

Room temperature sintering of Ag nanoparticles by drying solvent

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We have successfully developed a new Ag nanoparticle paste which can sinter at room temperature simply by drying the solvent from the paste. A small amount of alkylamine was incorporated into the Ag nanoparticle paste to form protective layers on the nanoparticles. By drying at room temperature, Ag nanoparticles are sintered, resulting in a low resistivity of $4.9 \times 10^{-6} \Omega\text{m}$. Since the new paste can be sintered even at room temperature without heat treatment, it should prove versatile for applications in electronics wiring.

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Sintering of metallic and inorganic material particles occurs through diffusion of elements across particles, forming necking between them. Sintering can usually be accelerated by heating. When particle size is reduced to the nanometer scale, sintering can occur at temperatures lower than that in bulk materials. Numerous studies on sintering of nanoparticles have been already reported [1,2]. Focusing on this unique characteristic of nanoparticles, wiring of electronic circuits with metallic nanoparticles has been attracting interest in the field of printed electronics in recent years.

For metallic pastes, long shelf life is one of the key features for practical applications. Nanoparticles have to be covered by organic dispersant to prevent aggregation or sintering under normal storage conditions. On the other hand, too stable an organic dispersant can prevent sintering of nanoparticles at low temperature. In terms of Ag nanoparticles, a temperature of over 150 °C is usually required to remove the dispersant [3–6]. Recently, the present authors have successfully developed a room temperature sintering method for Ag nanoparticle paste with simple chemical treatment [7]. In this process, the Ag nanoparticles are covered by alkylamine and dispersed in toluene solvent. By dipping the printed Ag nanoparticles into methanol, the alkylamine dispersant can be effectively removed from the particles and the Ag nanoparticles are sintered even at room temperature.

In the present study, the authors focused on developing a new paste that sinters at room temperature without dipping treatment. The basic concept of the new paste is quite simple. Once the solvent is evaporated, the nanoparticles begin to be sintered by adjusting the amount of the initial dispersant. The purpose of the present work is to develop a new nanoparticle paste, which has very small amount of organic dispersant, and possesses a substantial shelf-life.

Ag nitrate (AgNO_3), 0.13 mol, and dodecylamine ($\text{NH}_2\text{C}_{12}\text{H}_{25}$), 0.26 mol, were dissolved in acetonitrile (CH_3CN), $7.0 \times 10^{-4} \text{ m}^3$, and the solution was stirred at room temperature for $10.8 \times 10^3 \text{ s}$. The resulting white precipitate was filtered from solution to leave an Ag complex ($[\text{Ag}(\text{NH}_2\text{C}_{12}\text{H}_{25})_2]\text{NO}_3$), 0.13 mol, after drying [8]. A mixture of 20.0 g of the Ag complex, 30.0 g dodecylamine and $5.0 \times 10^{-7} \text{ m}^3$ ethanol was mixed together and heated while being stirred. The mixture surface turned to a metallic blue color at temperatures above 170 °C. Next, the complex was heated for 900 s between 190 and 200 °C, and then the mixture was cooled in air for 1200 s. The mixture was washed with acetone (CH_3COCH_3) three times to remove impurities, leaving blue powders and brown supernatant solution. After the third washing, the supernatant solution became colorless and transparent. The supernatant solution was removed and toluene ($\text{C}_6\text{H}_5\text{CH}_3$), $2.0 \times 10^{-5} \text{ m}^3$ was added to the sediment. The solution took on a metallic blue color. The solution was stirred for 600 s at room temperature. Finally, the Ag nanoparticle paste was obtained as the residue by filtering the solution with a paper filter. A silver-colored solid

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substance, 4.57 g, was present after drying off the toluene at room temperature.

In order to clarify the nature of the organic matter adsorbed to the Ag nanoparticle paste, the surface of the Ag nanoparticle paste dried for 12 h at room temperature was analyzed by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K_{α} X-ray beam (energy = 1486.6 eV, power = 150 W). Thermogravimetric analysis (TGA) was also conducted to measure Ag content in the dried paste in air. The rate of temperature increase was $10^{\circ}\text{C min}^{-1}$ and the ambient gas was air. The grain size was evaluated by X-ray diffraction (XRD) measurement before and after drying the solvent. In order to keep the paste wet during the XRD measurement, a few drops of tetradecane ($\text{C}_{14}\text{H}_{30}$) were added to the paste before the solvent dried. It was confirmed that tetradecane did not have any influence on the measurement. The samples were (A) the paste just after the fabrication (+tetradecane), (B) the paste dried for 12 h at room temperature and (C) the paste maintained for 30 days at 5°C avoiding drying of the solvent (+tetradecane). The measurement was performed by powder X-ray diffractometry. The X-ray source was Cu K_{α} ($\lambda = 0.15418\text{ nm}$), which was operated at 50 kV and 200 mA. Additionally, the dried paste was observed by field emission scanning electron microscopy (FE-SEM) at 15 kV and transmission electron microscopy (TEM) at 200 kV. TEM samples were prepared by cutting wired lines with an ultramicrotome at room temperature.

To monitor the sintering phenomenon of the paste, in situ electrical resistance and weight decrease were measured during the drying process. The Ag nanoparticle paste was printed onto glass substrates by screen printing to give a line 6.0 mm in length, 1.5 mm in width and 0.1 mm in thickness, as determined by laser microscopy. The resistance was measured by digital multimeter using a two-probe method. The current was 1.0 mA and the measured data was recorded at intervals of 0.5 s. To monitor the evaporation of the toluene, weight decrease was also recorded at intervals of 10 s during the drying process.

In order to understand the state of the organic substances adsorbed onto Ag nanoparticles in the paste, surface analysis was conducted using XPS on the paste dried for 12 h at room temperature. Toluene solvent in the paste evaporates at room temperature due to its high vapor pressure in air. The result of the surface analysis is

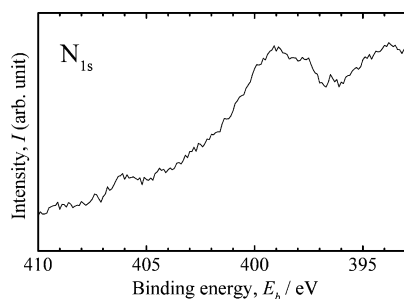


Figure 1. Nitrogen (N_{1s}) spectrum. The peak is attributed to the amine moiety.

shown in Figures 1 and 2. Figure 1 shows the spectrum of N_{1s} . The chemical shift analysis reveals that the observed peak is attributed to the amine moiety [9]. Figure 2 shows the spectrum of C_{1s} , which comes from the alkyl group [9]. These results clearly show that alkylamine is adsorbed to Ag nanoparticles after drying for 12 h at room temperature.

To measure Ag content in the dried paste, the dried Ag nanoparticle paste was analyzed. The TGA result of the dried paste is shown in Figure 3. The weight of the dried paste gradually decreases as the temperature is increased from 50 to 300°C . The weight loss can be attributed to vaporization of alkylamine adsorbed to Ag nanoparticles. TGA showed the existence of 2.1 wt.% alkylamine in the dried paste (average of three measurements). On the other hand, the conventional Ag nanoparticles, which we produced in a previous work [7], contain 19.0 wt.% alkylamine. Thus, the content of alkylamine of the new paste is much less than conventional Ag nanoparticle paste.

To estimate the grain size of Ag nanoparticles, the XRD peak of Ag(220) was analyzed. The XRD results are shown in Figure 4. Comparing the spectra of the initial state and the dried state, the half bandwidth of the dried state is obviously narrower than that of the initial state. This indicates that the grain size increases after evaporation of the solvent. The grain size can be calculated using the Scherrer equation [10]. It is a surprising fact that the grains grow from 15.9 to 45.4 nm after drying at room temperature.

Microstructure observations were performed by FE-SEM and TEM. Since the images do not change during the observations, the electron beams under the current conditions rarely affect the interactions between metallic particles. The microstructure of the dried paste is shown in Figure 5. Figure 5a shows FE-SEM image on the fracture surface of the dried paste. Particle-like Ag with various diameters, 30–100 nm, can be observed. From TEM observation, the dried paste forms a porous structure comprised of clusters. The particles observed in FE-SEM image are found to be protrusions on the clusters. These clusters connect through constriction points and their features indicate neck growth. The necking formation and the grain growth clearly show room temperature sintering by evaporation of the toluene solvent.

The stability of the nanoparticles is one of the key aspects for practical applications. Since the content of the alkylamine is much less than that of the conventional

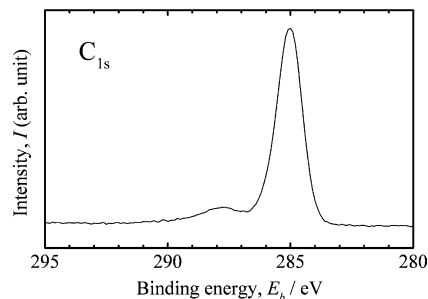


Figure 2. Carbon (C_{1s}) spectrum. The peak is attributed to the alkyl group.

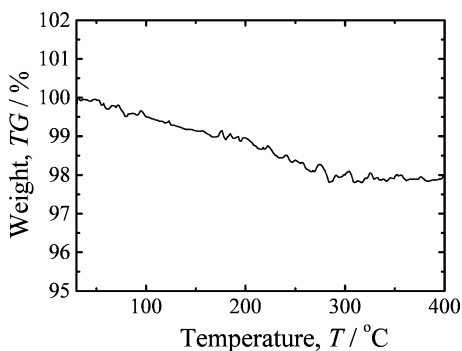


Figure 3. Weight loss of the dried paste measured by TGA.

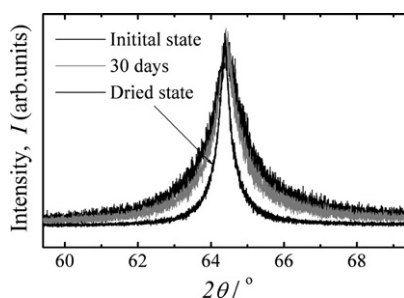


Figure 4. The XRD spectra come from Ag(220). The half bandwidth of the dried state is narrower than that of the initial state. The grain size drastically increases after drying at room temperature. The half bandwidth of the paste stored for 30 days is almost the same as the initial state.

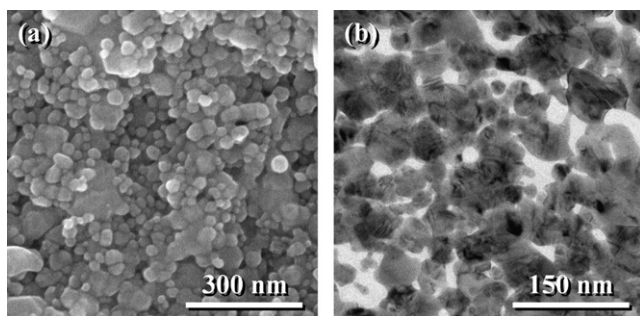


Figure 5. Ag particles in the dried paste: (a) FE-SEM image and (b) TEM image. Ag forms a porous structure comprised of many clusters, which have protrusions over 30 nm. These clusters connect each other by neck growth.

paste, the stability of the paste becomes one of the main concerns. The paste was held at 5 °C for 30 days, avoiding toluene evaporation. The measurement of the grain size was carried out by XRD in the same way. Although the grain size changes a little from 15.9 to 21.9 nm, it can be said that Ag nanoparticles maintain the initial grain size in the storage. Thus, it can be concluded the current Ag nanoparticle is substantially stable, avoiding toluene evaporation at 5 °C.

Weight change and electrical resistance of the printed lines during the drying process were measured to understand the sintering. The result of the in situ measurement is shown as a function of time in Figure 6. It is observed that the change in weight starts just after the

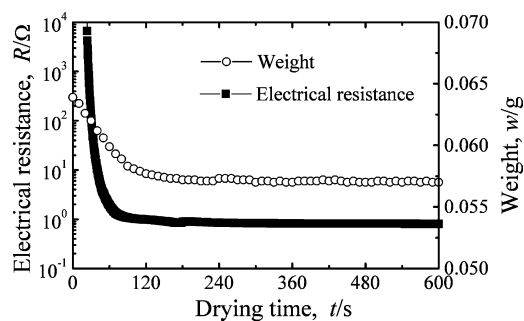


Figure 6. In situ measurements of the electrical resistance and the weight for the wired paste. The electrical resistance and the weight of the wired paste drastically decrease just after printing.

printing and continues until approximately 120 s. Since alkylamine adsorbed onto Ag nanoparticles does not evaporate at room temperature, this weight loss can be attributed to the evaporation of toluene in the paste. In contrast, the electric resistance drastically decreases just after the printing and gradually decreases after 90 s. The electric resistivity reaches $4.9 \times 10^{-6} \Omega\text{m}$ measured by the four-probe method after drying for 2 h at room temperature.

The conventional Ag nanoparticle paste, containing a larger amount of adsorbed alkylamine dispersant, is stable even after solvent drying [7]. This is guaranteed by the presence of the protective layer covering each Ag nanoparticle. In contrast, the current new paste with less dispersant can be stable in the presence of solvent, i.e. toluene. Once toluene evaporates, these nanoparticles begin to coalescence by contacting each other.

In the present study, the properties of a new Ag nanoparticle paste were investigated. The new nanoparticles contain much less alkylamine than conventional independent nanoparticles. Before drying of the solvent in the new paste, the Ag nanoparticles can maintain their initial state due to the presence of the adsorbed alkylamine and the toluene solvent. Once the toluene solvent evaporates, the nanoparticles can be sintered and coarsened even at room temperature. The paste dried at 23 °C has a conductivity of $4.9 \times 10^{-6} \Omega\text{m}$.

Thus, from the current work, a new Ag nanoparticle paste, which can sinter with evaporation of the solvent even at room temperature, has been successfully developed. Also, the paste can be stored for at least 30 days at 5 °C, avoiding solvent evaporation. This finding indicates that not only dispersants, but also solvents, play an important role in preventing nanoparticles from coming into contact with one another and sintering.

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