Electrical conductivity of copper nanoparticle thin films annealed at low temperature

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Abstract

Copper nanoparticles with a mean diameter of 20 nm were used to prepare electrical conductive films at low temperature. After dispersal in an organic solvent, the copper nanoparticle pastes were coated onto a glass substrate, which was then annealed under various conditions to investigate the effects of various atmospheric conditions, such as air, nitrogen gas or hydrogen gas, as well as different annealing temperatures. Two-step annealing, which first involves oxidation in air followed by reduction, is effective in the preparation of high electrical conductive copper nanoparticle films. The copper nanoparticle films that were calcined in air for 1 h and then hydrogen gas for 1 h at a low temperature of 200 ˚C showed a low resistivity of 2×10^{-5} Ω cm.

Keywords: Copper; Nanoparticles; Conductive film; Oxidation; Reduction

1. Introduction

The manufacture of electrical circuits is a process that is fundamental and important to the electronics industry. A photolithography/etching process is generally employed in the creation of tiny circuits. However, this results in a poor yield and a significant increase in production cost, since the process involves many steps such as development, etching, removal of resistant layers, and so on. Furthermore, developing liquid chemicals, such as etchants and cleaning liquids, must be used in large amounts at each of the many steps. Also, this method imposes a heavy burden on the environment with the necessity of waste liquid treatment, which has recently become a matter of serious concern. Therefore, a low-cost, convenient and environmentally friendly process for the fabrication of electrical circuits has attracted increasing attention in recent years.

As an alternative technique for the photolithography/etching process, an ink-jet printing method has been investigated for the fabrication of electronic circuits on a substrate [1, 2]. There are many reports on the use of different materials as electronic conductive inks: molten metal [3–5], conductive polymers [6,7], organometallic compounds [8,9], metal precursors [10], and metallic nanoparticle suspensions [11]. However, the operating temperature when using molten metal is too high for organic substrates. Conductive polymers have advantages in flexibility, but their conductivity is relatively low [12-14]. When using organo-metallic compounds or a metal precursor, additional heat-treatment is required for the reduction of metallic species, and films prepared by this method contain large amounts of organic residue, which adversely affects conductivity [8].

In consideration of the aforementioned limitations, a printing method using metallic nanoparticle paste is promising [1, 15-17]. Silver and gold nanoparticles can be applied to a printing circuit because of their high conductivity and anti-oxidation properties. However, these nanoparticles are expensive to use commercially, and when using silver, electro-migration reduces the reliability of an electrical circuit. Copper nanoparticles are a good candidate material due to lower cost and a diminished electro-migration effect. However, the disadvantage is that copper is easily oxidized in air, leading to a deterioration of electrical conductivity. Several methods for the preparation of copper nanoparticles have been reported: the wet phase (polyol method) [18], thermal decomposition [19, 20], chemical reduction (metal salt processes) [21], and the RF thermal plasma method [22, 23]. The surface of the prepared copper nanoparticles is generally covered by the protective layer of an organic surfactant, or by carbon, to prevent the oxidation of copper nanoparticles in air. To achieve high conductivity of the film, it is necessary to remove this protective layer by using a high operating temperature, but for application onto organic substrates, the operating temperature must be within a range of 200-300 ˚C. However, copper nanoparticles prepared by the RF thermal plasma method are protected by a thin carbon layer that can be removed at temperatures as low as 200 ˚C by oxidation in air [24], which, therefore, makes them a suitable candidate for this process.

In the present study, copper nanoparticles synthesized by the RF thermal plasma method were used in the preparation of electrical conductive thin films. The copper nanoparticles were dispersed in an organic solvent. Using a doctor blade film applicator, the nanoparticle pastes were deposited on glass substrates, which then were annealed under various atmospheric conditions. The effect of the annealing temperature on electrical conductivity was investigated and the microstructures of the thin films were observed.

2. Experimental details

2.1. Materials

Mono-dispersed copper nanoparticles prepared by the RF thermal plasma method (Nisshin Engineering, Inc.) were used as received. The mean diameter of the nanoparticles was 20 nm and their surfaces were covered with a thin carbon layer to prevent oxidation. Copper oxide nanoparticles (CuO, Nisshin Engineering Inc.) with a mean diameter of 29 nm, which were not covered with a carbon layer, were used for comparison. The thermal properties of the nanoparticles were measured by thermal gravimetric (TG) and differential thermal analysis (DTA) (TG-DTA 6200, Seiko Instruments, Inc.). For TG-DTA analysis, a sample of approximately 3 mg was placed in an aluminum pan, which was then subjected to a flow rate of 200 mL/min of air, nitrogen gas or 5% hydrogen-argon mixed gas, in a temperature range of 30 to 600 ˚C at a heating rate of 5 ˚C/min.

2.2. Preparation of nanoparticle paste and film

To prepare the nanoparticle paste, copper nanoparticles were dispersed in α-terpineol of 50 mass%. The prepared nanoparticle paste was coated onto a cleaned glass substrate using a doctor blade film applicator with a gap of 17 μm. To form conductive film, the paste coat was dried at 70 ˚C for 15 min, and the film was annealed under a flow rate of 200 mL/min of air, nitrogen gas or 5% hydrogen-argon mixed gas at 200 to 300 ˚C for 1 h using a tubular furnace. For comparison, film from copper oxide nanoparticle paste was annealed in 5% hydrogen-argon mixed gas.

2.3. Film characterization

The electrical conductivity of film annealed under various conditions was measured using a 4-point probe (MCP-T600, Loresta-GP, Mitsubishi Kagaku). The thickness of the film was measured by observation of cross-sections; this was intended to calculate the volume resistivity of the film. The morphology of the film was observed using field-emission scanning electron microscopy (FE-SEM, JEOL JSM6340F) at an accelerated voltage of 20 kV.

3. Results and discussion

3.1. Thermal properties of copper nanoparticles

TG/DTA analysis of the copper nanoparticles in air is shown in Fig. 1. The mass gain was seen from 180 to 300 ˚C in the TG measurement. This was caused by oxidation of the copper nanoparticles. Two peaks were observed in the DTA analysis, and the slope of TG changed at 210 ˚C. This shows that the oxidation of the nanoparticles proceeded in two steps. The mass gain of copper nanoparticles was approximately 10% at 210 ˚C, and 20% at 300 ˚C. Copper oxides were divided into two types, Cu_2O and CuO [25], with theoretical mass gains of 13% (= (71.5/63.5 - 1) x 100; 71.5 is the half-molar mass of Cu_2O, and 63.5 is the molar mass of Cu) and 25% (= (79.5/63.5 - 1) x 100; 79.5 is the molar mass of CuO and 63.5 is the molar mass of Cu), respectively. The first stage of the oxidation of copper nanoparticles was from conversion to Cu_2O, and the second stage was due to conversion from Cu_2O to CuO. In the thermal analysis, the mass gain was lower than the theoretical gain, because initially the copper nanoparticles were slightly oxidized. The mass of the nanoparticles decreased slightly at temperatures higher than 300 ˚C, which could have been caused by the removal of impurities inside the nanoparticles. The oxidized nanoparticles, as shown in Fig. 1, were cooled in air, and then heated to 600 ˚C in hydrogen gas to reduce the oxidized nanoparticles. TG/DTA analysis of the oxidized nanoparticles in

5% hydrogen-argon mixed gas is shown in Fig. 2. A major mass loss was found between 240 and 300 ˚C. The DTA curve showed only one peak, and the slope in TG measurement did not change during this period. The mass loss of the nanoparticles was approximately 20%, which was almost equal to the theoretical mass loss of 20% (= (1-63.5/79.5) x 100; 63.5 and 79.5 are the molar mass of Cu and CuO, respectively). This shows that the nanoparticles were directly converted from copper oxide to copper.

3.2. Sintering of copper nanoparticles under various atmospheric conditions

In order to investigate the influence of atmosphere on the sintering of copper nanoparticles, prepared nanoparticle pastes were annealed under various atmospheric conditions such as air, nitrogen gas or 5% hydrogen-argon mixed gas. Nanoparticle annealing was carried out at 300 ˚C, since that was the temperature at which both oxidation and reduction of the nanoparticles proceeded substantially, as indicated in the TG/DTA analysis shown in Figs. 1 and 2. For comparison, copper oxide nanoparticles also were annealed in hydrogen gas at 300 ˚C.

Table 1 shows the volume resistivity and film thickness of the films annealed under various atmospheric conditions. The volume resistivity of copper nanoparticle film annealed in nitrogen was quite high. The resistivity of copper nanoparticle film annealed in hydrogen was 5-orders lower than that in nitrogen, although the film thickness was similar. The resistivity of the film, prepared by annealing copper nanoparticle paste in air for 1 h, followed by annealing in hydrogen for 1 h, was lowered further. The resistivity of 1.4×10^{-5} Ω cm was 10-fold that of bulk copper, 1.72×10^{-6} Ω cm. During annealing, the copper nanoparticle paste was changed to copper oxide by oxidation in air, and was then reduced in hydrogen. The film was thinner than that annealed in nitrogen and hydrogen. The film prepared from copper oxide nanoparticles by reduction in hydrogen showed low resistivity, compared with the copper nanoparticle films annealed in nitrogen or hydrogen. However, the low resistivity of film prepared from copper oxide nanoparticles by reduction in hydrogen was seven times higher than the copper nanoparticle film annealed in air and hydrogen. The thickness of the copper oxide nanoparticle film reduced in hydrogen was twice that of the copper nanoparticle film annealed in air and hydrogen.

Fig. 3 shows the morphologies of the films after annealing under various atmospheric conditions. The particles in the films annealed in nitrogen were approximately 40 nm in mean diameter, and developed a neck formation between adjacent particles (Fig. 3(a)). The particles in the films annealed in hydrogen were grown to approximately 60 nm in mean diameter, and also were necked adjacent to one another (Fig. 3(b)). The volume resistivity of these films was high following the two types of treatments, as shown in Table 1. This was because the thin carbon layers coated on the surface of the copper nanoparticles were not eliminated and remained at the interfacial surface of the nanoparticles following annealing. The resistivity of copper nanoparticle film annealed in hydrogen was lower than that in nitrogen, which was caused by a reduction in the surface of copper nanoparticles that could have been slightly oxidized prior to annealing. In the film from copper nanoparticle paste annealed in air and hydrogen, we observed three-dimensional sintered particles 100 nm in size and consisting of primary nanoparticles (Fig. 3 (c)). Fig. 4 shows the SEM image of film from the same paste annealed only in air. The sintering of nanoparticles that have grown from the oxidation of copper nanoparticles in air, expansion in the oxidation step, is a result of nanoparticles contacting one another. In addition, the annealing of copper nanoparticles in air caused the removal of the thin carbon layers that were coated on the surface of the copper nanoparticles, as when carbon dioxide reacts with oxygen. As a result, the film showed low resistivity by the reduction of the sintered oxidized film in hydrogen, although the nanoparticles were shrunk by deoxidation. The film of copper oxide nanoparticle paste annealed in hydrogen, as shown in Fig. 3 (d), was quite similar to the copper nanoparticle film annealed in nitrogen (Fig. 3 (a)). The low resistivity of the film was due to the fact that initially there was no thin carbon layer on the copper oxide nanoparticles. However, the resistivity of the film was higher than the film annealed in air and hydrogen (Fig. 3 (c)), which was because the sintering was insufficient and many voids were present due to shrinkage of the nanoparticles by deoxidation during reduction of the copper oxide nanoparticles. Fig 5 shows a cross-section of the film from copper nanoparticle paste annealed in air and hydrogen (a), and film from copper oxide nanoparticle paste annealed in hydrogen (b). The films annealed from copper nanoparticle paste were thinner, but the under-layer of the film was sintered enough to be dense. On the other hand, many voids were found in the film annealed from copper oxide nanoparticles.

In order to obtain a film with low resistivity, copper nanoparticles coated with a thin layer of carbon must be oxidized and reduced to remove the carbon impurity and to develop sintering by expansion and shrinkage in two steps.

3.3. Effect of temperature on oxidation and reduction of copper nanoparticles

The effect of the annealing temperature was investigated for films from copper nanoparticle paste annealed in air and hydrogen. The prepared paste was oxidized in air for 1 h at a temperature that ranged from 100 to 300 ˚C, followed by a reduction in hydrogen for 1 h at a temperature that ranged from 100 to 300 ˚C. The volume resistivity of film as a function of oxidation temperature is shown in Fig. 6. The three curves show the effect of a reduction in temperature. A drastic decrease in resistivity was recognized at an oxidation temperature of 200 ˚C. Fig. 7 shows the morphology of the annealed films from copper nanoparticle paste oxidized from 100 to 300 ˚C and then reduced at 200 ˚C. The grain sizes were almost identical. However, the sintering of copper nanoparticles seemed nonexistent after oxidation at 100 ˚C, because the interface of the annealed nanoparticles was clearly evident. Those results can be compared with the TG/DTA data of oxidized copper nanoparticles, as shown in Fig. 1, which indicated removal of the thin layer of carbon impurity coating the surface of the nanoparticles and the sintering of copper nanoparticles by oxidation at temperatures higher than 200 ˚C.

The resistivity of the films reduced at 200 and 300 ˚C were almost identical. In the reduction at 100 ˚C, the resistivity of the film was higher, but the trend was similar to the films reduced at 200 and 300˚C. Thus, the reduction reaction proceeded even at a low temperature of 100 ˚C. Considering the TG/DTA results of reduction, as shown in Fig. 2, it seems impossible to convert copper oxide to copper at 200 ˚C. The TG/DTA data in Fig. 2 were obtained from the copper nanoparticles oxidized to 600 ˚C, so the particle sizes became larger from sintering, which was confirmed as a characteristic of nanoparticles. The increase in resistivity of film annealed with oxidation at 300 ˚C followed by reduction at 100 ˚C might be due to the enlargement of the particle size. The high resistivity of the film reduced at 100 ˚C was caused by insufficient reduction in the inner oxidized nanoparticles. To obtain a low resistivity film at a temperature that is as low as possible, the optimal conditions were to oxidize the copper nanoparticle paste at 200 ˚C and follow with reduction at 200 ˚C. The volume resistivity obtained under these conditions was $2\text{x}10^{-5}$ Ω cm, which can be applied to an organic substrate. It was reported that the resistivity of 40-50 nm copper particle film synthesized by a polyol process reached $1.72\ \text{x}10^{-5}$ Ω cm at 325 ˚C for 1 h in vacuum [26]. The octanethiolated copper nanoparticle film that was calcined at 300 ˚C for 1 h in air, and then for 5 h under 90% N_2-10% H_2 obtained a resistivity of $4.8\ \text{x}10^{-4}$

Ω cm [27]. The resistivity reported in these studies was similar, or one order higher, than that achieved in our work, but the annealing temperature was higher than 300 ˚C. This indicates the difficulty in applying this process to an organic substrate. The two-step annealing method used in the present study has the advantage of low-temperature annealing. The resistivity of the copper nanoparticle film was 10-fold that of bulk copper (1.72 x 10^{-6} Ω cm). This was obviously due to the voids that remained between nanoparticles, as shown in Fig. 7, leading to less contact area between nanoparticles. In order to obtain a low resistive film consisting of copper nanoparticles at a temperature that is as low as possible, the removal of the thin protective carbon layers coated on the nanoparticles and the sintering of the nanoparticles by oxidation must both be precisely controlled.

4. Conclusions

Copper nanoparticles synthesized by the RF thermal plasma method were used to prepare high conductive film at a low temperature. In the present study, films of copper and copper oxide nanoparticle paste were annealed under various conditions to investigate the effect of atmosphere and annealing temperature. As a consequence, two-step annealing, which first involves oxidation in air followed by reduction in 5% hydrogen-argon mixed gas, is effective in the preparation of high electrical conductive copper nanoparticle films from copper nanoparticle paste. The oxidation of copper nanoparticles is an important process for removal of the thin-layered protective carbon coated on copper nanoparticles, and sintering the nanoparticles is important for volume expansion. The film from copper nanoparticle paste annealed at temperatures higher than 200 ˚C for oxidation and reduction showed a resistivity of less than $2\text{x}10^{-5}$ Ω▪cm.

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Table 1. Volume resistivity of film annealed under various atmospheric conditions at 300 ˚C.

Fig.1. Thermal analysis of copper nanoparticles annealed in air.

Fig.2. Thermal analysis of oxidized copper nanoparticles in 5%H_2-Ar.

Fig. 3. Morphology of film annealed at 300 ˚C under various atmospheric conditions:
(a) Cu nanoparticles in N_2, (b) Cu nanoparticles in 5%H_2-Ar,
(c) Cu nanoparticles in air and 5%H_2-Ar, (d) CuO nanoparticles in 5%H_2-Ar.

Fig. 4. Morphology of Cu nanoparticle film annealed at 300 ˚C in air.

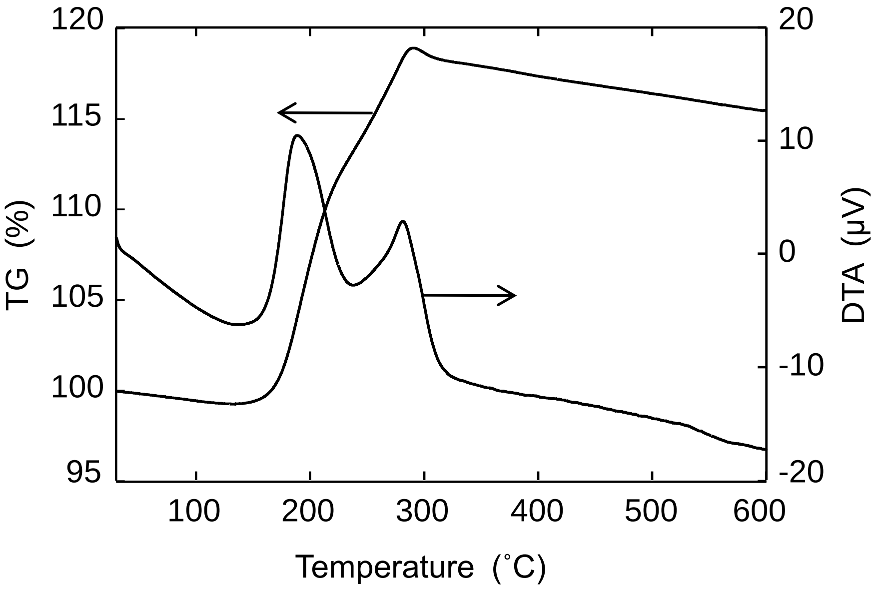
Fig. 5. Cross-section of film annealed at 300 ˚C under various atmospheric conditions:
(a) Cu nanoparticles in air and 5%H_2-Ar,
(b) CuO nanoparticles in 5%H_2-Ar.

Fig. 6. Volume resistivity of copper nanoparticle films in various oxidation and reduction temperatures.

Fig. 7. Morphology of copper nanoparticle films oxidized at (a) 100 ˚C, (b) 200 ˚C, and (c) 300 ˚C, and reduction at 200 ˚C.

Material	Atmosphere	Volume resistivity (Ω cm)	Film thickness (μm)
Cu	N_2	4.1×10^{3}	1.09
Cu	H_2	8.8×10^{-2}	1.21
Cu	Air → H_2	1.4×10^{-5}	0.80
CuO	H_2	9.8×10^{-5}	1.53

Table 1. Volume resistivity of film annealed under various atmospheric conditions at 300 ˚C.



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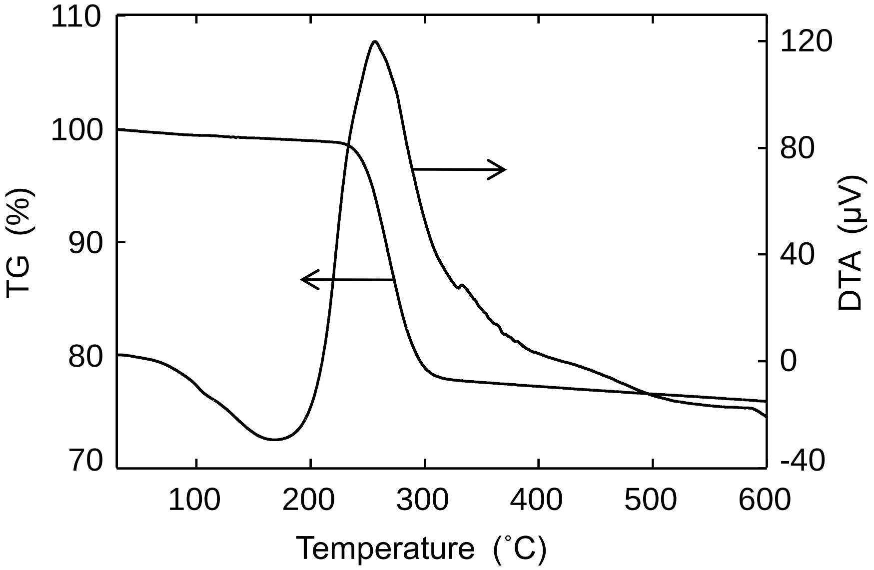
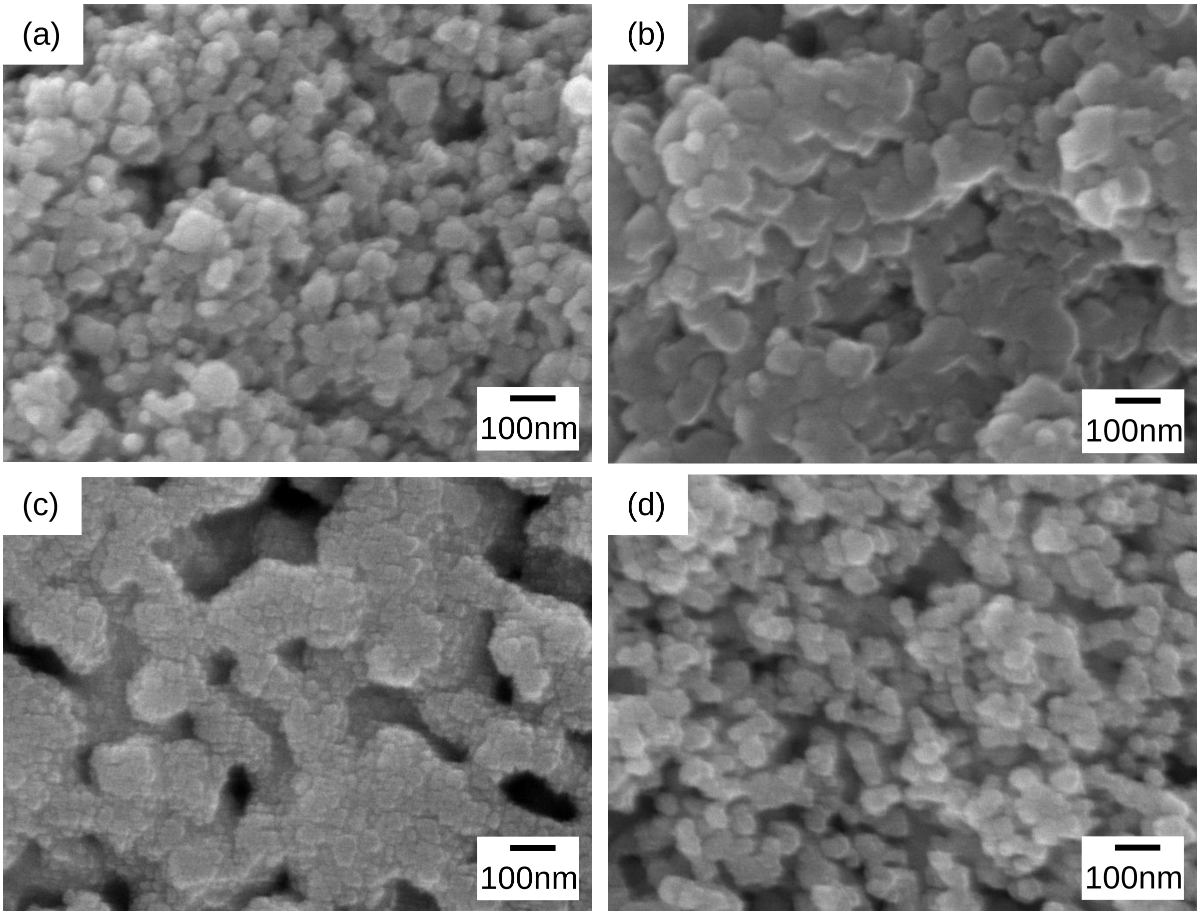


Fig.2. Thermal analysis of oxidized copper nanoparticles in 5%H_2-Ar.



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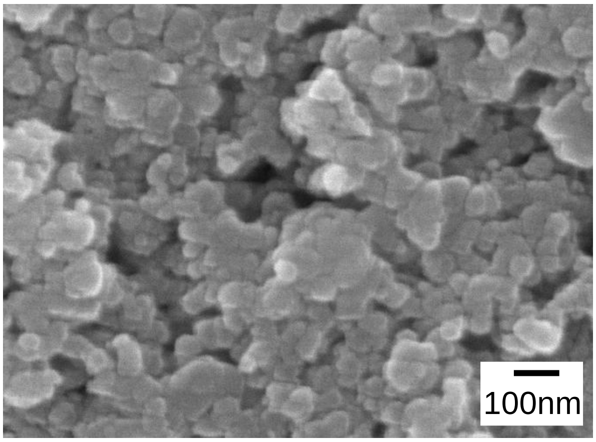


Fig. 4. Morphology of Cu nanoparticle film annealed at 300 ˚C in air.

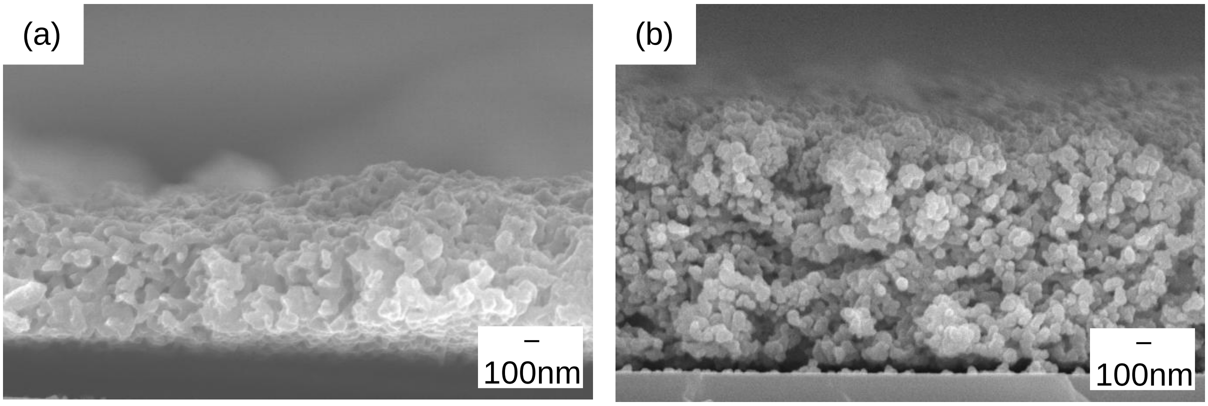


Fig. 5. Cross-section of film annealed at 300 ˚C under various atmospheric conditions: (a) Cu nanoparticles in air and 5%H_2-Ar, (b) CuO nanoparticles in 5%H_2-Ar.

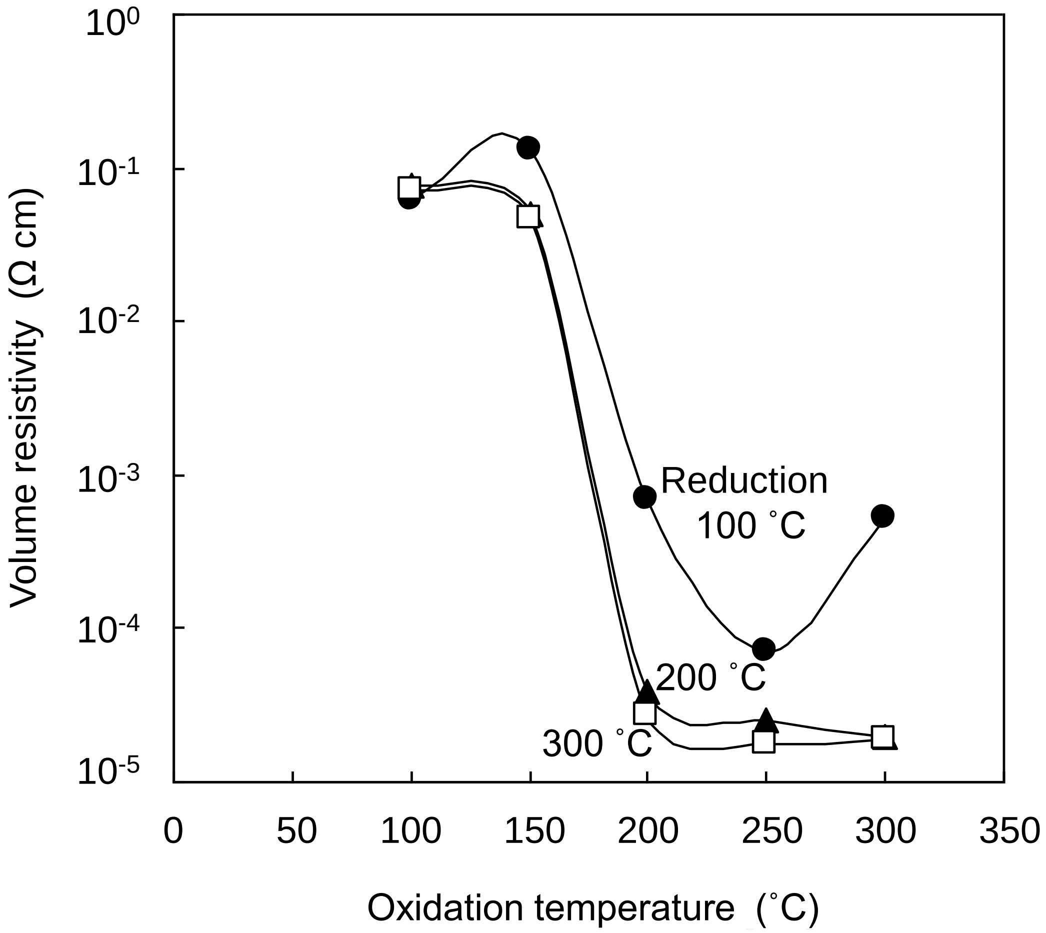
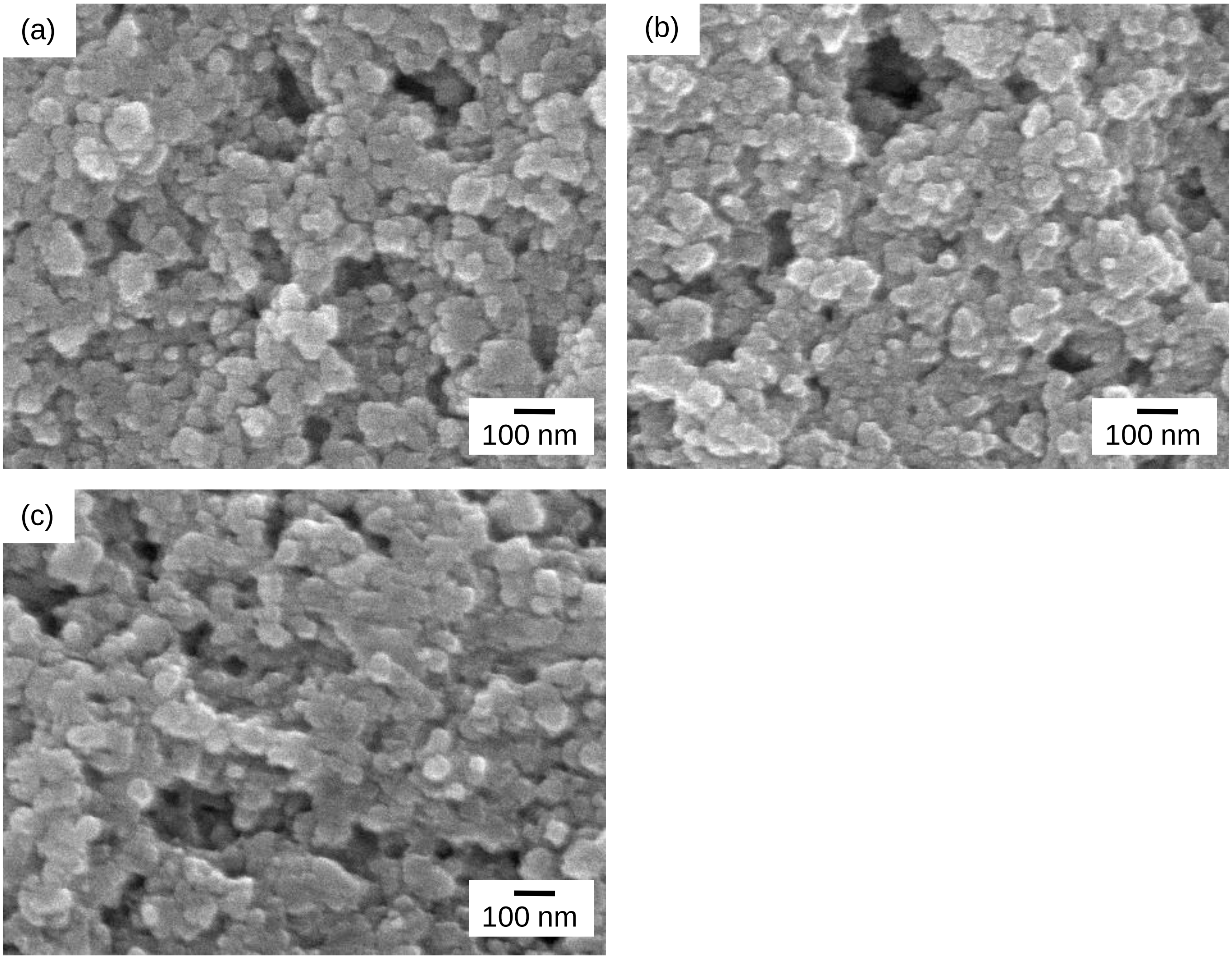


Fig. 6. Volume resistivity of copper nanoparticle films in various oxidation and reduction temperatures.



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