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# High temperature oxidation event of gelatin nanoskin-coated copper fine particles observed by *in situ* TEM

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Metallic copper fine particles were prepared using CuO slurry by hydrazine reduction in the presence of gelatin. To observe a behavior of these particles at high temperature, *in situ* heating TEM observations were carried out. Oxygen gas was introduced and the pressure of the TEM column was kept at  $10^{-3}$  Pa, corresponding the pressure around the sample at  $10^{-1}$  Pa. The gelatin, which acts as a protective nanoskin on the particle surface was gradually decomposed. Around approximately 140 °C, it was observed that Cu<sub>2</sub>O dots formed on the surface of the copper particle. This result is well consistent with the behavior of the TG-DTA curve of the copper fine particles under ambient conditions, and provides key information of oxidative behavior of copper fine particles. Copyright 2012 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported license. [<http://dx.doi.org/10.1063/1.4759498>]

## I. INTRODUCTION

Metal nano- and fine particles were widely used for various fields of science and technology, because of their unique physical and chemical properties depending on their size and shapes.<sup>1-4</sup> In particular, copper attracts much attention because of its high electro-conductivity, relatively low cost, and its many prospects. For example, applications of copper fine particles were proposed for conductive inks or pastes<sup>5-7</sup> bonding materials<sup>8,9</sup> and supported catalysts<sup>10-12</sup> that utilize high electro-conductivity, high formability, and unique surface reactivity, respectively. However, development of copper fine particles must contend with the inhibition of surface oxidation. Only a few reports on the subject have been published.<sup>13-15</sup> Note that the specific surface area of the particles greatly increases with the particles are miniaturized. Therefore, explosive oxidation or even burning occurs in the case of small copper fine particles. Even partial surface oxidation of copper fine particles inhibits sintering between particles. Hence, reducing atmosphere is required during sintering. In addition, CuO layer formed by surface oxidation of copper particles is easy to release cytotoxic Cu<sup>2+</sup> ions, which raises environmental concerns.<sup>16</sup>

Various processes are proposed for the preparation of copper fine particles. Among these, chemical reduction methods are suitable for mass production with a small initial cost. Moreover, to prevent surface oxidation, the particle surface can also be coated with thin layers of polymers, surfactants, and metal oxides. Authors reported the anti-oxidative copper fine particles stabilized by gelatin, which can be kept under air.<sup>17,18</sup> Manocha *et al.* successfully obtained copper octahedral by using a polyol process.<sup>19</sup> Wei *et al.* also used a polyol process but obtained copper nanorods stabilized by amines.<sup>20</sup> Lisiecki *et al.* used hydrazine and NaBH<sub>4</sub> as reducing reagents and prepared copper nanoparticles in both water-in-oil<sup>21</sup> and oil-in-water<sup>22</sup> emulsions. The size of the obtained copper nanoparticles was controlled by the concentration of the surfactants. Guajardo-Pacheco *et al.*

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proposed to use of an extracted compound from soy beans as a chelating agent to obtain copper fine particles by  $\text{NaBH}_4$  reduction.<sup>23</sup> Wang *et al.* also obtained copper fine particles by reduction with hydrazine in the presence of poly(acrylic acid)<sup>24</sup> or poly(acryl amine).<sup>25</sup> Single nanometer-sized copper nanoparticles could also be obtained by a polyol method.<sup>26</sup> In this case, ethylene glycol polymerized to oligo-oxyethylene to stabilize the particle surface.

It is very important to study the behavior of copper fine particles protected by an anti oxidative polymer layer at high temperature to understand the oxidizing process. For this purpose, *in situ* TEM observation of structural changes of nanomaterials has been proposed.<sup>27–34</sup> For example, powders can be heated up to 1000 °C in seconds by using a special TEM sample holder equipped with a heating filament, and high resolution TEM images could be obtained *in situ* without a large drift.<sup>27</sup> Ida *et al.* demonstrated the pointed sintering of aggregated copper fine particles coated with gelatin by using *in situ* TEM observation by the introduction of oxygen gas.<sup>28,29</sup> They succeeded in observing sintering behavior of copper fine particles resulting from the decomposition of the surface gelatin layer by controlling the oxygen partial pressure from of  $8 \times 10^{-5}$  to  $6 \times 10^{-4}$  Pa. We have previously reported the sintering behavior of copper/gelatin composites by *in situ* heating TEM under oxygen partial pressure at  $8 \times 10^{-4}$  Pa.<sup>30</sup> However, these reports showed no information of surface oxidation of copper particles due to the oxygen introduction.

In this study, we firstly report the direct observation of the oxidation behavior of gelatin-stabilized copper fine particles, which were prepared by the reduction of CuO by hydrazine, with which we obtained *in situ* heating TEM under  $10^{-3}$  Pa level oxygen partial pressure. This was higher than the previous reports. We also compared the oxidation phenomenon with the TG-DTA results at ambient condition.

## II. EXPERIMENTAL

### A. Materials

Cupric oxide (CuO, N-130) purchased from Nissin Chemco Ltd., Japan. Hydrazine monohydrate ( $\text{N}_2\text{H}_4 \bullet \text{H}_2\text{O}$ ), aqueous ammonia ( $\text{NH}_3$ , 28%) and citric acid monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \bullet \text{H}_2\text{O}$ ) were purchased from Kanto Chemical, Japan. All chemicals were used without further purification. A small amount of defoamer (Sannopco Co. Ltd., Japan) was added to the reduction process. Gelatin was supplied from Nitta Gelatin Co., Japan. Water was twice distilled and then purified with a Organo/ELGA purelabo system ( $>18 \text{ M}\Omega$ ).

### B. Synthesis of copper fine particles

Gelatin (32 g) was completely dissolved into 950 mL of warm water (60 °C). This solution was transferred into a 5-L beaker and a PTFE impeller was placed in it. Eighty grams (1.0 mole) of CuO black powder was added into this solution. Aqueous ammonia as a pH adjuster was added in the solution to adjust pH to 11 by stirring at 100 rpm. For inhibiting the formation of foams during the reduction of CuO by hydrazine, a small amount of the defoamer was added. This beaker was then covered with a plastic wrap and the reaction slurry was gradually heated up to 80 °C for 1 h by stirring. One hundred and twenty milliliters (2.5 mole) of hydrazine monohydrate was added to this slurry at a time. After stirring for 2 h at 80 °C, the color of the slurry contained copper particles changed to brown, and then saturated aqueous citric acid was added to adjust the pH to 8–9. Copper particles were then separated out by settling, and it was possible to collect them by decantation. Then, the obtained particles were washed twice with water and ethanol dried at 60 °C under a nitrogen atmosphere.

### C. Characterization

X-ray diffraction (XRD) patterns were obtained using a PANalytical X'pert Pro, equipped with a Cu  $K\alpha$  tube. Crystalline diameters were estimated by Scherrer's equation from the Cu (111) peaks. Particle diameters were determined from the SEM images obtained by a JEOL JSM-6701F.

TG-DTA curves were observed with a Shimadzu DTG-60H with a 1 °C/min temperature increasing rate. The heating behavior of the Cu fine particles were observed with a TEM (Hitachi, H-9500, 300 kV). The sample particles were put on a Pt (70 %)-Ir (30 %) filament, which was mounted to a heating TEM holder with a gas injection nozzle. The filament was heated by a DC current generated by dry cells. The behavior was recorded through a CCD camera with an NTST frame rate of 29.97 fps. The filament temperature was fixed by the current value, which was calibrated by a radiation thermometer camera and the sublimation temperature of Sb (330 °C at  $10^{-5}$  Pa) and Ag (790 °C at  $10^{-3}$  Pa) powders calculated from the data.<sup>35</sup> Furthermore, it was observed that the filament temperature increases proportionally to the current increase in the observation temperature range. Oxygen gas was directly introduced from an oxygen gas cylinder with a regulated pressure. The pressure of TEM column was measured with a ULVAC GI-M2 ionization vacuum gage. The pressure around the sample is about hundred times higher than that value,<sup>36</sup> which will be discussed later.

### III. RESULTS AND DISCUSSION

#### A. Synthesis of copper fine particles

In our previous report,<sup>17</sup> copper fine particles were prepared from CuO in ethanol/water mixed solvent (water : ethanol (vol/vol) = 1 : 1) in order to avoid the formation of foams during reduction and obtained particles were collected by suction filtration. In this study, the preparation of copper fine particles was carried out in water only. In which case no ethanol addition, it is necessary to inject a small amount of deformer because the reaction slurry was foamed intensively by decomposition of hydrazine. However, without ethanol, copper fine particles formed weak secondly aggregate via hydrogen bonds between surface gelatin layer by adjustment pH of reaction slurry below isoelectric point of gelatin (pH 7 ~ 9) by addition of saturated aqueous citric acid, and can be precipitated. As a result, it was enabled fine particles to collect simply by decantation. This process is very useful procedure for mass production.

Copper fine particles with a diameter of 100 – 200 nm were obtained by the reduction of CuO (Fig. 1(a)). The average diameter and standard division of these particles were 178 nm and 45 nm, respectively (Fig. 1(b)). The secondary aggregated large particles were not observed in the SEM images. In addition, the particle shape did not appear as spheres, but they showed clear facets. TEM observations of these particles revealed that their surface was coated with a uniform thin amorphous layer with a thickness of about 2.5 nm (Fig. 1(c)). As is the case in previous reports,<sup>5,28</sup> this amorphous layer can be consider gelatin as a protective agent. This uniform gelatin layer prevents the oxidation of the particle surface in ambient conditions. In the case of PVP-coated copper fine particles,<sup>13</sup> the surface was found to be copper oxide, and this result was also observed from the thermodynamic phase transition behavior.<sup>37</sup> However, in this study, it appeared that when gelatin was observed on the particle surface, oxidation of copper particles did not occur. This is attributed to strong adsorbability and poor gas permeability of gelatin.

As also shown in the XRD pattern (Fig. 2), no peak of copper oxides is observed. The grain size of metallic copper calculated by the Scherrer's equation from this XRD pattern is 85.5 nm.

#### B. TG-DTA

TG-DTA curve of the particles was measured in ambient atmosphere (Fig. 3). There is no weight loss under 100 °C, it suggest that water was removed by alcohol washing. In this TG curve, weight increase began at approximately 130 °C, and continued up to approximately 290 °C. At 350 °C, the weight of copper fine particles is increases by 122 % of the initial weight. This result indicates that the metallic Cu (atomic weight: 63.5) completely changed to CuO (molecular weight: 79.5). In the DTA curve, two exothermal peaks are observed at approximately 140 °C and 160 °C, and the rising rate of the TG curve increases around these temperatures. It is appeared that metallic Cu was oxidized to Cu<sub>2</sub>O around these temperatures. Then, another exothermal peak is observed at approximately 260 °C, and here Cu<sub>2</sub>O was again oxidized into CuO.

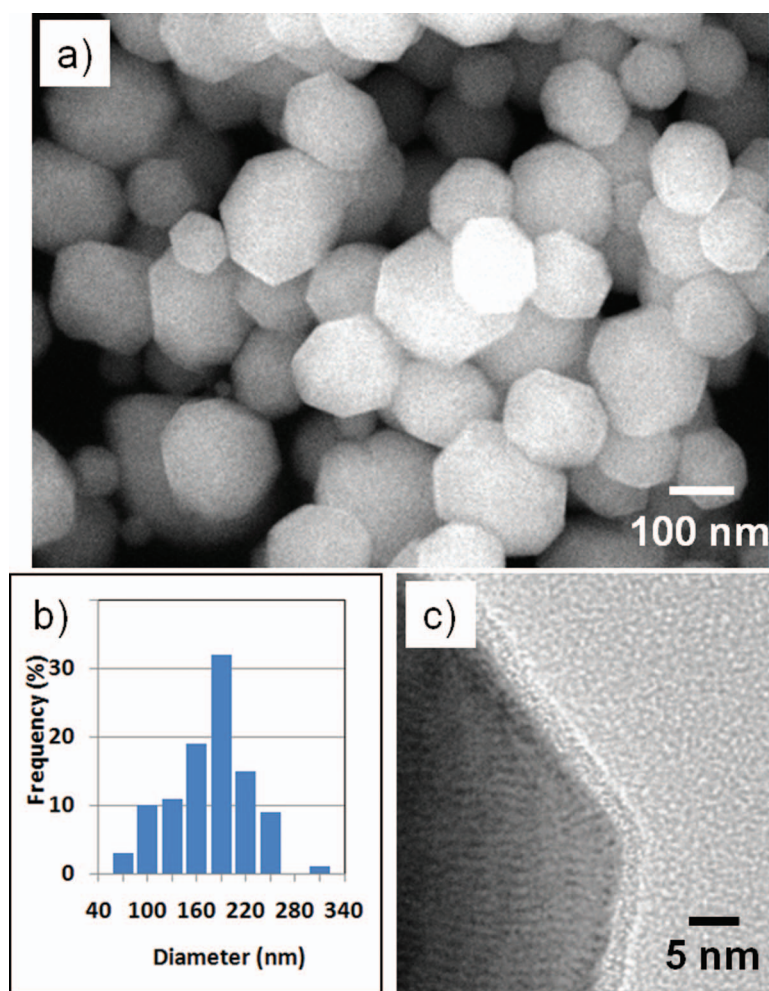


FIG. 1. (a) SEM image of copper fine particles. (b) Particle size histogram of copper fine particles (mean diameter:  $178 \pm 45$  nm). (c) TEM image of copper fine particle coated by gelatin nanoskin.

### C. *In situ* heating TEM observation

An illustration of the observation area of the specimen heating TEM holder with a gas injection nozzle is shown in Fig. 4. The filament coil was made of a Pt (70 mass%)-Ir (30 mass%) wire. Using tungsten filament would be inadequate for this study, because when oxygen gas is introduced at high temperature under vacuum, tungsten is oxidized, and tungsten oxide is evaporated and deposited near the sample. This Pt-Ir alloy does not produce oxidation under an oxygen atmosphere even at high temperatures, and the sample drift during observation is suppressed because the thermal expansion of Pt-Ir is smaller than that of pure Pt at high temperatures. Samples were heated by a DC current applied to both ends of a filament from dry cells for *in situ* TEM observation. The heating rate of the sample is adequately high but the observation spot is constantly kept in our field of view. The gas injection nozzle was opened directly beside the filament. Oxygen gas from a cylinder was introduced and blown toward the samples. The degree of vacuum near the samples was monitored during observation.

When no gas was introduced, the degree of vacuum around the samples was  $3.5 \times 10^{-5}$  Pa. When oxygen gas was introduced by a constant flow through a needle valve, the degree of vacuum around the samples was lowered to  $4.0 \times 10^{-3}$  Pa and was stably maintained around samples. Oxygen gas was injected quite near the sample as illustrated in Fig. 4. Therefore, the pressure around the sample becomes much higher than that of TEM column. Kishita calculated it using a Monte-Carlo simulation with a 3D rarefied gas dynamics simulation software (Pegasus software, Japan).<sup>35</sup> His

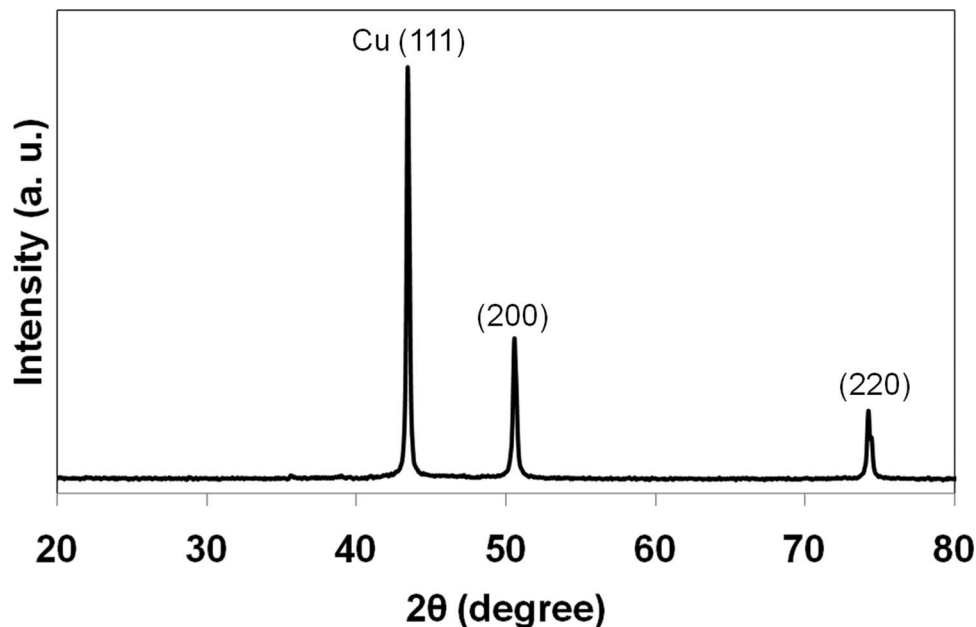


FIG. 2. XRD pattern of the copper fine particles coated by gelatin nanoskin.

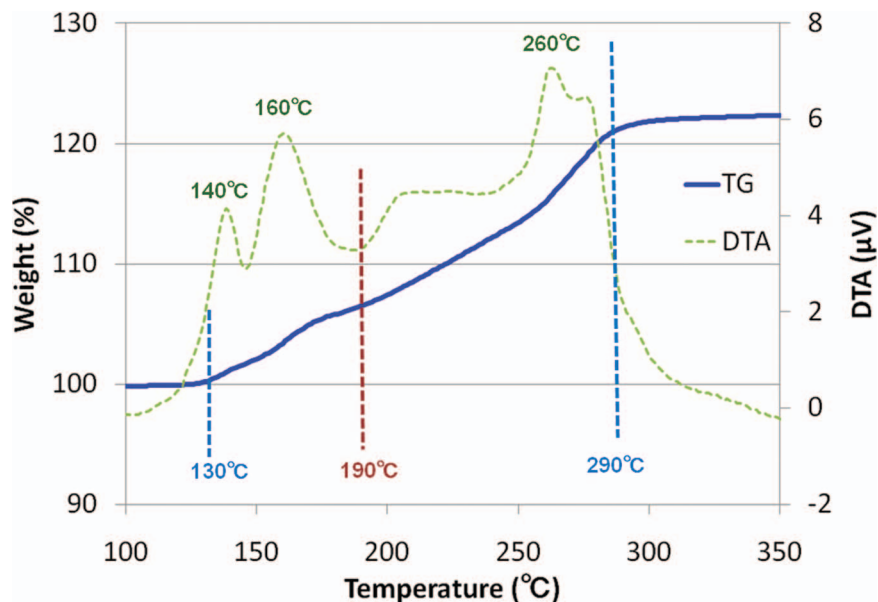


FIG. 3. TG-DTA curves of the copper fine particles coated by gelatin nanoskin measured in an ambient condition.

result showed that the pressure around the sample on the heating wire should be about 100 times larger than the pressure measured in the TEM column. Therefore, the oxygen partial pressure around the copper fine particles should be  $\sim 10^{-1}$  Pa. Therefore, *in situ* heating TEM observation of the copper fine particles was carried out at these four degrees of vacuum.

First, results of *in situ* heating TEM observation without oxygen gas are shown in Figs. 5(a)–5(c). The surfaces of the copper fine particles at room temperature are coated with a thin gelatin layer but the gelatin layer was slightly unevenly distributed. The gelatin layer was kept remained even at 150 °C. It seems that the shapes of the particles changed because the filament was deformed by heat expansion at high temperatures. When heated up to 180 °C, the particle surface did not show any particular change.

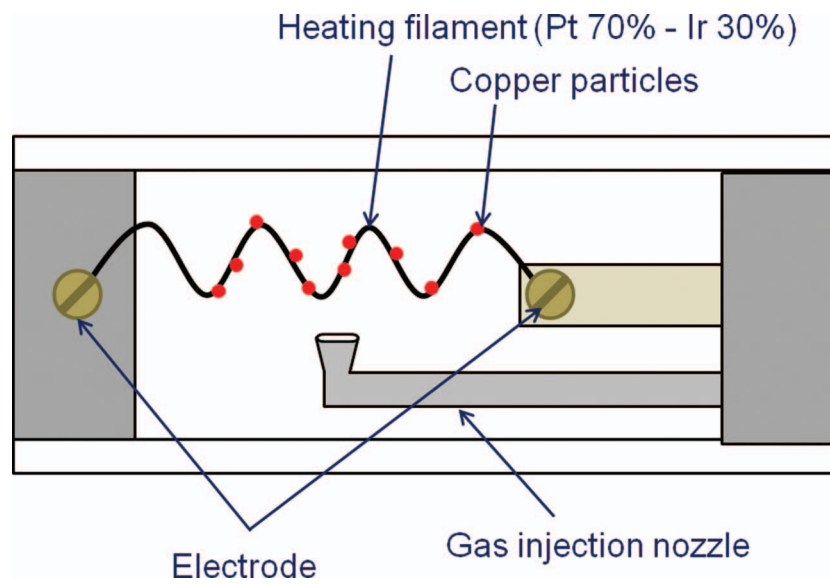
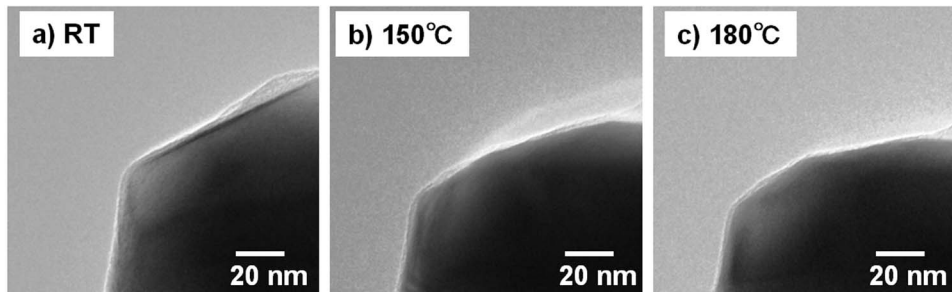


FIG. 4. Schematic illustration of the observation area of the specimen heating TEM holder.

Without  $O_2$  gas (Pressure of TEM column :  $3.5 \times 10^{-5}$  Pa)



With  $O_2$  gas (Pressure of TEM column :  $4.0 \times 10^{-3}$  Pa,  
Around the samples  $\sim 10^{-1}$  Pa)

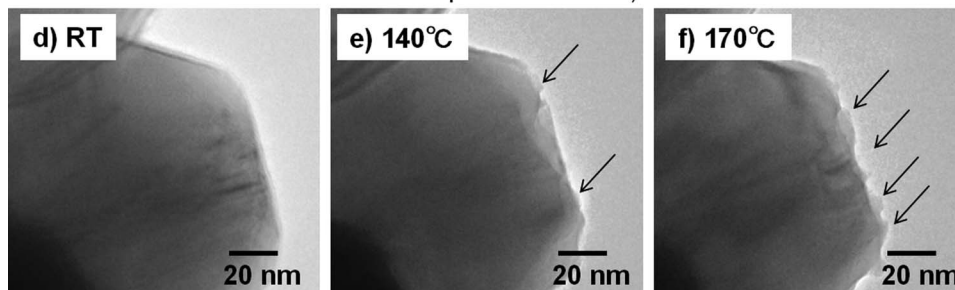


FIG. 5. TEM images of the copper fine particles during *in situ* heating observation with / without oxygen gas introduction. Upper (a-c): Without introduction of oxygen gas. The pressure of the TEM column was kept as  $3.5 \times 10^{-5}$  Pa. Lower (d-f): With introduction of oxygen gas from a cylinder. The pressure of the TEM column was kept as  $4.0 \times 10^{-3}$  Pa and that around the sample was about  $10^{-1}$  Pa. Arrows shows the asperities of copper oxide.

When the oxygen gas having a pressure of  $10^{-3}$  Pa was introduced, there was no change in the shapes of the particles at room temperature and no sample drift due to the introduction of gas was observed. At 140 °C, small asperities began to be observed on the particle surface. Again heated to 170 °C showed small bumps, as indicated in Fig. 5(f). At that time, the surface gelatin layer

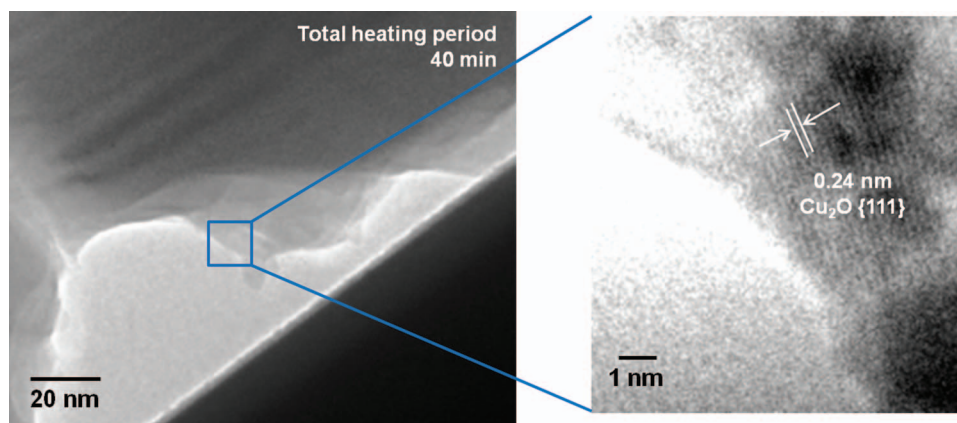


FIG. 6. HR-TEM images of copper fine particles after heated up 190°C with O<sub>2</sub> gas introduction (TEM column:  $4.0 \times 10^{-3}$  Pa, Sample region: about  $10^{-1}$  Pa).

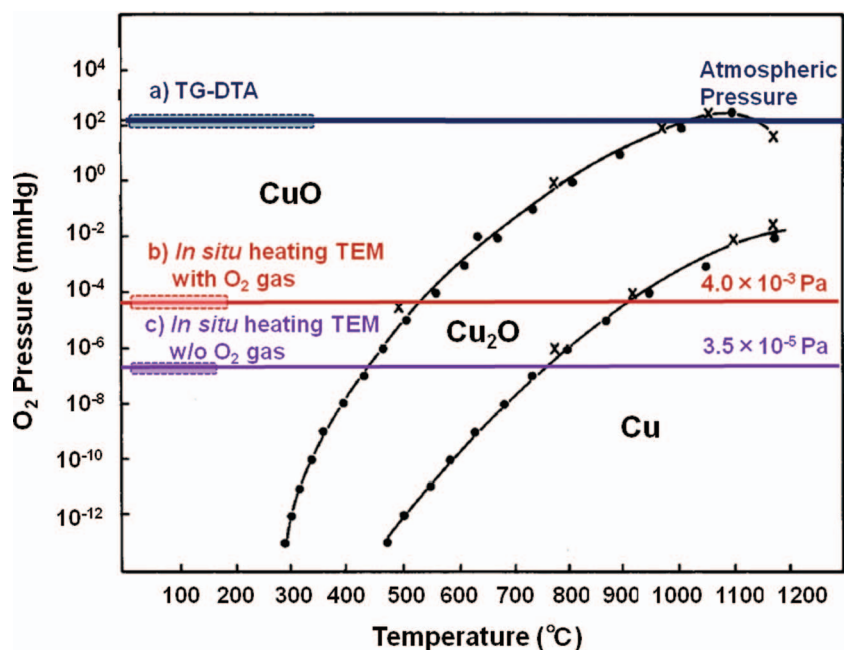


FIG. 7. Thermodynamic stability phase diagram of Cu-Cu<sub>2</sub>O-CuO system.<sup>37</sup> Corresponding experimental conditions of (a) TG-DTA (in Fig. 3), (b) *in situ* heating TEM observation with O<sub>2</sub> gas (in Fig. 5(d)–5(f) and Fig. 6) and (c) *in situ* heating TEM observation without O<sub>2</sub> gas (in Fig. 5(a)–5(c)) are shown in this figure. (Reprinted from Solid-State Electronics, 29, A. E. Rakhshani, “Preparation, characteristics and photovoltaic properties of cuprous oxide—a review,” 7, (Reference 37) Copyright (1986), with permission from Elsevier).

was disappeared because of the introduction of oxygen gas. These results strongly suggest that the amorphous layer on the particle surface shown in Fig. 1 is not copper oxide but gelatin. In general, crystalline structures and the presence or absence of surface oxidation of fine particles in a TEM image are estimated by the selected area electron beam diffraction (SAED) pattern. However, to obtain a SAED pattern image, the electron beam has to be focused on a small region of the sample. It is difficult to obtain the crystalline information of the sample target part at a preset temperature because of the damages caused by electron beam focusing and temperature increase. Therefore, in this study, the oxidation state of the copper fine particles after heating was estimated from the interstice of lattice fingers in the TEM image obtained at the preset temperature. Then, the surface of the copper particles heated to 190°C under a similar condition was observed again under high magnification (Fig. 6). A black shadow at the lower right side of the image shown in Fig. 6(a) is the

Pt-Ir filament. A bump indicated by a square in Fig. 6 showed clear lattice fringes that, in a high magnification image, seemed to be directed the growth direction of the bump. However, to obtain a SAED pattern image, the electron beam has to be focused on a small region of the sample. It is difficult to obtain the crystalline information of the sample target point of the bump. The interstice of lattice fingers in Fig. 6(b) is 0.24 nm, which is closer to the lattice spacing of Cu<sub>2</sub>O (111) (0.247 nm)<sup>38</sup> than CuO (002) (0.253 nm).<sup>39</sup>

Under the experimental condition of *in situ* heating TEM in this study, thermodynamically stable oxidation state of copper is CuO (Fig. 7).<sup>36</sup> However, heating period of copper fine particles was very short, 40 min maximum. Therefore, Cu<sub>2</sub>O was observed in this study as reported by Zhou *et al.*;<sup>40</sup> *in situ* heating TEM observation of copper thin film. In addition, from the TG-DTA curve (Fig. 3), the temperature of 190 °C (the observed temperature of the lattice fingers above) is lower than that at which the exothermic DTA peak associated with transmutation from Cu<sub>2</sub>O to CuO (260 °C) appears, and the gain of weight at 190 °C estimated by the TG curve is only 106% relative to initial entry. In fact, it is concluded that the copper has become cupric oxide at a hundred and several tens of degrees celcius into the TEM column under an oxygen partial pressure at  $4.0 \times 10^{-3}$  Pa, and then transmuted to cuprous oxide as observed in the TG-DTA curve under ambient conditions. Moreover, the cupric oxide formed by the oxidation of copper was not amorphous but crystalline.

#### IV. CONCLUSIONS

High resolution TEM image showed particle surface of the copper fine particles with the diameters of approximately 100 – 200 nm were coated with a thin gelatin layer and that oxidation of copper was inhibited. A TG-DTA curve indicated that oxidation began at approximately 130 °C and completed at approximately 290 °C. From the obtained results of *in-situ* heating TEM observations with the introduction of oxygen gas, it could be seen that crystalline Cu<sub>2</sub>O grew on the particle surfaces at around 140 °C. However, when there was a lack of oxygen gas, there was no change in the morphology of the particle surface. These results indicate that *in-situ* heating TEM observation is effective in determining the oxidation condition of copper fine particles.

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