In-situ TEM observation of the sintering process of Cu nanoparticle film printed on a polyimide sheet in reducing atmospheres

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The application of metal nanoparticles (NPs) to printable electronics has attracted considerable attention as a low-cost fabrication of integrated circuits [1]. In this technology, not only the flexible electronic devices but also the wiring of the devices will be fabricated on a flexible polymer sheet using printing technology. Such wiring material will require low temperature heat treatment in order to avoid damage to the device and the base sheet. We have observed the behavior of Cu NPs film printed on a polyimide sheet during low temperature heat treatment in H_2 and CO atmosphere.

Cu NPs of 50 nm in diameter were synthesized by wet chemical method and coated with biopolymer film [2]. Cu NPs ink was prepared using this NPs dispersing into toluene. The Cu NPs film was prepared by dropping this Cu NPs ink and applied using a bar coater on a polyimide sheet. The film was pre-heated at 200 ºC using 10 ppm O_2-N_2 mixed gas to obtain the gas transparent property of biopolymer coating and partially oxidized Cu NPs in order to enhance the sintering [3]. The cross-sectional TEM (XTEM) specimens of the film were prepared using focus ion beam (FIB) technique and fixed onto heating element of the so-called “filament cassette” [4] for direct heating holder (Kamino-Saka holder) [5]. Both the surface of the thin membrane was coated by the plasma-polymerized hydrocarbon (PPH) film to seal the specimen, and a part of the edge which was corresponding to the surface of the bulk sample was exposed by removing the coated film using FIB. In-situ transmission electron microscopy (TEM) was performed in a newly developed environmental cell of the reaction-science high voltage electron microscope JEM-1000K RS. The specimens were observed at around 300ºC in the flow of 1000 Pa of N_2-5at%H_2 and CO, respectively.

As illustrated in schematic drawing of XTEM specimen of Cu NPs film in Fig. 1a, whole the surface was coated with protective film of the plasma-polymerized hydrocarbon layer (cross-section of the specimen in left hand side of the figure) except a part of the edge indicated as the gas window. Figure 1b shows the XTEM image of the specimen before heating. The partially oxidized Cu NPs film with 500 ~ 800 nm of thickness was observed on the polyimide film (Fig. 1b). After the heating experiment in the flow of 1000 Pa of N_2-5at%H_2 up to 500ºC, re-crystallized and sintered microstructure with voids were observed in the area indicated as A in Fig. 1b only below the gas window as shown in Fig. 1c. On the contrary, no significant maicrostructural change has not been observed in the area indicated as B in Fig. 1b, in which the specimen was completely sealed with protective layer, as shown in Fig. 1d. The results indicate that the sintering process was reproduced in the TEM. Also it is suggested that the specimen can be sealed with the PPH film in the hydrogen environment. In the early stage of sintering (Fig. 2a), the particles with few nm in size were formed (Fig. 2b) and disappeared (Fig. c), repeatedly, and coalesced (Fig. 2d). After the initial stage of coalescence of few nm particles, 50 nm sized particles which

construct the film showed the sintering. Same specimen was observed (Fig. 3) in pure CO flow up to 1000 Pa, however, sintering behavior has never been observed. At higher than 300ºC, the surface of the specimen covered with deposited C as shown in Fig. 3b. Thermodynamical calculation gives the ΔG^0 of CuO and Cu_2O reduction in CO to be about -130 and -108 kJ/mol at 300ºC, respectively. This is lower than the ΔG^0 of carbon deposition in CO that is about -34 kJ/mol. Ida et. al. [3] suggested that the decomposition of biopolymer coating by hydrolysis caused with H_2O which formed during the reduction of Cu oxide by H_2 should take an important role in the sintering of Cu NPs film. It is deduced that decomposition of biopolymer coating by hydrolysis is required to start the sintering, however, the reduction by CO can not produce H_2O for hydrolysis, which resulted the strong depression of not only the sintering of Cu NPs but also the reduction of Cu oxide due to the remaining biopolymer coating. When the reaction with CO is prohibited, the chemical equilibrium results the 0.1% of CO decomposition as C deposition at 300ºC

We have reproduced the sintering process of the film consisted of Cu NPs coated with biopolymer coating on the polyimide sheet. The decomposition of biopolymer coating by hydrolysis required to start the sintering, and not only the reduction of Cu oxide but also the sintering of Cu NPs with CO were failed without hydrolysis.

References

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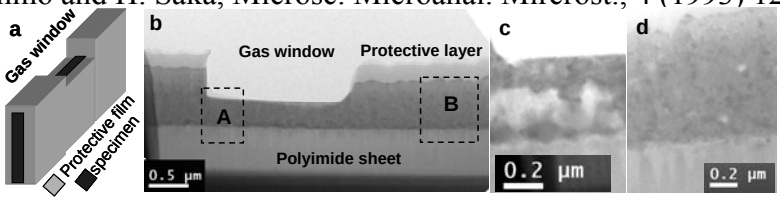

FIG. 1. (a) schematic drawing (b) XTEM image of the specimen before heat treatment. (c) and (d) Enlarged image corresponding to A and B after heating in N_2-5at%H_2, respectively.

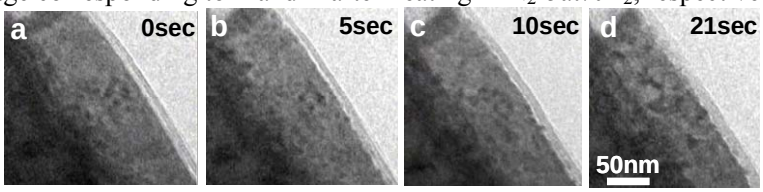

FIG. 2. In-situ TEM images in the early stage (a) of sintering, The few nm of particles (b) formation (c) disappearance and (d) coalescence.

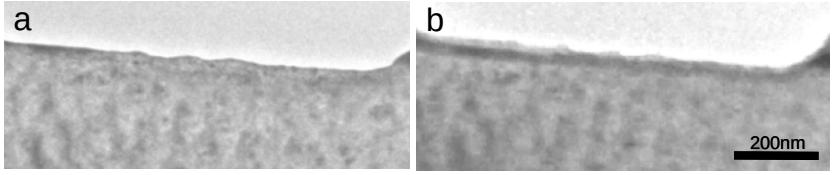

FIG. 3. TEM images (a) before and (b) after heat treatment in 1000 Pa of CO. Deposition of carbon was observed without sintering.