

Effects of process parameters on Cu-nanoparticle synthesis in tetraethylene glycol through microwave irradiation

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Copper nanoparticles were successfully synthesised through microwave irradiation of a copper-oxide particle precursor dispersed in tetraethylene glycol. Initial results obtained after 4–6 min of irradiation, without the use of a surfactant, indicated nanoparticle aggregation and particle-size bimodality by incomplete reduction. However, the said aggregation and bimodality were observed to be significantly suppressed with accelerated reduction upon addition of an alcohol-type surfactant. Consequently, Cu nanoparticles measuring 74 and 79 nm in size were successfully synthesised by performing short irradiations lasting 3 and 4 min, respectively.

1. Introduction: In electronic packaging, copper (Cu) powder has conventionally been used as an important conducting material owing to its superior electrical conductivity and low electrochemical migration similar to that of silver (Ag) [1–7]. Apart from the conductivity of Cu being similar to that of Ag (Cu is only 6% less conductive than Ag) [8–16], its considerably lower cost of procurement, in particular, has encouraged greater use of Cu powder instead of Ag recently. For example, the use of Cu powder has been investigated as a low-cost alternative to Ag fillers used in sinter-bonding pastes for attachment of wide-bandgap (WBG) semiconductor chips made of SiC or GaN to be employed in next-generation high-power devices [16–20]. The bonding ability of these pastes strongly depends on the particle size – the smaller the size, the higher the sinter-bonding ability [21–23]. That said, the use of nanoparticles exclusively as filler material for the paste is not usually recommended because of difficulties encountered in the mixing process and reduced cost-effectiveness. On the other hand, it is desirable for Cu nanoparticles to be used as additives to enhance sinter-bonding ability by increasing the initial packaging density [24–27]. Therefore, use of an effective wet-synthesis method for production of Cu nanoparticles assumes great significance as a crucial manufacturing technology [15, 28–30], as regards sinter-bonding of WBG semiconductor chips and high-heat-generating devices [31–33].

Wet chemical methods are effective processes employed for low-cost synthesis of nanoparticles that cannot be fabricated through molten-metal atomisation. However, the wet chemical processes usually employed are often complex and involve complicated use of chemicals, such as reducing agents, protective agents, and other functional agents [34, 35]. Furthermore, the long heating time required for completion of necessitates modifications to the traditional wet-synthesis approach.

In view of the above, Cu-nanoparticle synthesis by microwave irradiation has recently been considered as a possible alternative to address concerns associated with the wet-synthesis approach. Zou *et al.* [36] and Blosi *et al.* [37] reported fabrication of Cu particles measuring 10 and 46 nm on average, through the use of an advanced microwave-irradiation-synthesis approach referred to as microwave-assisted polyol synthesis. However, their use of a reducing agent in addition to an expensive Cu precursor chemical such as a metal salt is considered as a drawback of the proposed technique. If the Cu precursor can be completely reduced by the polyol itself through short microwave-assisted synthesis, the additional use of a reducing agent can be avoided, lowering the

cost and complexity of the process. Therefore, this study proposes the development of a simple and fast method using low-cost CuO precursor for fabricating Cu nanoparticles through microwave irradiation synthesis without the addition of a reducing agent. The proposed method will utilise the reducing characteristic of polyols. Additionally, the effects of process parameters on the realisation of optimum Cu-nanoparticle synthesis are investigated.

2. Experimental study: CuO powder with particles measuring 35 µm on average (as depicted in Fig. 1) was selected in this study as a precursor for synthesising Cu nanoparticles, and 98% tetraethylene glycol (C₈H₁₈O₅) (Daejung Chemicals & Metals Co. Ltd.) was used as a solvent for wet synthesis. CuO particles weighing 5.96 g were added to 150 ml of tetraethylene glycol, and the resulting mixture was subsequently irradiated by microwaves for different times under an air atmosphere. The microwave irradiation power was 1500 W. To suppress the aggregation of final Cu particles and modify size distribution during synthesis, two types of surfactant were evaluated as additives to the mixture. Particles dispersed in the final solution were washed using ethanol after centrifugation at 10,000 rpm for 10 min followed by decantation. The sequential processes of centrifugation, decantation, and washing were repeated thrice. Washed particles were subsequently dried within a low-vacuum chamber maintained at room temperature.

The sizes and morphologies of the original CuO and synthesised nanoparticles were examined using a field emission-scanning electron microscope (FE-SEM; SU-8010, Hitachi High-Technologies Corporation), and the composition of synthesised particles was confirmed by X-ray diffraction (XRD; DE/D8 Advance, Bruker). The average size of synthesised particles was measured by direct measurement using high resolution FE-SEM micrographs.

3. Results and discussion: Fig. 2 shows images of nanoparticles synthesised at different microwave irradiation times, and Fig. 3 shows XRD results (JCPDS card no. 85-1326 for Cu, 78-0428 for Cu₀, and 78-2076 for Cu₂O). An irradiation time of the order of 4 min led to the formation of nanoparticles measuring 25 (±5) nm in size; however, severe aggregation of particles was observed (Fig. 2a). Moreover, the XRD results of Fig. 3 indicate significant peaks for the CuO phase. Considering sequential reduction behaviour on the surface of a large CuO particle, it is inferred that the CuO peaks come from initial CuO particles which were not reduced to Cu nanoparticles. With an increase in irradiation

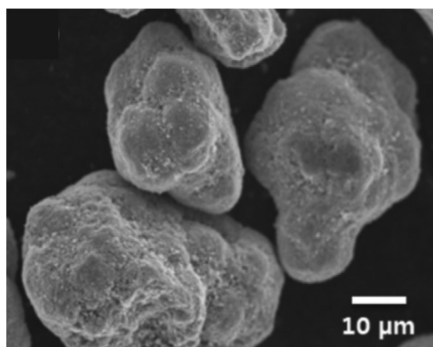


Fig. 1 Initial shape of CuO particles used in this study

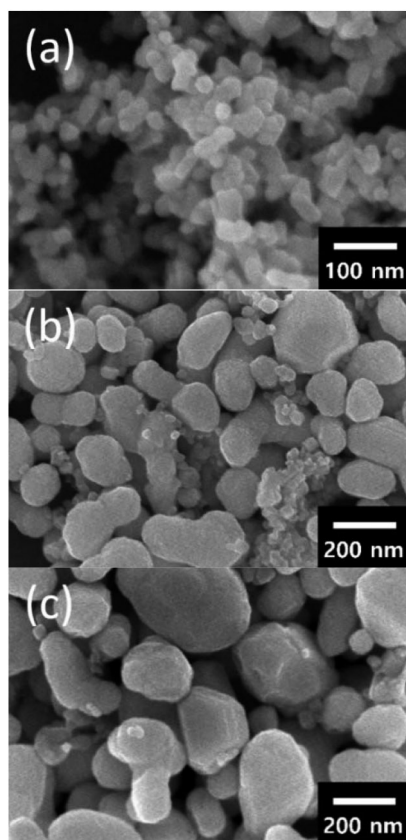


Fig. 2 SEM images for nanoparticles synthesised using different microwave irradiation times

a 4 min
b 5 min
c 6 min

time to 5 min, the sizes of the resultant particles are transformed into a bimodal state with corresponding average sizes of the small and large particles being $25 (\pm 8)$ nm and $123 (\pm 36)$ nm, respectively (Fig. 2b). Moreover, the XRD results demonstrate the existence of some residual CuO particles, although the amount decreases with an increase in irradiation time. Upon further increasing the irradiation time to 6 min, some CuO is still observed to be present (Fig. 3c). Bimodality is still present, and the average sizes of the small- and large-sized particles are $35 (\pm 12)$ nm and $186 (\pm 59)$ nm, respectively. Based on these findings, we infer that longer irradiation times generally increase the degree of reduction and induce additional growth of Cu particles. The growth seems to proceed by rapid agglomeration and coarsening of preferentially formed Cu particles.

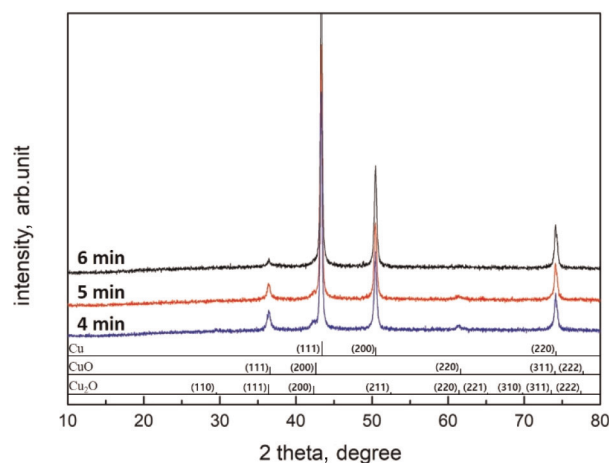


Fig. 3 XRD results of nanoparticles synthesised in polyol solvent through microwave irradiation for different times

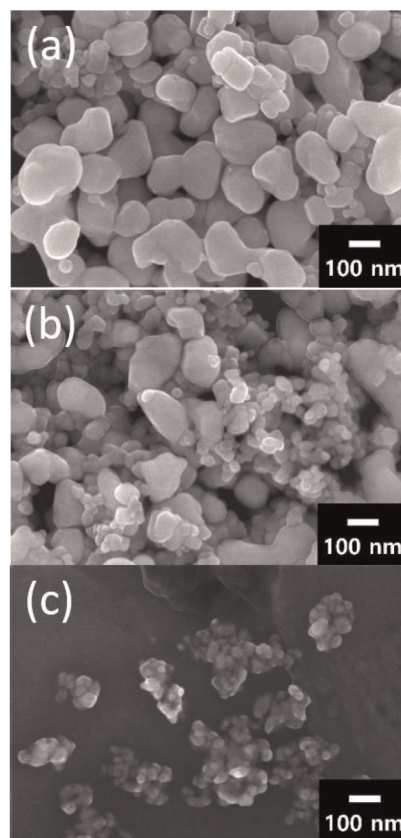


Fig. 4 SEM images of nanoparticles synthesised through microwave irradiation for 4 min with addition of different amounts of PVP surfactant

a 0.3 g
b 1.5 g
c 3.0 g

To suppress the above-mentioned aggregation and bimodality, a surfactant was added to the CuO–tetraethylene glycol mixture prior to microwave irradiation. When polyvinyl pyrrolidone (PVP) was added as the surfactant, SEM images of the nanoparticles synthesised through microwave irradiation for 4 min were captured and are presented in Fig. 4, with various amounts of PVP surfactant added. When compared with the image in Fig. 2a without surfactant, the small addition of 0.3 g generates a completely different result, as shown in Fig. 4a. Most particles

are bigger than those shown in Fig. 2a, and the shapes are also different. Aggregates of smaller particles are present among larger particles in Fig. 2a. These aggregates of small particles increase with an increase (1.5 g) in the amount of PVP surfactant (Fig. 4b). Consequently, neither the aggregation of the particles nor the bimodality was improved with surfactant use.

Moreover, the addition of 3.0 g of PVP surfactant reveals severely aggregated tiny particles (Fig. 4c). The aggregated final particles produce extremely smooth surfaces, indicating that residual PVP is present on the particle surfaces due to excessive addition.

Fig. 5 shows the XRD results for nanoparticles synthesised through microwave irradiation for 4 min. When no surfactant was added, CuO peaks, as well as Cu peaks, are detected, meaning that residual CuO is present that was not reduced to Cu. However, the intensities of the peaks slightly decrease with the addition of 0.3 g of PVP. The particles approaching or exceeding a size of 100 nm are analysed as Cu. With the addition of 1.5 g of PVP, an inverse trend is observed. The intensities of Cu peaks decrease and those for CuO increase considerably. Therefore, the addition of 1.5 g of PVP presents a more delayed reduction synthesis than the synthesis without PVP. When the added amount of PVP reaches 3.0 g, the intensities of the CuO peaks increase further. Thus, the addition of PVP exceeding a critical amount demonstrates undesirable results in terms of the degrees of reduction, aggregation, and bimodality.

Because these results were unlike the excellent surfactant performance observed in earlier reported reports, an effective alcohol-type surfactant was selected through a process of trial and error. Fig. 6 depicts SEM images of Cu nanoparticles synthesised through microwave irradiation performed for 4 min with various amounts of alcohol-type surfactant added. Upon addition of a small amount (1.82 g) of alcohol-type surfactant, particle bimodality is still observed to be maintained with the formation of large particles, although a completely different microstructure is formed when compared with the result (Fig. 2a) obtained without surfactant. The degree of aggregation is slightly reduced (Fig. 6a). With an increase in the amount of surfactant to 9.11 g, the presence of aggregated tiny particles is nearly eliminated (Fig. 6b). The existence of a few tiny particles induces aggregation between larger particles. When the surfactant is increased to 18.21 g (Fig. 6c), the tiny particles are thoroughly eliminated, and bimodality and aggregation are in turn reduced. The average size of the synthesised particles was 79 (± 21) nm. The additional increase in surfactant was not effective in reducing bimodality and aggregation (Fig. 6d).

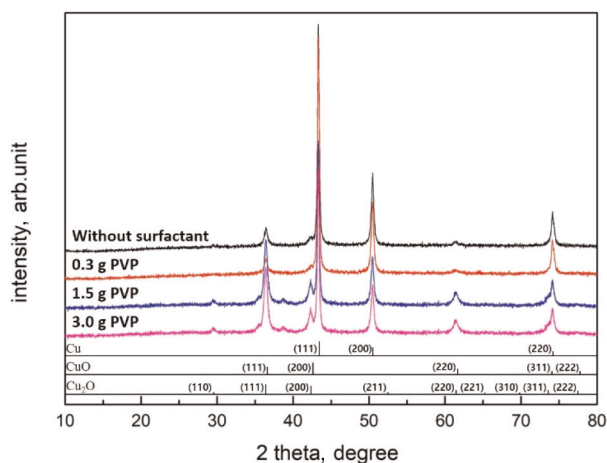


Fig. 5 XRD results of nanoparticles synthesised through microwave irradiation for 4 min without and with PVP surfactant

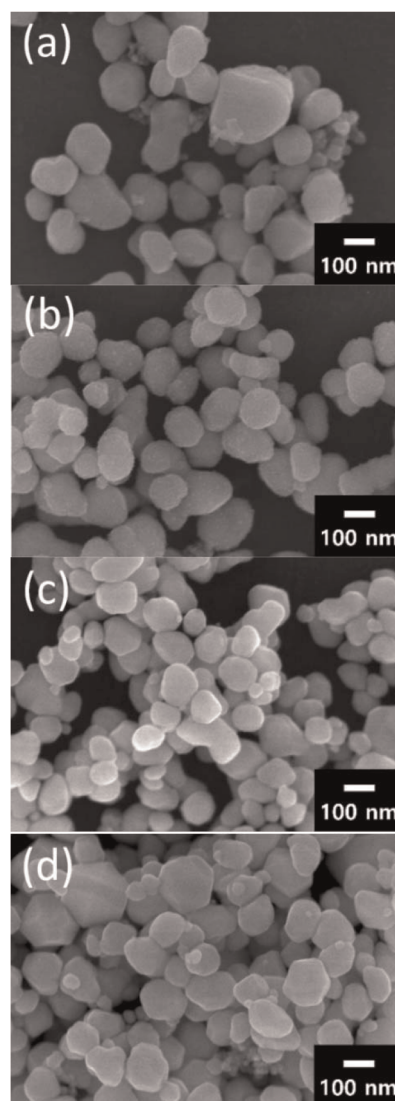


Fig. 6 SEM images of nanoparticles synthesised through microwave irradiation for 4 min with different amounts of alcohol-type surfactant added
a 1.82 g
b 9.11 g
c 18.21 g
d 54.65 g

Another effect of the surfactant was verified by comparing XRD results, as shown in Fig. 7. With the absence of surfactant, the particles that dried after synthesis indicate clear CuO peaks, from unreacted CuO precursor. However, the oxide peak is removed after a small amount (1.82 g) of the surfactant is added and is eliminated in both the SEM image and XRD result after a sufficient amount (18.21 g) is added. Based on the different results obtained with otherwise identical synthesis parameters, we conclude that the added surfactant accelerates the reduction synthesis.

When the optimal amount of 18.21 g was added, SEM images of Cu particles obtained at different synthesis times were captured and are displayed in Fig. 8. At 3 min (Fig. 8a), slightly aggregated, differently shaped particles, in contrast to the tiny and severely agglomerated particles of residual CuO, are observed. The average particle size is 74 (± 26) nm. With an increase in time (Figs. 8b and c), the average size of the synthesised Cu particles proportionally increases; the average sizes after synthesis for 4 and 5 min are 79 (± 21) and 89 (± 32) nm, respectively.

The XRD results shown in Fig. 9 reveal that the resultant particles consist of the only Cu after irradiation for just 3 min.

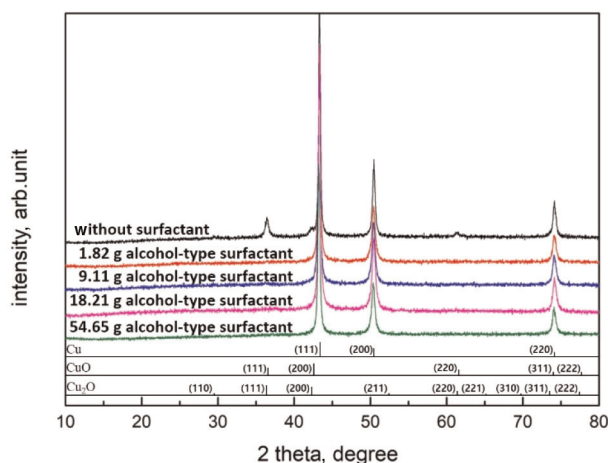


Fig. 7 XRD results of nanoparticles synthesised through microwave irradiation for 4 min with and without alcohol-type surfactant

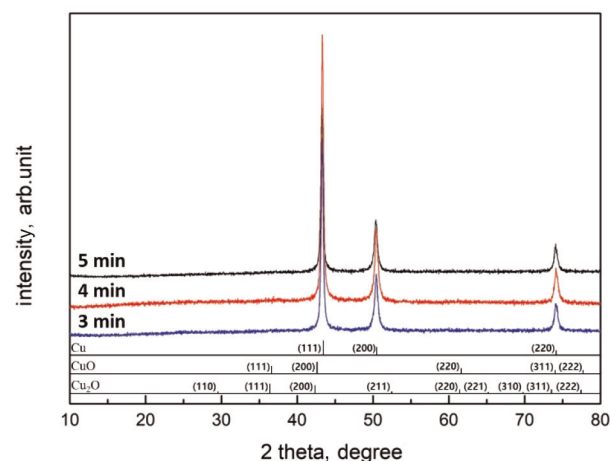


Fig. 9 XRD results of nanoparticles synthesised through microwave irradiation at different times with alcohol-type surfactant

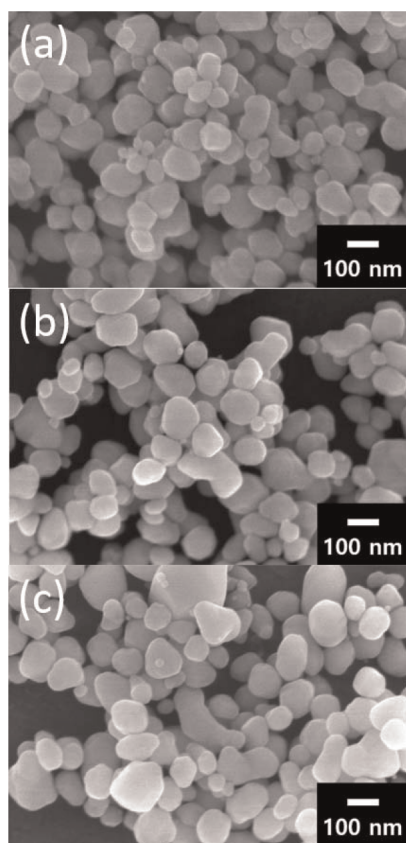


Fig. 8 SEM images of nanoparticles synthesised by microwave irradiation at different times with the addition of alcohol-type surfactant of 18.21 g
a 3 min
b 4 min
c 5 min

With an increase in the irradiation time exceeding 3 min, no noticeable change is observed in the XRD results. In summary, microwave irradiation for only 3 min can synthesise pure Cu particles of sub-100 nm size, and the effective process can be incorporated into mass production by the flow of precursor solution through a narrow pipe [38–40].

We propose a simple and fast process without any addition of reducing agent by utilising only the reducing characteristic of polyol to synthesise Cu nanoparticles using a low-cost CuO

precursor. The short synthesis time of 3 min indicates that microwave-assisted Cu synthesis is a method applicable to a continuous flow microwave-assisted reactor for industrial production [41]. The non-aggregated Cu particles smaller than 100 nm can be applicable as a low-cost filler material for the fabrication of electrode or conduction patterns by intense pulsed light sintering [42–44] as well as sinter chip-bonding [31–33].

4. Conclusion: The synthesis of pure Cu nanoparticles by the reduction in tetraethylene glycol using large CuO particles (average size: 35 μm) was successfully performed through microwave irradiation at 1500 W. The addition of alcohol-type surfactant in the synthesis promoted the reduction reaction, resulting in a reduced synthesis time. The alcohol-type surfactant was also effective at decreasing aggregation of the synthesised Cu nanoparticles and bimodality when compared with the previously used surfactant (PVP). As a representative result, an irradiation time of only 3 min induced the synthesis of Cu nanoparticles with an average size of 74 nm.

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6 References

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