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Novel method for room temperature sintering of Ag nanoparticle paste in air

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Abstract

We successfully developed a new method of sintering Ag nanoparticles protected by dispersant in an air atmosphere without heating. Ag nanoparticles on glass substrates were dipped in methanol for 10–7200 s to remove the dodecylamine dispersant. After 7200 s dipping, the removal of the dispersant became clear by surface analysis and Ag nanoparticles were densely sintered. The sintered Ag wire had excellent low resistivity of 7.3×10^{-7} Ωm. Microstructural observations revealed that the Ag nanoparticles had agglomerated and coarsened with increased dipping time. Clear connections were found among the grown particles.

1. Introduction

Recently, the sintering temperature descent phenomenon of metallic nanoparticles has attracted a great deal of attention. Iwama et al. reported the room temperature sintering of ultrafine powders of Au, Ag, Al and Cu in high vacuum [1]. Thus, many metallic nanoparticles can be sintered, even at room temperature, when their surface is clean and without any oxide layer or protective organic dispersants. From a practical point of view, the application of the sintering temperature descent phenomenon to the wiring of circuits combined with certain kinds of printing methods, such as by ink-jet, has been studied. For excellent printability, a suitable paste of the metallic nanoparticles is required. This means that the nanoparticles must be covered by organic dispersants to avoid aggregation and must be able to disperse in solvents. Heating has always been required after wiring metallic nanoparticle pastes to remove the organic dispersants and solvents. When metallic nanoparticle pastes are heated at 150–300 °C, the dispersants can be effectively removed, and the remaining active metallic nanoparticles can then be successfully sintered. As a result, metal circuits of excellent low resistivity, for example 10^{-8} Ωm, can be obtained. In the case of the most promising Ag nanoparticle pastes, heating beyond 150 °C is required to remove the dispersants from the Ag nanoparticles and to vaporize them [2–5]. These heating treatments mean that the unique phenomenon presented by Ag nanoparticles is not exploited as much as it could be. The only reason that Ag nanoparticles are unable to be sintered at low temperatures is due to the presence of the dispersants and solvents. Furthermore, a heating temperature beyond 150 °C is too high for many organic devices and printed circuit boards, which are generally unstable at these temperatures.

In the current study, we developed a novel room temperature chemical method that removes the dispersant material covering the Ag nanoparticles without requiring heating or vacuum. The microstructural development and electrical characteristics of the resulting wired circuits were examined. We expect that the chemical method we present here for Ag nanoparticle pastes will become a standard method for nanoparticle wiring.

2. Experimental

Ag nitrate ($AgNO_3$), 0.13 mol, and dodecylamine ($NH_2C_{12}H_{25}$), 0.26 mol, were dissolved in acetonitrile

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(CH_3CN), 7.0×10^{-4} m^3, and the solution stirred at room temperature for 10.8×10^3 s. The resulting white precipitate was filtered from solution to leave an Ag complex ($[Ag(NH_2C_{12}H_{25})_2]NO_3$), 0.13 mol, after drying [6]. A mixture of 20.0 g of the Ag complex, 30.0 g dodecylamine, and 5.0×10^{-7} m^3 ethanol was mixed together and heated while being stirred. The mixture surface took on a metallic blue color at temperatures above 170 °C. Next, the complex was heated for 900 s with the temperature maintained between 190 °C and 200 °C, and then the mixture was allowed to cool naturally for 1200 s. The mixture was washed with acetone (CH_3COCH_3) three times to remove impurities, leaving a blue powder and a brown supernatant solution. After the third washing, the supernatant solution became colorless and transparent. The supernatant solution was removed and toluene ($C_6H_5CH_3$), 2.0×10^{-5} m^3 was added to the sediment. The sediment dispersed in toluene and the solution took on a metallic blue color. The solution was stirred for 600 s at room temperature and was then filtered with glass fiber filter to remove particulate matter over 0.3 μm. A minute quantity of blue powder, 0.938 g, was present after vacuum concentration. Finally, an Ag nanoparticle paste was produced by dispersing the 0.938 g of blue powder into 3.6×10^{-6} m^3 (3.16 g) of toluene.

The fabricated Ag nanoparticle paste was printed onto glass substrates to give a circuit 50 mm in length, 300 μm in width and 0.2 μm in thickness, as determined by laser microscopy (Keyence Co. VK-9500) and field emission scanning electron microscopy (FE-SEM, Hitachi High-Tech. Co. S-5000). The wired glass substrates were dipped in methanol for sintering at room temperature (23 °C). To study the influence of methanol, the dipping time was varied from 10 s to 7200 s. After dipping, the substrates were removed from the methanol bath and dried naturally for 7200 s at room temperature. Electrical resistivity measurements were conducted using a four probe method, and the microstructural observation was carried out by FE-SEM after the drying process. The electrical resistivity was measured 10 times for each sample, and the averages and standard deviations were plotted on a graph. For TEM samples, the Ag nanoparticle paste diluted with toluene was dropwise deposited onto Cu grids of ultrathin amorphous carbon films. The grids were then dipped in a methanol bath for set periods of time and after natural drying for 7200 s, observations were performed by transmission electron microscopy (TEM, JEOL LTD., JEOL-JEM3000F) operated at 300 kV. To confirm the removal of the dispersant, surface analysis was conducted. Sample disks, 9 mm in diameter, were coated with Ag nanoparticle paste using a spin coater at 600 rpm. The disks were then dipped in methanol for 7200 s and analyzed by X-ray photoelectron spectroscopy (XPS, VG Scientific, Microlab mark III).

3. Results and discussion

Fig. 1 shows the microstructural changes of Ag nanoparticles as a result of methanol dipping. As shown in Fig. 1a, which is the initial state of the paste, Ag nanoparticles of average diameter 7 nm were observed packed in a highly dense structure. After 3600 s dipping, as shown in Fig. 1b, the Ag nanoparticles completely disappeared and a high density Ag structure appeared.

To clarify the microstructural changes after dipping, TEM observations were carried out as shown in Fig. 2. In the initial state, each particle can be clearly seen as being independent from the others because of the presence of dodecylamine as a dispersant, as shown in Fig. 2a. With the passage of dipping time, the Ag nanoparticles grew, as shown in Fig. 2b. Moreover, the coarsened particles became connected with each other by forming metallic bonds. It was surprising that the coalescing of the Ag nanoparticles started after only 30 s of dipping.

The results of the surface analysis study are shown in Figs. 3 and 4. Comparing the surface spectra of the initial sample and dipped sample, the intensity was normalized by the peak intensity of $Ag_{3d_{5/2}}$. Fig. 3 shows the spectrum of

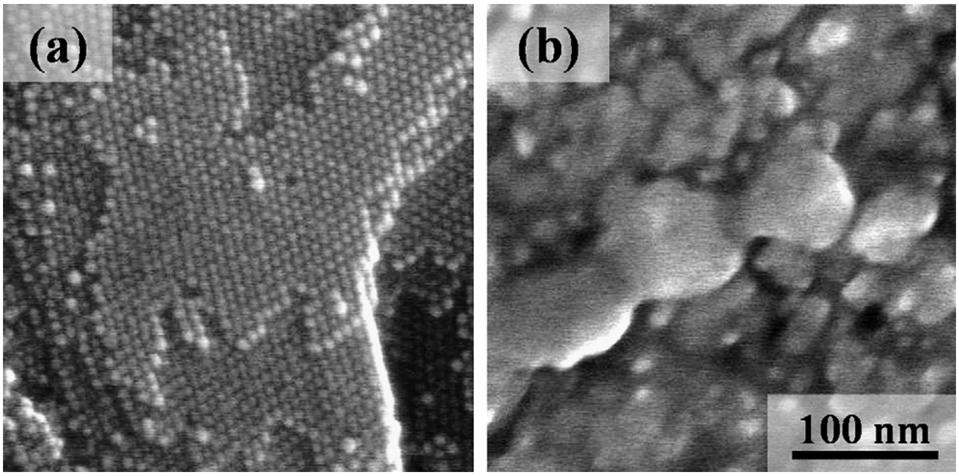

Fig. 1. Microstructural changes in an Ag nanoparticle paste as observed by FE-SEM: (a) initial state, and (b) after dipping in methanol for 3600 s.

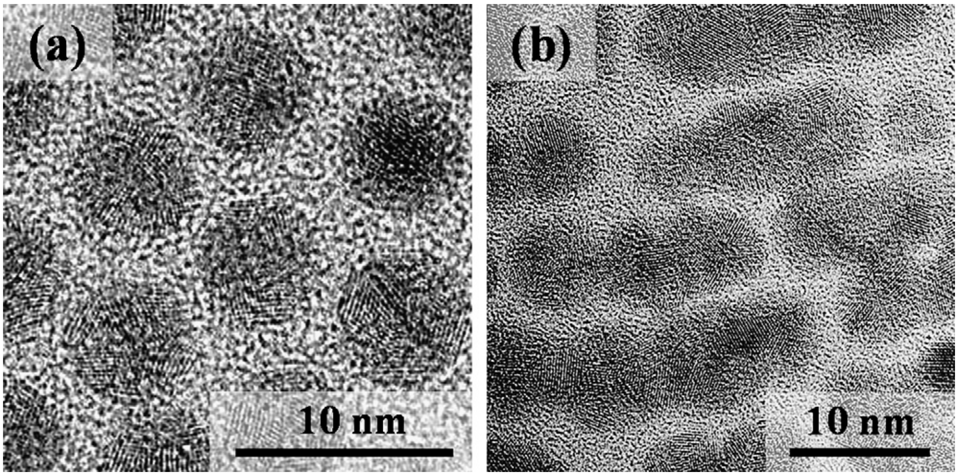

Fig. 2. Microstructural changes in an Ag nanoparticle paste as observed by TEM: (a) initial state, and (b) coalescing of nanoparticles that starts after 30 s of methanol dipping.

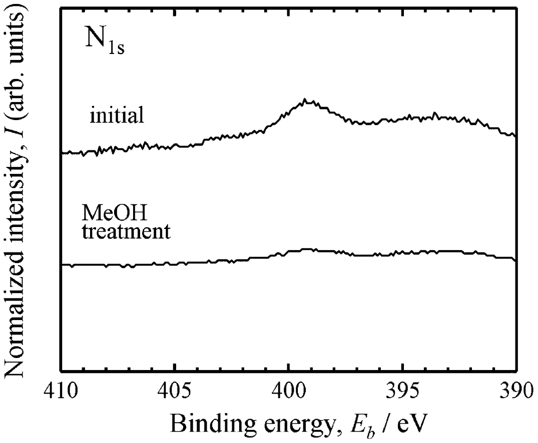

Fig. 3. Nitrogen (N_{1s}) spectrum. The N_{1s} peak disappears after methanol dipping for 7200 s.

N_{1s}. The chemical shift analysis reveals that the observed peak is attributed to the amine moiety. From Fig. 3, the peak of N_{1s} can be seen to have disappeared after methanol dipping for 7200 s. Fig. 4 shows the spectrum of C_{1s}. The peak intensity of C_{1s}, which comes from hydrocarbons (contamination) and the alkyl group, clearly decreases after methanol dipping. This decrease is attributed to the removal of the alkyl group of dodecylamine, which is further supported by the disappearance of the N_{1s} peak. Although there is a small peak after methanol dipping, the peak can be thought of as contamination in the chamber. These surface analyses prove that the dispersant was effectively removed by our methanol dipping method.

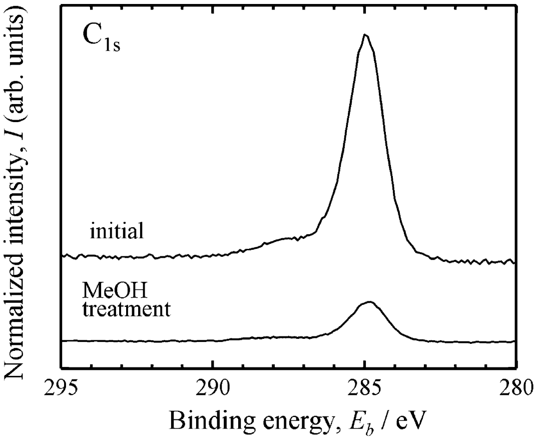

Fig. 4. Carbon (C_{1s}) spectrum. The C_{1s} peak intensity decreases after methanol dipping.

Fig. 5 shows the change of electrical resistivity as a function of dipping time, which is expected to fall with dipping time. The circuit obtained from this experiment possesses a quite low resistivity, in the order of 10^{-6} Ωm, after only 300 s of dipping. This decrease in resistivity corresponds to the microstructural observations, which shows that the Ag nanoparticle growth occurs in just a short space of time. After 7200 s of dipping, the circuit finally acquired an excellent resistivity of 7.3×10^{-7} Ωm. This resistivity is nearly equal to the electrical resistivity, 5.5×10^{-7} Ωm, obtained by the same paste after heat treatment at 150 °C for 1800 s.

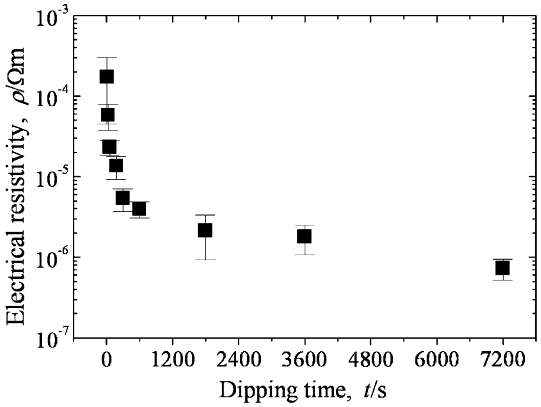

Fig. 5. Electrical resistivity changes as a function of dipping time.

In summary, the above experimental results demonstrate the mechanism of room temperature sintering of Ag nanoparticle pastes. The initial Ag nanoparticles are protected by dodecylamine in the paste. While there is still debate about the mechanism of the bonding between Ag nanoparticles and a dispersant [7,8], the nature of the bonding seems relatively weak compared to strong chemical bonding such as covalent bonding. Dodecylamine molecules are found to dissolve easily during dipping in methanol, a solvent which has high affinity with dodecylamine. Generally, there is no chemical reaction between dodecylamine and methanol at room temperature under a regular atmospheric pressure. Once Ag nanoparticles are freed from the dispersant, the bare Ag nanoparticles, which possess active surfaces, can be sintered even at room temperature. Finally, once the Ag nanoparticles are sintered, the electrical resistance is observed to decrease.

4. Conclusions

We demonstrated the successful development of a novel sintering method for Ag nanoparticle pastes that is carried out at room temperature in an air atmosphere. As the dipping time increases, the Ag particles grow and become connected with each other through the formation of metallic bonds. The coarsening of the Ag nanoparticles was observed after only 30 s. The fabricated circuits obtained an excellent resistivity of $7.3 \times 10^{-7}\ \Omega\mathrm{m}$ after 7200 s dipping. Thus, our methanol treatment effectively removes the dispersant and allows for the sintering of Ag nanoparticles without heating or vacuum. This method could become a standard procedure for wiring Ag nanoparticle pastes as it is both economic and rapid, while also being environmentally friendly.

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