



Exothermic low temperature sintering of Cu nanoparticles

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ABSTRACT

Sintering of the Cu nanoparticle at low temperatures resulted in exothermic behavior after its initiation. The calorimetry study of the heating of a 20 nm copper nanoparticles agglomerate revealed the evolution of 41.17 J/g of heat between 170 °C and 270 °C. High resolution transmission electron microscopy (HRTEM) images indicated that the heat generation was accompanied by sintering. The surface energy of the 20 nm copper nanoparticles was estimated to be 1.23×10^3 erg/cm² based on the heat released during sintering. The *in situ* high resolution transmission electron microscope (HRTEM) investigation showed that vigorous sintering occurred between 217 and 234 °C, which took place through the dislocation sintering mechanism.

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1. Introduction

Because of their large surface area, metal nanoparticles display several unique properties, such as a low melting point and sintering temperature [1,2]. The large surface area provides higher surface energy and reactivity to the nanoparticles by which they can be sintered below the bulk melting point [3–5]. This may be beneficial for semiconductor packaging because the low temperature could help avoid thermal stresses and reduce substrate warpage. Because of the excellent electrical conductivity (6% less than that of Ag) of copper, it is widely used as metallization for flip chip and ball grid array (BGA) technologies [6,7] in modern 3D products. Cu nanoparticles are considered to be one of the most suitable metals for electronic manufacturing. They have been investigated for practical applications because of their high surface area and low sintering temperature [8,9]. Preparation of Cu nanoparticles [10–12] and their applications in printed electronics have been studied [13–15].

The sintering of 4–20 nm copper nanoparticles directly on a single crystal (001) copper substrate has been studied in real time using a novel *in situ* transmission electron microscope (TEM) [16]. These studies showed the reorientation of the nanoparticles upon heating to assume the same orientation as the substrate. An *in situ* TEM investigation found that the sintering behavior of copper nanoparticles covered by gelatin strongly depends on the partial pressure of oxygen. Cu nanoparticles can be sintered at around 250 °C without sublimation between 1.0×10^{-4} and 6.0×10^{-4} Pa [17]. In another study [18], *in situ* reduction of Cu oxide nanoparticles using forming gas (95N₂5H₂) was carried

out for the purpose of producing Cu nanoparticles. A cross-section analysis on a bonded interface showed the onset of Cu nanoparticle sintering at 400 °C. An *in situ* X-ray study [19] of the sintering of Cu nanopowder under various environments including air, N₂ and formic acid showed that the crystallite size increases along with the resistivity.

The shift towards lower sintering temperature has been ascribed to enhanced reactivity of nanoparticles having surface defect densities and high curvature [20]. It has been recommended that the sintering temperature of Cu nanoparticles should be limited to a range of 300–350 °C, and the sintering pressure should be not less than 600 MPa in a plasma process [21]. The sintering mechanism of two single crystal Cu nanoparticles was analyzed [22] using a molecular dynamics simulation. The rapid sintering of nanoparticles in this study was ascribed to the high shear stresses developed in small particle contacts. Sintering thus occurs via a dislocation mechanism. Flash-light sintering [23] of Cu nano ink using an *in situ* monitoring system showed that the resistivity decreases drastically at around 250 °C.

It is generally understood that powder sintering requires energy to enable diffusion of metallic atoms. However, there has been no investigation of the heat involvement of Cu nanoparticles in alignment with the sintering behavior and the microstructure evolution. The present study reports exothermic sintering of Cu nanoparticles at low temperatures. The unique feature is the relation of the heat flow during sintering with the surface energy of the nanoparticles and the direct *in situ* observation of occurrence of sintering in the sintering temperature range.

2. Experimental procedure

Commercial Cu nanoparticles of average size 20 nm prepared by electrical explosion method were used for the present study. The heat

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flow during heating of the Cu nanoparticles was measured by a differential scanning calorimeter (DSC) using a heating rate of 10 °C/min under an argon atmosphere. Heating of the Cu nanoparticles for the sintering investigation was conducted at a heating rate of 10 °C/min to desired temperatures under 95N₂5H₂. The samples for the X-ray diffraction and microscopic investigations were cooled in a furnace to room temperature after heating. Scanning electron microscope (SEM) and high resolution transmission electron microscope (HRTEM) investigations were conducted with a 10 keV and 200 keV beam energies, respectively. The HRTEM micrographs were further analyzed using electron diffraction, a fast Fourier transform (FFT) and an inverse FFT (IFFT).

3. Results and discussion

3.1. DSC study

As shown in Fig. 1, the calorimetry of the heating of Cu nanoparticles using 10 °C/min under Ar atmosphere reveals two bands in the temperature range 50–300 °C. A broad endothermic band appears at 50–170 °C with a peak at 99.66 °C. The total heat adsorbed as delineated by this band is 10.92 J/g. There is no chemical reaction expectable under an Ar atmosphere in this temperature range. The broad band implies relatively uniform heat flow occurrences. This broad band is believed to be due to the evaporation of surface adsorbed water.

The second band is an exothermic peak between 170 °C and 270 °C, with the peak temperature at 224.24 °C. The total heat flow estimated from the exothermic band is 41.14 J/g. Sintering is expected to occur in this temperature range. On the basis of the DSC studies, two heating processes were selected for studying the effect of heating on variations in Cu nanoparticles and their structures. The first sample was heated from room temperature to 170 °C (Cu 170 hereafter) and the other to 260 °C (Cu 260 hereafter). The powders were cooled in the furnace after reaching the desired temperature. Similar calorimetric behavior was observed in both the Ar and N₂/H₂ gases. The N₂/H₂ gas was used to remove the possible existing surface oxygen in the Cu nanoparticles and to minimise the effect of oxygen on the reactions among the nanoparticles at higher temperatures.

3.2. X-ray diffraction study

In light that the DSC process shown in Fig. 1 was conducted under Ar atmosphere, the exothermic behavior is attributed to phase transformation or physical behavior occurring during the heating process. It is of interest to examine the corresponding physical occurrences. It is observed that the colors of nanoparticles changes during heating. Cu nano is dark

black which changes to brown for Cu170 and then to red for Cu 260 which is standard color of Cu. This is believed to be a result of the surface reduction as stated below. The nanoparticles, after being cooled in the furnace, were examined for the crystalline structure using XRD, as presented in Fig. 2. The XRD of the as-received Cu nanoparticles (Cu nano hereafter) shows the three major orientations (111), (200), and (220) [24]. There is a small peak corresponding to Cu₂O(110) at $2\theta = 36.44^\circ$ [16]. The Cu₂O (110) vanishes after heating at 170 °C, as shown in the Cu170 spectrum, instead, the CuO(–111) and (111) appear. The CuO was completely reduced after heating at 260 °C as indicated by the Cu 260 spectrum. The oxide layer on the Cu nanoparticles was reported to be completely reduced at 150 °C [20]. The Cu 170 spectrum seems to indicate the existence of Cu (110) in the Cu nanoparticles after heating at 170 °C. The XRD spectra indicate that the full width half maximum (FWHM) of the three major peaks Cu (111), (200), and (220) is reduced at higher temperatures. In other words, the peak intensity increases. The decrease in FWHM and the corresponding increase in peak intensity reflect the occurrence of sintering and the growth in crystallite size. The occurrence of sintering of Cu nanoparticles has been previously achieved at 250 °C [11,18] although a practice at higher temperatures of 300–350 °C has been recommended for producing bulk copper [20] from Cu nanoparticles. The XRD results from Fig. 2 suggest that sintering of the Cu nanoparticles seems to start at the beginning temperature of the exothermic peak, 170 °C, as shown in Fig. 1.

3.3. SEM study

SEM micrographs in Fig. 3a–c demonstrate the Cu, Cu170 and Cu260 nanoparticles in bundles. Small window on the left top of micrograph shows Cu nanoparticles in high magnification. No change in sizes in Cu170 in Fig. 3b compared to Cu in Fig. 3a is observed but bundles of nanoparticles are seemed to be slightly joined with each other. Size increases many folds in Cu260 as seen in Fig. 3c, by joining these bundles with each other. This confirms the sintering of Cu nanoparticles between 170 °C and 260 °C.

3.4. HRTEM study

The HRTEM image of the as-received Cu nanoparticles (Cu nano), Fig. 4a, shows the appearance of the discrete particles of which the dimension is around 20 nm. The distinct particle morphology is quite clear along the outskirts of the particle agglomerate. The image in Fig. 3b of the particles heated up to 170 °C, Cu 170, shows the slight sintering of the particles as evidenced by the less distinct particle morphology along the outskirts of the agglomerate as compared to the Cu

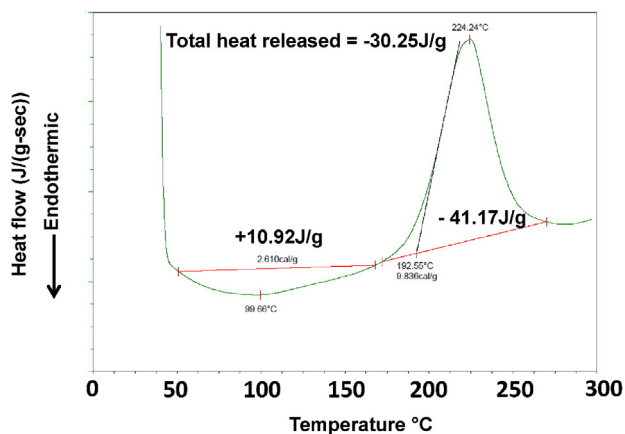


Fig. 1. Differential scanning calorimetric (DSC) study showing a broad endothermic at 50–170 °C and one exothermic band at 170–270 °C during heating of Cu nanoparticles using a heating rate of 10 °C/min under an Ar atmosphere.

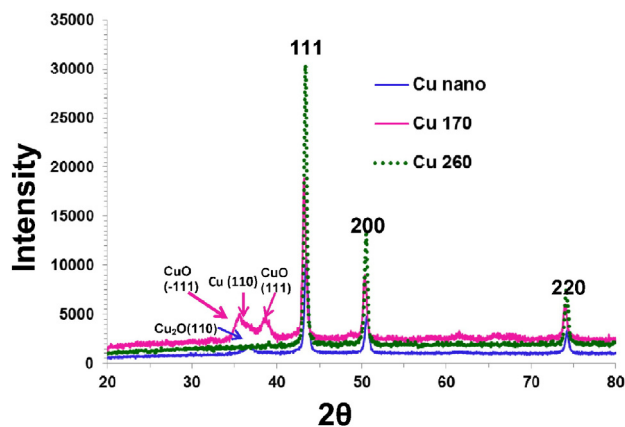


Fig. 2. X ray diffractions of raw Cu nanoparticles (Cu nano) after heating to 170 °C (Cu 170) and 260 °C (Cu 260) showing the changes in the crystal planes.

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