Development of Copper Nanoparticle Fabrication Technique Using Electrochemical Reduction

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ABSTRACT   Recently, the R & D on the sintered materials are very active to realize the soldering of electronic components and the forming of fine wiring circuits at a low temperature using metal nanoparticles as a raw material. Especially, the prospects for copper nanoparticles, which have advantage in a material cost in comparison with that of gold or silver, is increasing. So the mass production technique of the copper nanoparticles is required at a low cost and at a low environmental impact. In this research, the fabrication process adopting the electrochemical reduction is investigated as a method to synthesize the copper nanoparticles. As a result, it is confirmed that the copper nanoparticles of smaller than 100 nm in the primary particle diameter can be fabricated by the electrochemical reduction method and that the copper nanoparticles fabricated in it can be sintered at a low temperature around 200℃.

1. INTRODUCTION

It is already known that the metal shows some characteristics different from those of bulk materials and those of fine particles of the size in nanometer. These changes of characteristics are caused by the remarkably increased ratio of atoms which are exposed to the surface of the particles and have a large surface energy in comparison with that of bulk materials. They show various features such as the improved catalytic activity and the lower melting point. Especially, the characteristics of lowering the melting point have been investigated for a long time. The equation of Pawlow, which is a classic model to show the relation of the particle size and the melting point, is shown as follows:

$$T = T_0 \left[1 - \frac{4}{\rho_s L d} \left\{ \sigma_s - \sigma_l \left(\frac{\rho_s}{\rho_l} \right)^{\frac{2}{3}} \right\} \right] \qquad (1)$$

T: The melting point of the nanoparticle, T_0: The melting point of the bulk, L: the Latent heat, d: the Diameter of particle, ρ_s: the Density in the solid phase, ρ_l: the Density in the liquid phase, σ_s: the Surface tension of the solid phase, σ_l: the Surface tension of the liquid phase

The relation of the melting point of copper against the diameter of the particle based on Equation (1) is shown in Figure 1. It is expected that the melting point may decrease suddenly where the diameter of particle is around 10 nm. Recently, the R & D on the sintered materials is very active to realize the soldering of electronic components and the forming of the fine wiring circuits at a low temperature with the use of such a feature of the metal nanoparticles where the melting point decreases. From the view point of metal types, the research of silver is ahead of the others but it presents a problem because of the high cost of raw material and of the ion migration phenomenon in silver. Therefore, the expectation from the nanoparticles of copper which is low in cost and resistant to the migration is increasing as a metal to replace gold and silver.
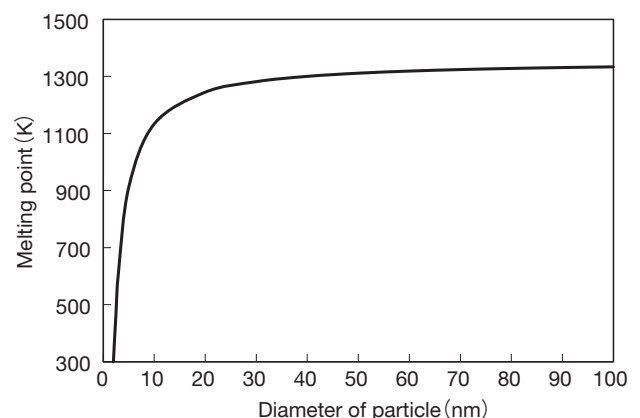

Figure 1 Melting point of copper particles against the particle size.

As for the fabrication methods of metal particles, they are roughly classified into three types, the solid-phase method in which bulk materials are broken into particles,

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the liquid-phase method in which particles are formed in a solution and the gas-phase method in which particles are formed from a metallic vapor. The solid-phase method is a simple process but there are some problems in its productivity in case of breaking the material from its bulk size. The range of distribution of its particle diameter is so broad that in general it is difficult to fabricate fine particles in the order size of nanometer. In the gas-phase method, particles in the order size of nanometer with little impurities are easily formed. But, it has also the weak point that its production equipment is large in size in addition to the tendency of its widening range of distribution of its particle diameters. The liquid-phase method is a process to fabricate particles by some chemical treatment in a solution. The liquid-phase reduction method is the most popular process in which a strong reducing agent is put in a solution of the target metal ion to deposit this metal particle by reduction. However, ordinarily in the batch processing is required in the liquid-phase reduction method, there are major problems that the quantity of the waste liquid and complexity of the process increases with the building up of the capacity of production because the reuse of raw materials applied in the fabrication is difficult. That is the reason behind developing the research of a fabrication technique of the metal nanoparticles by the electrochemical reduction which may realize the continuous synthesis under the use of the features of the wet process[2]. A schematic illustration of the electrochemical reduction process is shown in Figure 2. In this method such a procedure is applied that electrodes are set in a solution of a target metal ion to deposit the metal nanoparticles by the electrochemical reduction on the surface of a cathode by applying potential between the electrodes. In the electrochemical reduction method, the quantity of wasted liquid can be drastically reduced in comparison with that in the liquid phase reduction method because the raw materials can be reused similar to the

present electroplating process. And the productivity is expected to improve drastically as well, because the scale of production can be easily expanded. If the fabrication technique of copper nanoparticles using the electrochemical reduction is established, it is expected to supply the metal nanoparticles at a very low cost in comparison with a copper nanoparticle by a conventional process.
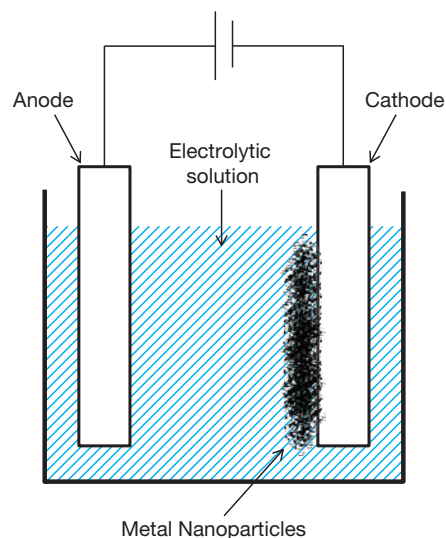

Figure 2   Schematic illustration of electrochemical fabrication method for metal nanoparticles.

Considering the above mentioned background, in this paper, we are going to report mainly the results of the analysis of the basic behavior of the copper nanoparticles in the electrolytic deposition in various kinds of electrolytic baths. Further, the characteristics of the low temperature sintering of the copper nanoparticles formed in the electrochemical reduction are checked as well.
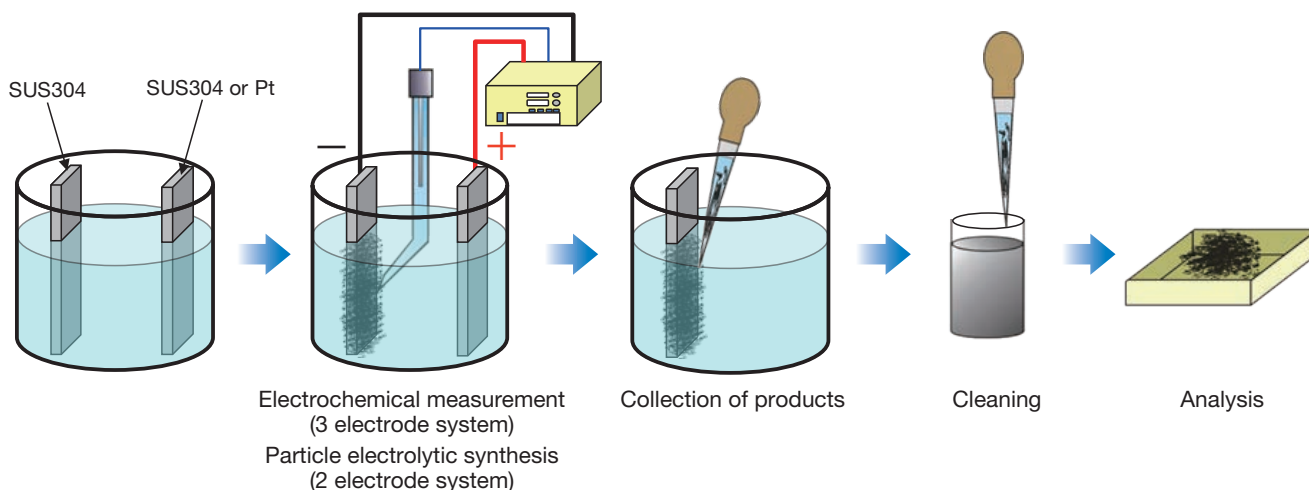

Electrochemical measurement
(3 electrode system)
Particle electrolytic synthesis
(2 electrode system)

Collection of products   Cleaning   Analysis

Figure 3   Schematic illustration of the experimental process.

2. THE METHOD OF EXPERIMENT AND ANALYSIS

2.1 The Process of Experiment

A schematic illustration of the process of experiment is shown in Figure 3. Plates made of SUS304 after degreasing and acid cleaning are installed in an electrolytic bath as the electrodes. And applying potential between the electrodes in the initially made-up electrolyte, the copper deposition reaction by the electrochemical reduction is investigated. Further, the most important parameters in the electrochemical reduction reaction are the type of electrolytic bath which affects largely the ionic state of the copper and the supporting electrolyte which is necessary to control the solution resistance and the pH value. Therefore, as shown in Table 1, the copper sulfate bath, the copper pyrophosphate bath and the copper cyanide bath, which are types of bathes used in a general electrolytic copper plating and in addition the copper acetate bath are applied. In each of these kinds of bathes, the Linear Sweep Voltammetry (LSV) is carried out with a three-electrode system using a reference electrode and a suitable condition of current density for synthesizing the particles is estimated based on the form of copper deposition accompanied by the cathodic polarization. Based on the obtained suitable condition, the copper particles are formed on the electrode with the application of potential between the two electrodes. After finishing the electrolysis, products formed on the electrode are separated and collected and these products are washed with alcoholic organic solvent. Then, the particles are dried under the reduced-pressure atmosphere.

Table 1　The composition of electrolytic bath for electrochemical deposition of copper particles.

No.	Type of bath	Copper salt	Concentration	Supporting electrolyte	Concentration	pH
1	Copper sulfate bath	$CuSO_4 \cdot 5H_2O$	0.1 mol/L	Na_2SO_4	0.005 mol/L	4.1
2	Copper pyrophosphate bath	$Cu_2P_2O_7 \cdot 3H_2O$	0.05 mol/L	$K_4P_2O_7$	0.24 mol/L	10
3	Copper acetate bath	$Cu(CH_3COO)_2 \cdot H_2O$	0.1 mol/L	$CH_3COONa \cdot 3H_2O$	0.01 mol/L	5.5
4	Copper cyanide bath	$CuCN$	0.1 mol/L	$NaCN$	0.2 mol/L	10

2.2 Method of Evaluation

A Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray analyzer (EDX) is used for the observation of form of products and the analysis of elements. Samples for the SEM observation are prepared by trapping the products in a filter with holes of 20 to 200 nm in diameter. And the Raman spectrum of the products on the electrode is measured in situ in the solution. A working electrode with the uneven nanometer-size structure which shows the effect of Surface-Enhanced Raman Scattering (SERS) is used to increase the detection sensitivity. Some electrolytic solution is added after a counter electrode and a reference electrode are installed in addition to this working electrode in an electrochemical cell. And the measurement is carried out by a Raman microscopy (Tokyo Instruments, nano-finder 30) under a constant potential of the working electrode.

As for the evaluation of low temperature characteristics of sintering, the copper nanoparticle ink made of the copper nanoparticles dispersed in an organic solvent is used for investigation. After applying the copper nanoparticle ink on a glass substrate, it is heated up in nitrogen atmosphere to make a sintered film. The measurement of electric resistance and the analysis of crystal structure with the X-Ray Diffraction (XRD) are carried out.

3. RESULTS

3.1 Behavior in the Electrochemical Deposition of Copper Nanoparticles

3.1.1 Investigation into the Condition for Particle Deposition by the Cathodic Polarization

The LSV of the copper sulfate bath, the copper pyrophosphate bath and the copper acetate bath with a silver-silver chloride reference electrode are carried out to estimate the condition of current density suitable for the forming of particles. The measurement is carried out at the set scan rate of 5 mV/second with a working electrode of 16 mm × 16 mm in area in an electrolytic bath without stirring. The cathodic polarization curves obtained by the LSV are shown in Figure 4. The reduction current increases clearly at -50 mV (vs. Ag/AgCl) in the copper sulfate bath, at -950 mV (vs. Ag/AgCl) in the copper pyrophosphate bath and at -200 mV (vs. Ag/AgCl) in the copper acetate bath approximately. And then, the current density does not increase through the plateau region and it is drastically increasing after reaching -1.5 V (vs. Ag/AgCl). At this moment, the deposition in powder form becomes obvious and bubbles of hydrogen are heavily generated in accordance with the following equation.

$$H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (2)$$

In the plateau region in which the current density is constant, it is explained that the current density has reached the critical current density at which the supply rate of copper ions by their diffusion reaches its limit. Since a long time ago, it has been explained that the electrolytic deposition of powder is caused by some obstruction in supplying the reactants and that the critical current density is one of its aims[3]. In the electrolytic bath of this experiment, the concentration is adjusted to such a level as to cause the diffusion-controlled reaction more easily than that in a general plating bath. It is not a rare case that the potential for hydrogen production is exceed-

ed under the electrolytic condition in which the current density reached the critical one although it may depend on the concentration of the electrolyte or the condition of stirring. Further, it is also a feature that bubbles of hydrogen are generated along with the deposition of powder. The influence of the generated hydrogen over the powder deposition is not yet clearly known. But, it is explained based on the present knowledge that the bubbles of hydrogen give some supplementary actions such as exfoliation and mechanical destruction of deposited products[4]. In the phase where the current density exceeds 100 mA/cm^2, the quantity of powder is as much as to cover the electrode as shown in Figure 5, while the generation of hydrogen gas becomes more intense. In this investigation, the current density of 100 mA/cm^2 or over is applied as the condition of particle forming.
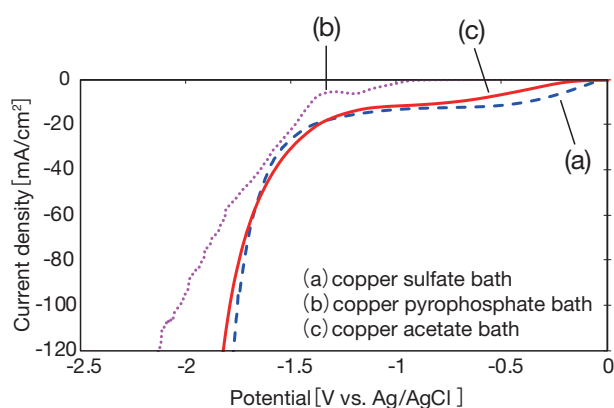

Figure 4 **Cathodic polarization curves obtained from each of the copper salt solutions. (scan rate = 5 mV/s)**
(a) copper sulfate bath
(b) copper pyrophosphate bath
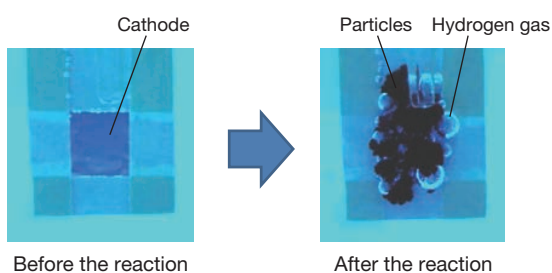**(c) copper acetate bath**

Figure 5 **Appearance of a cathode before and after the electrolytic reaction.**

3.1.2 Analysis of Products Obtained by the Electrochemical Reduction

The observation of the SEM image and the result of the element analysis using the EXD of the products are shown in Figure 6, which are obtained by applying a power of current density of 100 mA/cm^2 or higher using the copper sulfate bath, the copper pyrophosphate bath and the copper acetate bath in the two-electrode system.

In a specimen (a) from the copper sulfate bath, there are a lot of dendrite crystals of 1 to 20 μm intermingled and very few particles are formed. On the other hand, in a specimen from either the copper pyrophosphate bath (b) or the copper acetate bath (c), there are much less dendrite crystals intermingled and nanoparticles whose primary particle diameters are 100 nm or under are formed. Especially the nanoparticles formed in the copper acetate bath are the smallest and the diameter of the primary particle is approximately 30 to 40 nm. Based on the result of the point analysis by the EDX of the nanoparticles obtained from the copper acetate bath, it is confirmed that they are mainly composed of copper as well. There is such a characteristic in a specimen from the copper pyrophosphate bath that there is large-size powder of micron size intermingled with nanoparticles whose primary particle diameters are 40 to 100 nm more than that from the copper acetate bath.
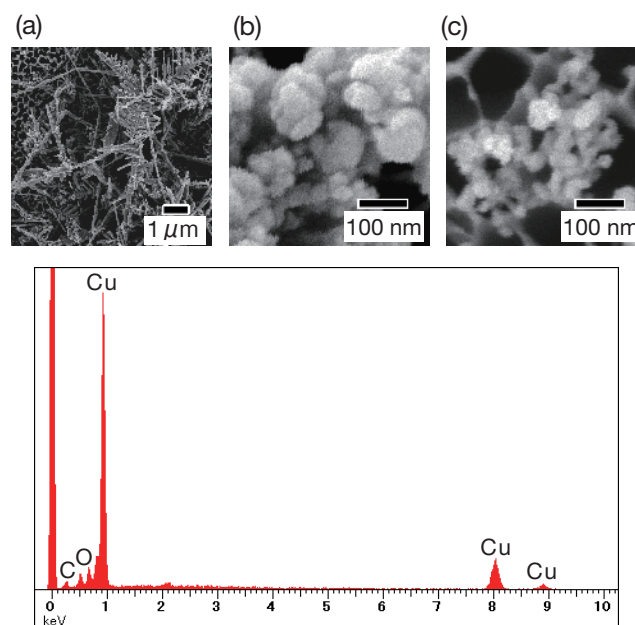

Figure 6 **SEM images of particulate substances synthesized from (a) copper sulfate bath, (b) copper pyrophosphate bath and (c) copper acetate bath. (EDX spectrum corresponds to the sample (c).)**

3.1.3 Influence of pH value and Complex Formation

Although it is confirmed that nanoparticles can be formed by the electrochemical reduction, conclusive factors which contribute to the deposition of nanoparticles have not been discovered, yet. The quantity of copper included in each of the electrolytic bathes of No.1 to No.3 in Table 1 is same but the shapes obtained in the electrolytic deposition are quite different. The pH value of the electrolytic bath is the first factor we focused to explain clearly the factors that influence the deposition of nanoparticles. The pH value of the copper acetate bath in which the smallest copper nanoparticles among No.1 to No.3 in Table 1 have been deposited is pH 5.5 of a slightly acidic

solution. The influence of the pH value over the deposition form is investigated by carrying out the same reduction process under the control of the pH value by adding acetic acid or sodium acetate in the copper acetate bath. The result of the investigation is shown in Figure 7. The specimen (a) from the bath adjusted at pH 4.7 shows there is a lot of micron-size dendrite intermingled as same as that from the copper sulfate bath. No dendrite is confirmed in the specimen (b) from the bath adjusted at pH 6.0 and mainly the nanoparticles formed in it are found out. It is explained that it is necessary to keep the pH value of the bath not to drop to be acidic in order to suppress the dendritic growth. The upper limit of the pH value can be estimated only from the results of other bathes because copper ions are precipitated as copper hydroxides when the pH value is adjusted to a higher level in the copper acetate bath. The specimen (c) shows the large-size powder of micro size obtained from the copper pyrophosphate bath together with the nanoparticles. The specimen from the copper pyrophosphate bath shows the existence of a lot of large-size powder intermingled and clearly a lower characteristic in the deposition of nanoparticles than that of the copper acetate bath. The copper cyanide bath (shown in No.4 in Table 1) which used as a typical alkaline copper plating bath is also investigated to check whether the phenomenon is peculiar to the copper pyrophosphate bath where the characteristic in the deposition of nanoparticles tend to drop even though its pH value is much higher than that of the copper acetate bath. The cathodic polarization curves obtained from the copper cyanide bath in which the concentration of copper is adjusted similar to each of the electrolytic bathes of No.1 to No.3 are shown in Figure 8. Those of the copper cyanide bath are different from any of the copper sulfate bath, the copper acetate bath and the copper pyrophosphate bath and a very little reduction current flows until -1.5 V (vs. Ag/AgCl) and no powder is deposited even when the excessive potential of -6.0 V (vs. Ag/AgCl) or lower is applied. Those pictures inserted in the graph of the polarization curves show the conditions of the electrodes at the measurement. It is found out from them that only copper plating coat is uniformly formed and that there is no powdered deposition. The investigation is carried out in case the concentration of copper is reduced down to 0.01 mol/L and also increased up to 0.20 mol/L, however, only copper plating coat is formed as well. The result is that the deposition of copper nanoparticles in the copper cyanide bath is very difficult even though the pH value is approximately the same as that of the copper pyrophosphate bath. It is expected based on these results that the stability of the copper complex has some effects in the deposition of nanoparticles as a factor. It is very clear from the potential-pH value diagram (Pourbaix Diagram) of copper-water system that fundamentally in an aqueous solution including copper ions, copper hydroxides are formed and deposited under the alkaline environment. But the copper ions

become soluble even in alkaline solution if a chemical agent including such a ligand that is strongly coordinated with copper to form complex ions is introduced. The complex formation constants of copper and ligands in the electrolytic bathes used in this investigation are shown in Table 2[5), 6)]. The larger the value is, the more stable the complexes with the stronger coordinating property are formed. The complex formation constant of copper cyanide is the largest and that of copper pyrophosphate is the second and that of copper acetate is the third. This order corresponds to the tendency of deposition of the nanoparticles. The reaction process of deposition of the copper nanoparticles is not clearly known, but it is explained that assuming that several cathodic reactions necessary for forming the nanoparticles proceed after the complex is decomposed, the forming ability of the nanoparticles is reduced in the electrolytic bath of too stable complexes because the overpotential necessary for the decomposition of complexes is also high.

(a)   (b)   (c)

500 nm   200 nm   500 nm

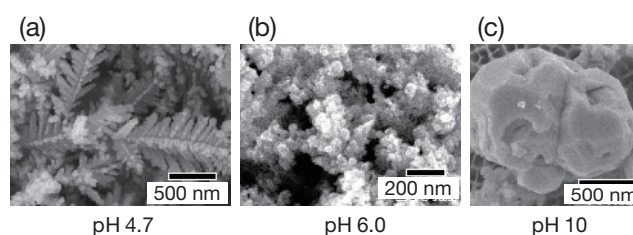pH 4.7   pH 6.0   pH 10

Figure 7   Influence of pH of a bath on the deposition characteristics.
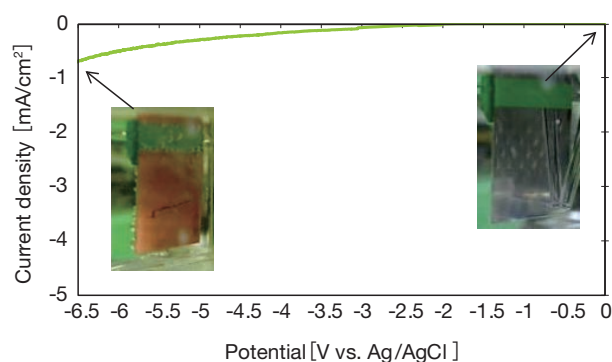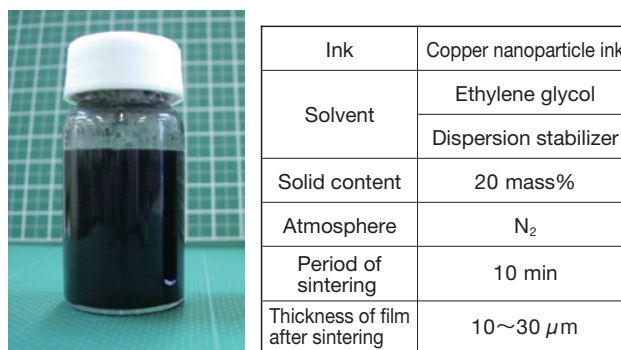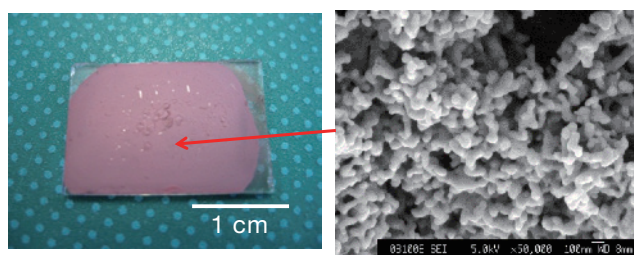

**Figure 8   Cathodic polarization curves obtained from copper cyanide bath. (scan rate = 5 mV/s)
(Inset) appearance of a cathode before and after measurement.**

Table 2　Complex formation constant of each of various copper salts, and relevant information on the deposition characteristics.

Copper salt	pH	Ligand	Complex formation constant (log β)	Form of deposition
$CuSO_4 \cdot 5H_2O$	4.1	$SO_4{}^{2-}$	2.36	dendrite
$Cu(CH_3COO)_2 \cdot H_2O$	5.5	CH_3COO^-	3.09	nanoparticle
$Cu_2P_2O_7 \cdot 3H_2O$	10	$P_2O_7{}^{2-}$	6.2	nanoparticle coarse particle
CuCN	10	CN^-	30.3	plating film

3.2　Sintering Properties of Copper Nanoparticles

The nanoparticle ink containing 20 mass % Copper (shown in Figure 9) is prepared by mixing the copper nanoparticles and an organic solvent to evaluate the low-temperature sintering characteristics of the copper nanoparticles synthesized by the electrochemical reduction. There was a problem that the oxidation reaction of the copper nanoparticles easily progressed because no coating treatment was provided on the surface of the particles in the synthesis condition for the copper nanoparticles in this investigation. A too thick layer of oxides may be a large factor to prevent the sintering. Therefore, ethylene glycol is added to the solvent as an agent for removing oxide films at heating. Ethylene glycol is a typical and known polyol as it shows a reduction action in its decomposition process at high temperature heating. In addition, the dispersion stability of the particles is raised by adding various organic solvents. A specimen is prepared with dropping the copper nanoparticle ink on a glass plate and is transferred in a nitrogen atmosphere of oxygen density of 1000 ppm or less. After that, the prepared specimen is heated to the prescribed temperature and held on that temperature for 10 minutes. The appearance and the surface SEM image of a 200℃ sintering film on the copper nanoparticles prepared in the above mentioned procedure are shown in Figure 10. From the SEM image, it was suggested that the copper particles have formed necking together and started fusing. Next, the result of the XRD measurement before and after the sintering of the copper nanoparticles is shown in Figure 11. The main peaks of not only Cu but also Cu_2O are intensely detected before the sintering, but only the peak of Cu is detected on the sintered coat at 200℃ and 300℃. And, the results of the measurement of the electric resistivity of the sintered film are shown in Figure 12. The specific resistance is 68 μΩ・cm at 180℃, 27 μΩ・cm at 200℃ and 22 μΩ・cm at 300℃.

Ink	Copper nanoparticle ink
Solvent	Ethylene glycol
	Dispersion stabilizer
Solid content	20 mass%
Atmosphere	N_2
Period of sintering	10 min
Thickness of film after sintering	10〜30 μm

Figure 9　Copper nanoparticle ink (Cu Nano-Ink) manufactured by electrochemical reduction.

1 cm

Figure 10　Appearance and SEM image of the sintered copper nanoparticle film after heat treatment at 200℃ for 10 min.
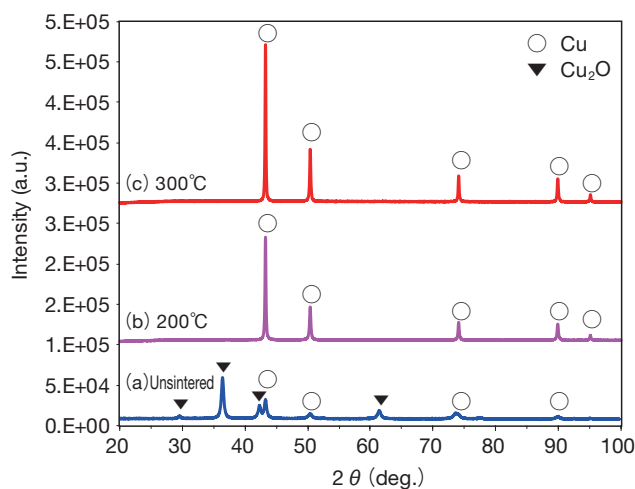
Figure 11　XRD pattern of the sintered copper nanoparticle film (a) unsintered (b) 200℃ (c) 300℃

Based on the above mentioned results, it is found out that even though some degree of oxidation on the surface of copper nanoparticles has already progressed, the copper nanoparticles can be reduced and sintered to the metal copper sufficiently even at a low temperature of 200℃ if they are combined with such a solvent, as polyols, which has the reduction effect of oxide.
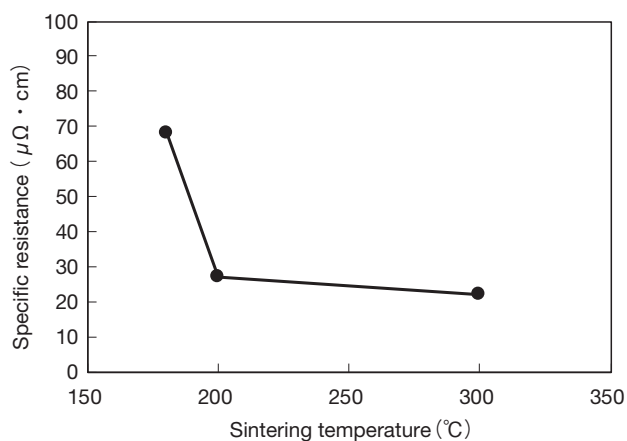
Figure 12 Specific resistance against the sintering temperature.

4.　DISCUSSION

4.1　Analysis of the Deposition Process of the Copper Nanoparticles in the Electrochemical Reduction Reaction

Although it is already found out that the pH value and the stability of the complexes are important factors in the synthesis condition, the details of the reaction process until the copper nanoparticles are electrochemically deposited, is not sufficiently explained yet. In the analysis of this type of electrode reaction, where nanosize deposits are formed and which might easily drop off from the electrode and deteriorate, this type of evaluation method is very effective when the reaction site is directly measured in situ. Therefore, we built an electrochemical cell of the three electrode system type and have been developing the direct measurement of the reactants on the surface of the electrode with a Raman microscopy. This electrochemical cell can detect the Raman scattering light at a high sensitivity, whose objects are the molecular species on the surface of the electrode in a solution as this electrochemical cell has nanostructure electrodes inside, which increases the Raman effects.

The result is obtained, which indicates the existence of several copper compounds as the intermediate products around the cathode after analyzing the deposition reaction of the copper nanoparticles from the copper acetate bath by the measurement in situ with the Raman microscopy. The detected compounds change depending on the pH value and the concentration of the electrolytic solution and the potential applied on the working electrode at measurement. The existence of CuO, Cu_2O, and Cu (OH)$_2$ are confirmed so far[7]. The spectrum is shown in Figure 13, which is obtained from the measurement of the Raman spectroscopy when keeping the potential of cathode at -0.2 V (vs. Ag/AgCl) in the copper acetate bath. Referring to the result of earlier research[8], a peak mainly originated from Cu_2O has been already detected under the condition of this potential control. Even when the cathode potential is -1.0 V (vs. Ag/AgCl) or lower, the result is that the peak of Cu_2O is also intermingled. The process is explained that such a reaction environment is formed at the early stage of the electrolytic reaction in which oxides and hydroxides are formed as precursors of the copper nanoparticles one after the other. Probably, this reaction environment may be created by the condition where the pH value around the cathode becomes higher than that of a bulk solution along with the generation of hydrogen shown in Equation (2). A schematic description of this reaction path is illustrated in the potential-pH value diagram (Pourbaix Diagram) of copper-water system in Figure 14. Please note the fact that the actual potential-pH value diagram is a phase diagram including the equilibrium state with anions and ligands generated by the solution of copper salt. The alkali reaction field is built up by the enrichment of OH ions along with the generation of hydrogen when the hydrogen generation potential is reached in the initial stage of the electrolytic reaction. Therefore, the environment which pH value is higher than that of the bulk solution is generated around the cathode and the electrochemical reaction to form the hydroxides and the oxides is progressing, which are expected as precursors of the creation of the nanoparticles. However, in case that the pH value in the bulk solution is too low, no stable phase of hydroxides or oxides can be reached and the deposition follows the process which is in conformity with a general mechanism of dendritic growth[9]. And, in case that the pH value in the bulk solution is too high, the decomposition of complexes hardly progresses a situation in which the stability of the complexes is inevitably high. It is explained that as a result, the efficiency of forming of the precursors shows decline and the frequency of deposition of the large-size powder becomes higher. Based on the above mentioned discussion, the deposition processes of the copper sulfate bath, the copper pyrophosphate bath and the copper acetate bath used in this investigation are summarized in Figure 15.
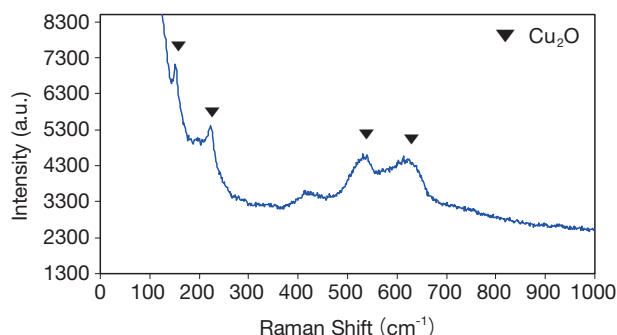

Figure 13 In situ Raman spectrum on the surface of electrode under the electrochemical reduction using copper acetate bath. (cathodic potential: -0.2 V vs. Ag/AgCl)

4.2 Behavior of Sintering of the Copper Nanoparticles

When the copper nanoparticles synthesized by the electrochemical reduction method are made to a kind of ink with an organic solvent to evaluate their behavior in the sintering, it is shown that there are exhibiting the low temperature characteristics of sintering as the necking among the particles is confirmed. However, the specific resistance of sintered film tends to be higher in comparison with 1.7 µΩ・cm of bulk copper. It is found out from the SEM image shown in Figure 10 that the sintered film still has the high porosity and the porous structure and it seems to have no sufficient conducting paths. Consequently, it can be expected that the perspective for the reduction of the resistance of sintered films are acquired by the analysis of the influence of oxides existing on the surface of the particles and that of the size of particles obtained by synthesis against the condition of sintering.

5. CONCLUSION

In this paper, fundamental guidelines are shown to deposit the copper nanoparticles electrochemically. It is possible to obtain the copper nanoparticles of smaller than 100 nm in primary particle diameter if the composition of electrolytic bath and the condition of applying potential are controlled. Especially, the pH value of the electrolytic bath and the stability of the complexes are important as the conditions of fabrication. The result of the analysis by the measurement in situ with a Raman microscopy indicates the possibility for oxides and hydroxides to be formed on the electrode as intermediate products. Further, it is also confirmed that the copper nanoparticles obtained in the electrochemical reduction process can be sintered at a low temperature such as 200℃.

At present, we are making our best effort in the development to establish this method as a fabrication technique of metal nanoparticles because of its low cost and its low environmental impact.
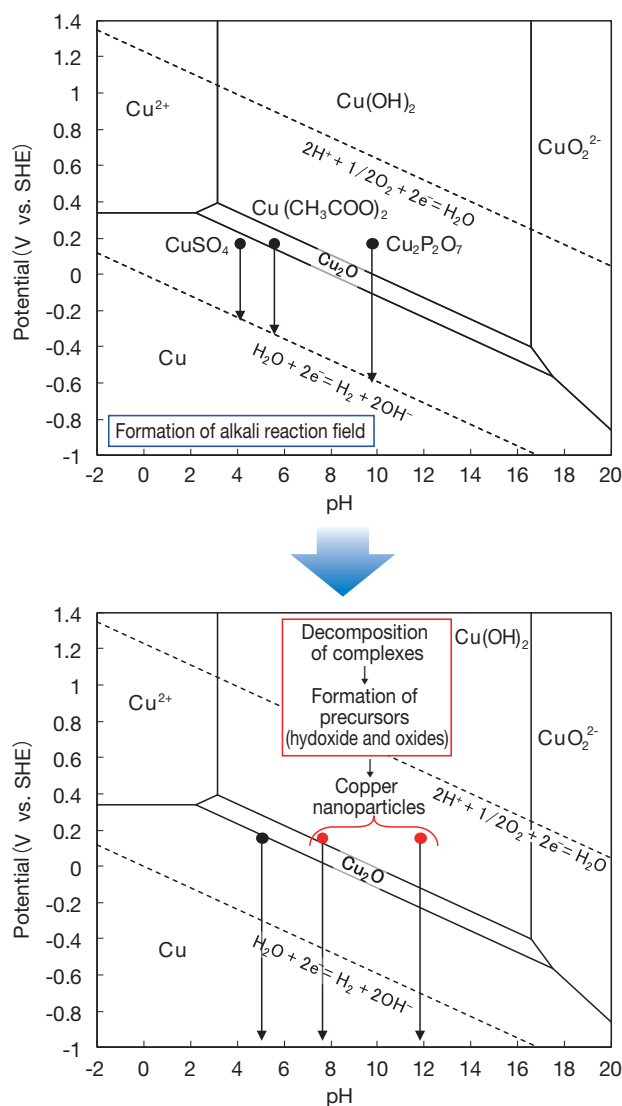
Figure 14 Overview of the reaction path and the mechanism of the synthesis of copper nanoparticles using the electrochemical reduction.
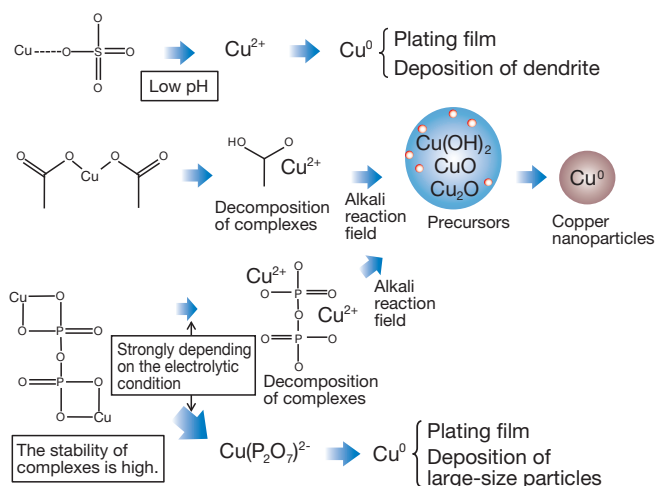

Figure 15 The Schematic illustration of reaction path for the synthesis of the copper nanoparticles using each of the various copper salt solutions.

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