivity of the conductive pastes with Cu nanoparticles prepared under different sintering conditions was studied for determining the relationship between the sheet resistance and Cu₂O volume fraction depending on the heating temperature.

2. Experimental details

2.1. Preparation of Cu nanoparticles with oxidation stability

Copper sulfate pentahydrate (CuSO₄ · 5H₂O, 99.9 %, Aldrich) was used as the metal precursor. Ethylene glycol (EG, JUNSEI) and poly(N-vinylpyrrolidone) (PVP, Mw = 220,000, JUNSEI) were used as the solvent and dispersing agent, respectively. All chemical reagents were used as such. Cu nanoparticles were prepared using e-beam irradiation in EG. Typically, 1.7 g PVP was added to 100 mL EG at 40 °C. Next, we added 0.2 M of copper sulfate to the prepared PVP solution in the presence of N₂ gas with stirring for 30 min. The mixture was irradiated with the different absorbed e-beam doses at ambient temperature (20~25 °C), and the Cu nanoparticles were synthesized using a batch process. Under e-beam irradiation, the precursor solution was stirred to diffuse the solvated electrons into the reaction mixture. The reacted solution was filtered through centrifugation at 10,000 rpm, treated using formic acid (99 %, Aldrich), and dried at 40 °C in a vacuum oven. In the current work, e-beam irradiation was carried out in the Korea Atomic Energy Research Institute (KAERI). Under an e-beam energy of 1 MeV and a current of 1 mA, various absorbed doses were produced by the e-beam accelerator.

2.2. Preparation of conductive paste using Cu nanoparticles as metal fillers

The as-prepared Cu nanoparticles through e-beam irradiation were used as metal fillers for producing conductive pastes. Epoxy, acrylic, polyester, and urethane resins were purchased from SK-Cytec and used as binders. Ethyl carbitol acetate, butyl carbitol acetate, triethylene glycol monoethyl ether, and terpineol were purchased from JUNSEI and used as solvents. We swelled 15 wt% of the binder in 15 wt% solvent for 30 min at a rotation of 1,100 rpm and at a revolution of 1350 rpm using a paste mixer (DAEHWAE Tech. co., PDM-1KV). The solvent and epoxy binder were mixed with the same wt%. The mixture was subjected to an antifoaming process at a rotation speed of 100 rpm for 30 min and a revolution speed of 12,000 rpm using a paste mixer. Then, we added 70 wt% Cu nanoparticles and processed the paste using a three-roll mill.

2.3. Characterization

The size, morphology, and crystallographic properties of the final samples were characterized using transmission electron microscopy (TEM, JEOL 2200FS), equipped with selected area electron diffraction (SAED). Ultraviolet-visible (UV-vis) analysis was carried out in the range from 200 to 800 nm with an X-ma 6300PC spectrophotometer (Human Corporation, Korea). The crystalline structure of the final products was characterized using X-ray powder diffraction (XRD). The XRD patterns were recorded in the 2θ range of 10°–80° with a PHILIPS (Netherlands) X'Pert-MPD diffractometer using Cu Kα irradiation at 40 and 150 kV. The surface oxidation state in the final samples was analyzed using X-ray photoelectron spectroscopy (XPS, Multilab 2000, Thermo Electron Corporation, England). The morphology of sintered Cu paste film was characterized using scanning electron microscopy (SEM). The resistivity of the paste was measured on a 24203A Source Meter with four-point probes.

3. Results and discussion

In the initial step, e-beam irradiation of the aqueous solution generated many active species. Among these active species, the solvated electron (e_{solv}[•]) and hydrogen atom (H[•]) act as strong reductive agents [17]. Under e-beam irradiation, Cu cations were generated in the CuSO₄ solution. As the irradiation dose was increased for reducing the Cu ions, abundant amounts of neutral copper (Cu₀) atoms were produced through the following reactions:

During irradiation, the Cu atoms were nucleated and aggregated continuously into clusters. Then, Cu nanoparticles were grown from the metallic Cu atom clusters.

Based on the radiolysis mechanism of EG, the ionization and excitation of EG molecules generated the solvated electrons, and the

Figure 1. Typical TEM images of Cu nanoparticles prepared through e-beam irradiation with different absorbed doses (a) 100 kGy, (b) 200 kGy, and (c) 300 kGy. Scale bar is 40 nm. (d) SAED and (e) XRD patterns of Cu nanoparticles formed using 300 kGy of irradiation. (f) UV-vis spectra of Cu nanoparticles with different absorbed doses (red line) 100 kGy, (green line) 200 kGy, and (blue line) 300 kGy.

radical and protonated EG molecules [17]. Three types of reduction species from EG allowed the metal cations to form metallic species.

Such a reduction reaction can be conveniently conducted under ambient conditions. During nanoparticle preparation, PVP functioned as the surfactant to control the size and morphologies of the final product.

The TEM images in Fig. 1 show typical morphologies of Cu nanoparticles prepared from different absorbed doses of e-beam irradiation. The as-prepared Cu nanoparticles are spherical with sizes ranging from 5 to 47 nm. With an absorbed dose of 100 kGy, the size of the Cu nanoparticles was less than 7 nm, whereas the size increased to 47 nm as the absorbed dose increased to 300 kGy. Thus, microscopic observations indicate that the sizes of the as-prepared Cu nanoparticles increase as the absorbed dose increases. The UV-vis spectra [Fig. 1(f)] of Cu nanoparticles prepared using different absorbed doses show that the plasmon absorption band of the nanoparticles appears at approximately 570 nm as the irradiation increases. This band indicates that metal nanoparticles were formed and stabilized by PVP after the metal atoms coalesced during reduction of the Cu^{2+} cations. Because of their size-dependent optical properties, a red shift in the plasmon absorption of the prepared Cu nanoparticles implies an increase in the size of the Cu particles.

The as-prepared Cu nanoparticles via e-beam irradiation with 300 kGy of the absorbed dose were characterized using SAED and XRD. The four fringes in the SAED pattern of the prepared sample correspond to the (111), (200), (220), and (311) planes in the face-centered cubic (FCC) structure of metallic Cu, thus agreeing with the XRD results. The XRD patterns of the prepared samples do not contain the peaks for copper oxide. The diffractions angles of 44.28, 50.40, 74.12, and 89.90° in the XRD patterns correspond to the diffraction angles of the FCC phase (the standard powder diffraction card, ASTM 03-1005). The XRD results show that Cu metallic nano-

Figure 2. (a) XPS spectra of Cu nanoparticles prepared using 300 kGy of irradiation. (b) Cu2p. (c) C1s. (d) O1s. (e) N1s. (f) illustration of prepared air-stable copper nanoparticles.

particles could be crystallized using e-beam irradiation without employing any chemical reducing agent and special experimental conditions such as high vacuum or high temperature.

In the current work, PVP was used as both the dispersing and capping agent. The surface oxidation state of Cu nanoparticles prepared using PVP shows the copper ($\text{Cu}2s$, $\text{Cu}2p_{1/2}$, and $\text{Cu}2p_{3/2}$), carbon ($\text{C}1s$), oxygen ($\text{O}1s$), and nitrogen peaks ($\text{N}1s$) in the XPS spectra of Fig. 2(a). The XPS spectrum of Cu in Fig. 2(b) shows doublet peaks centered at 933.2 and 953.0 eV, corresponding to $\text{Cu}2p_{3/2}$ and $\text{Cu}2p_{1/2}$ in CuO . The peaks centered at binding energies of 285.8 [Fig. 2(c)], 531.8 [Fig. 2(d)], and 400.2 eV [Fig. 2(e)] correspond to $\text{C}1s$, $\text{O}1s$, and $\text{N}1s$, respectively, indicating the C-C bond, O 1s in the C=O bond, and C-N bond. The strong interaction between Cu and O in the PVP solution enclosed the surface of the Cu nanoparticles, indicating chemical adsorption between the metal core and an oxygen atom in PVP as shown in Fig. 2(f). Figure 3 shows the XRD patterns of Cu nanoparticles after exposure to ambient conditions for 75 days. The XRD patterns of samples obtained after exposure for 75 days period did not show peaks related to oxides. Thus, the prepared Cu nanoparticles are air-stable. This result reveals that PVP with Mw = 220,000 imparted oxidation stability to the formed Cu nanoparticles during

Figure 3. XRD patterns of Cu nanoparticles depending on sintering time.

Figure 4. Photograph and top-view SEM image of Cu pastes sintered under different atmospheres.

the nucleation and growth step, with no formation of even a thin oxide layer on the surfaces of the Cu nanoparticles.

The oxidation resistance and electrical conductivity of the conductive Cu paste prepared through e-beam irradiation were studied under different sintering conditions, as shown in Fig. 4. A copper paste was printed onto a glass substrate using screen printing and sintered under air, nitrogen gas, and formic acid. Figure 4 shows the changes in the color of the copper paste under the three different sintering atmospheres at 200 °C for 30 min. The copper paste exposed to air and nitrogen gas changed to a blue color from its original reddish-brown color. Therefore, we can infer that the Cu paste could undergo oxidation during heat treatment based on its color change. However, the Cu paste heat-treated under a formic acid atmosphere retains the original reddish-brown color of Cu. SEM images of all the samples were compared for evaluating their morphologies depending on the sintering conditions. The SEM image of the paste heat-treated under air shows typical aggregated nanoparticles. Samples heat-treated under nitrogen show aggregates with smaller particles. Interestingly, a porous, thin film of the Cu paste on glass after heat treatment under formic acid. In addition, the Cu nanoparticles were well connected to each other after heat treatment in the formic acid atmosphere. In this work, formic acid provided a reducing atmosphere according to the following reaction.

Figure 5. Comparison of typical XRD patterns of (a) as-prepared Cu nanoparticles and Cu pastes sintered under (b) air, (c) nitrogen, and (d) formic acid atmospheres.

Figure 6. (a) Sheet resistance of Cu pastes sintered under different atmospheres, sintering temperatures, and durations. Atomic structure (blue ball: Cu atom, red ball: O atom) of Cu metal (black square) and Cu_2O (red square). (b) Volume fraction and crystalline domain size of Cu paste according to sintering temperature.

As such, unexpected minor oxides generated during formulation of the conductive paste could be reduced. Figure 5 shows the XRD patterns of the heat-treated copper pastes under different atmospheres. The metallic Cu particles were transformed into Cu_2O during heat treatment under air or nitrogen gas. However, the Cu nanoparticles were not oxidized during heat treatment under the formic acid atmo-

sphere. Therefore, formic acid was effective in preventing oxidation and enabled reduction during sintering.

Figure 6(a) shows the sheet resistance of the sintered Cu pastes under different atmospheres, sintering temperatures, and sintering times. The sheet resistance increases with temperature and the duration of heat treatment because oxidation occurs on the metal surface. Such a relationship between sheet resistance and sintering conditions was observed in our results. The sheet resistance of the three types of pastes increased as the heating temperature and time increased. The Cu pastes heat-treated under air and nitrogen gas showed sheet resistances over $1.39 \text{ M}\Omega\cdot\text{cm}^2$. However, when the paste was sintered for 15 min at 200°C under formic acid, the sheet resistance was $5.95 \Omega\cdot\text{cm}^2$. Although the sheet resistance consistently increased as the heating temperature exceeded 250°C , it is worth noting that Cu pastes with such sheet resistance values can effectively replace conventional conductive Ag pastes. The volume fractions of the metal and metal oxide in the conductive paste prepared through treatment under formic acid were determined to evaluate the extent of oxidation, as shown in Fig. 6(b). The volume fraction and crystalline domain size of the Cu_2O phase increased as the temperature and heating duration increased. At a high sintering temperature, the Cu nanoparticles aggregated with each other and crystal growth occurred in the matrix. Further, the extent of oxidation of the Cu nanoparticles simultaneously increased in the Cu_2O crystalline state. Hence, considering the variation trend of sheet resistance with respect to heat treatment, we can conclude that sheet resistance increases as the Cu_2O volume fraction and crystalline domain size increase.

4. Conclusions

In this work, air-stable Cu nanoparticles were prepared through e-beam irradiation without a chemical reductant. This method is suitable for mass production of nanoparticles owing to its simplicity and fast reaction time. The sizes of the Cu nanoparticles could be changed by adjusting the absorbed dose of the e-beam irradiation. The oxidation state of the Cu surface was confirmed through XPS analysis. The XPS results revealed that PVP enabled the synthesis of air-stable Cu nanoparticles capable of maintaining oxidative stability even after exposure to air for 75 days. The as-prepared Cu nanoparticles were used as fillers for preparing conductive pastes. Among the Cu conductive pastes coated on glass substrates under various heat treatment

conditions and atmospheres, the paste prepared through heat treatment under formic acid formed a porous, thin film on the glass substrate with well-connected particles. Such structural features show that the prepared Cu conductive paste can replace conventional conductive pastes prepared from noble metals based on the relationship between the sheet resistance, Cu_2O volume fractions, and heat treatment conditions.

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