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TEM Characterization of Sintered Copper Nanoparticles Covered by Biopolymer Nanoskin

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Silver and copper nanoparticles have been studied greatly to apply to electronic materials such as wiring materials and bonding materials in the field of printed electronics. In particular, copper which is a sufficiently cheap and widely used industrial metal has advantageous properties such as low melting point, high electrical conductivity and less electromigration property. However, because the copper is easily oxidized that is a disadvantage, only few papers on practical synthetic methods and applications of copper nanoparticles [1, 2].

Recently, oxidation-resistant copper nanoparticles with biopolymer nanoskin have been prepared by the authors [3] using the simple wet-process which is suitable for mass production. In this method, average radii of the copper nanoparticles obtained can be controlled by the concentration of a complex agent. The oxidation-resistance due to the prevention of the oxidation by gelatin which covers the copper nanoparticles allows us easier treatment of the copper powders in ambient atmosphere. We expect application of our nanoparticles to wiring, bonding and electrode materials.

In this study, we report the characterization of the above mentioned copper nanoparticles sintered using in-situ heating TEM.

Copper nanoparticles used as specimens were synthesized using the wet-chemical method as mentioned in reference [4]. Average radii of used copper nanoparticles were 46nm, 125nm, and 175nm, and the surface of it was covered by gelatin layer with thickness of 5nm. In-situ heating TEM observations were performed in H-9000NAR at an accelerating voltage of 300 kV. The pressure atmosphere during in-situ TEM observation was controlled between 2.0×10^{-5}Pa, which is the raw vacuum pressure of the TEM column, and 8.0×10^{-4} Pa with oxygen flow through the Kamino holder. The characterization of the sintered copper nanoparticles was performed using the electron energy loss spectroscope (EELS) and selected area electron diffraction (SAED).

As the results of in-situ TEM observation, all size of copper nanoparticles sublimated without sintering at about 1273 K under vacuum pressure of 2.0×10^{-5}Pa without oxygen gas, and carbonized gelatin remained the shape of initial layer on the heating wire.

Under more than 2.0×10^{-4}Pa of vacuum pressure, sintering of copper nanoparticles were observed between 523K and 673K. Sintering temperature of copper nanoparticles was similarly regardless of particle size. As a result of TG-DTA analysis, the gelatin which was used as the protective agent in the synthesis of copper nanoparticles was decomposed at higher than about 523K by oxidation in 1 atm of air. Therefore, it is suggested that the decomposition temperature of gelatin are more predominant than the

particle size in the sintering temperature of copper nanoparticles covered by gelatin.

In general, it is well known that impurities such as carbon element and metal oxide in the circuit deteriorate the electro-conductivity. Therefore, we examined carbon element and copper oxide in the sintering copper. Figure 1(a) and Figure 1(b) show sintering behavior of copper nanoparticles. As a result of EEL spectrum shown in Figure 1(c), the carbon element was not confirmed in the grain boundary soon after sintering between copper nanoparticles. Analysis of Copper oxide was performed after the completion of sintering. Figure 2(a) shows high resolution TEM image of completely sintered copper nanoparticles. From this result, it is found that the gelatin layer is exactly covered on the surface of the sintered copper. Moreover, as results of SAED pattern (Figure2(b)) and EEL spectrum (Figure2(c)) of sintered copper, it was confirmed that copper nanoparticles have not been oxidized. On the other hand, when copper nanoparticles were oxidized during the sintering, the gelatin layer was sparsely formed on the surface. From these results, it was suggested that the gelatin layer could work as a prevention layer against oxygen. Based on obtained findings in this study, further work is underway to apply for real fabrication of wiring.

References

[1] B.K.Park, et al., Thin Solid Films. 515, (2007)7706.
[2] H.S.Kim et al., Composites Sci. Tech. 69, (2009)1256.
[3] M. Tomonari et al., J. Sur. Fin. Soc. of Jap. 59, (2008)18(in Japanese).
[4] M. Tomonari et al., Nanosci. nanotech. 8, (2008)2468.

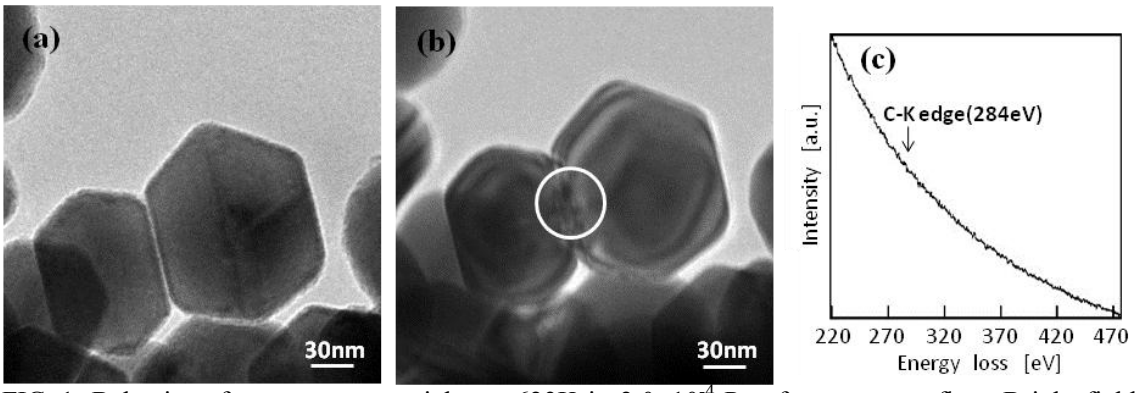

FIG. 1. Behavior of copper nanoparticles at 623K in 2.0×10^{-4} Pa of oxygen gas flow. Bright field TEM images (a) before heating, and (b) in the initial stage of sintering. (c) EEL spectrum of grain boundary corresponding to the area indicated by the circle in (b).

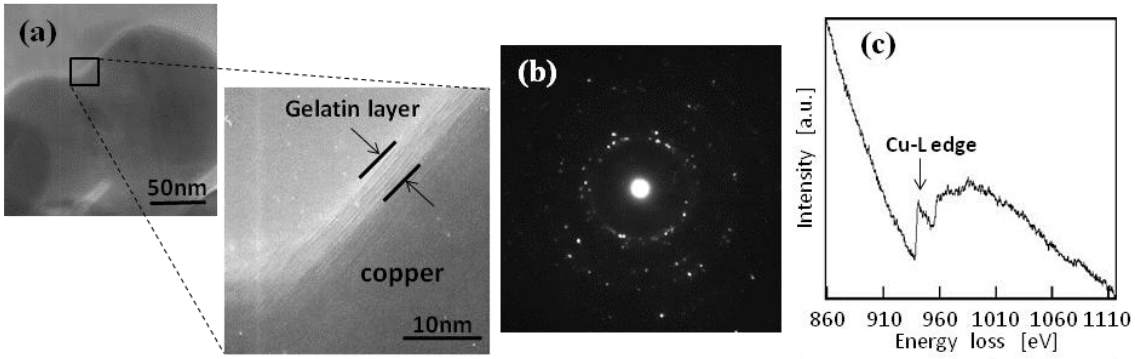

FIG. 2. (a)High resolution TEM image after the completion of sintering. (b) corresponding SAED pattern, and (c)EEL spectrum.