

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

Woo Lim Choi, Jong-Hyun Lee ✉

Department of Materials Science & Engineering, Seoul National University of Science & Technology, Seoul 139-743, Republic of Korea

✉ E-mail: pljh@snut.ac.kr

Published in Micro & Nano Letters; Received on 23rd July 2019; Revised on 1st May 2020; Accepted on 6th May 2020

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

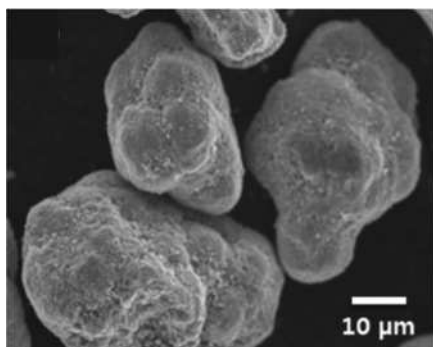


Fig. 1 Initial shape of CuO particles used in this study

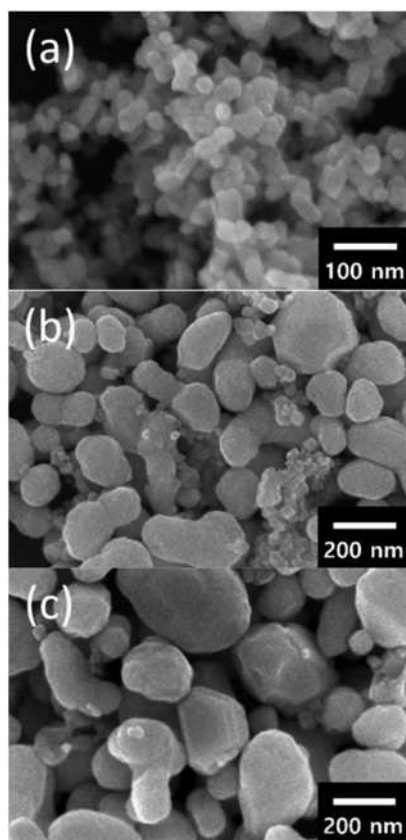


Fig. 2 SEM images for nanoparticles synthesised using different microwave irradiation times

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.

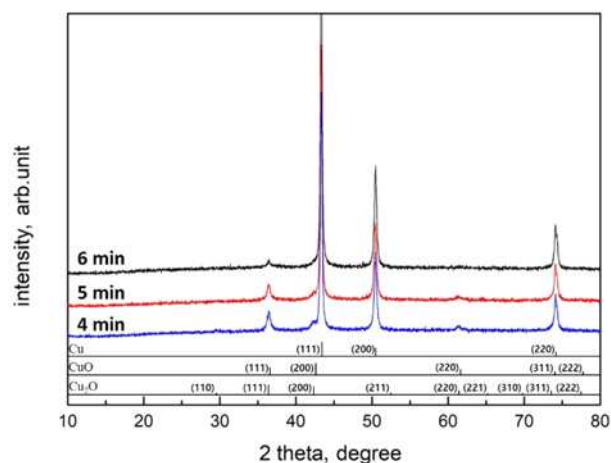


Fig. 3 XRD results of nanoparticles synthesised in polyol solvent through microwave irradiation for different times

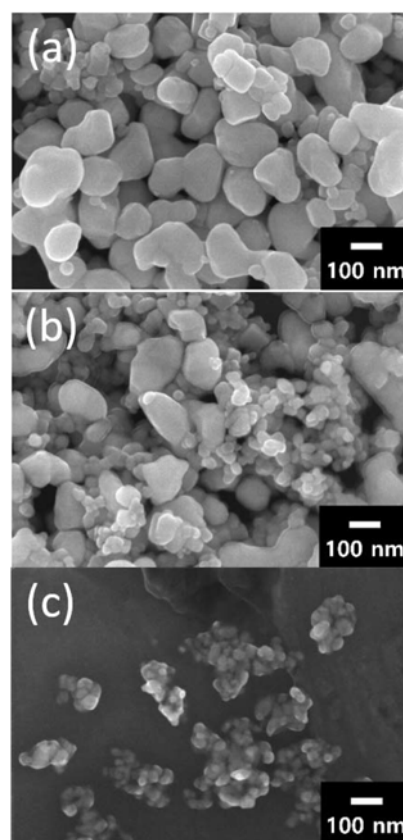


Fig. 4 SEM images of nanoparticles synthesised through microwave irradiation for 4 min with addition of different amounts of PVP surfactant

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 $79 (\pm 21)$ nm. The additional increase in surfactant was not effective in reducing bimodality and aggregation (Fig. 6d).

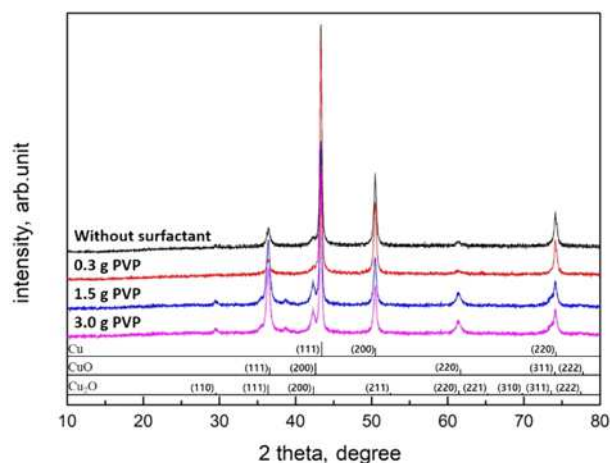


Fig. 5 XRD results of nanoparticles synthesised through microwave irradiation for 4 min without and with PVP surfactant

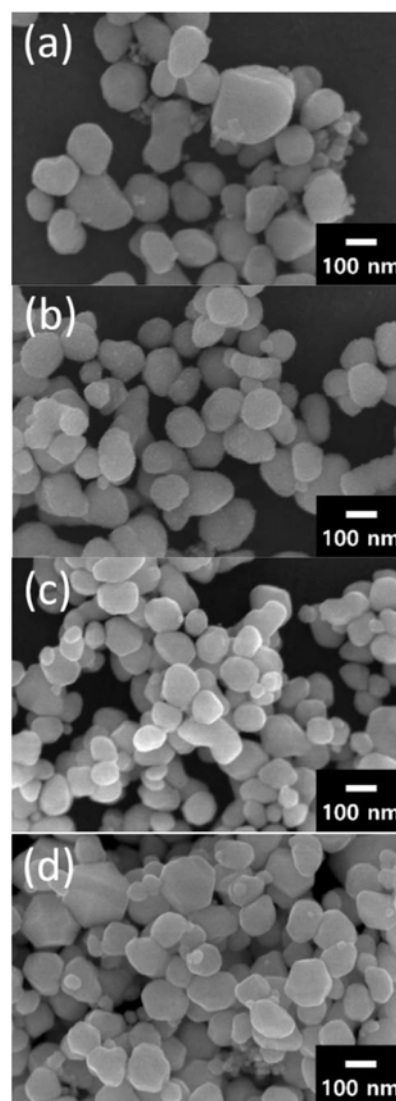


Fig. 6 SEM images of nanoparticles synthesised through microwave irradiation for 4 min with different amounts of alcohol-type surfactant added
a 1.82 g
b 9.11 g
c 18.21 g
d 54.65 g

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 $74 (\pm 26)$ 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 $79 (\pm 21)$ and $89 (\pm 32)$ 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.

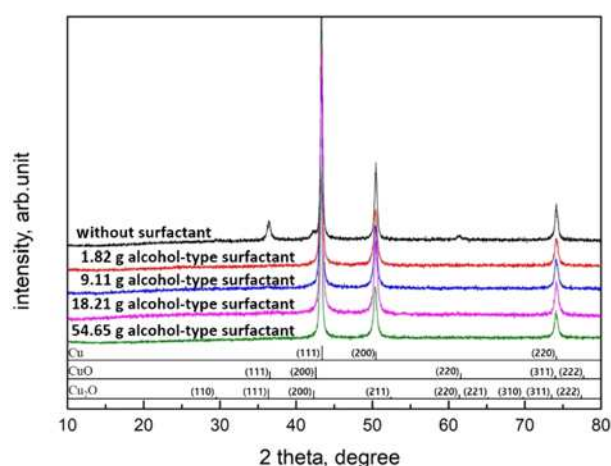


Fig. 7 XRD results of nanoparticles synthesised through microwave irradiation for 4 min with and without alcohol-type surfactant

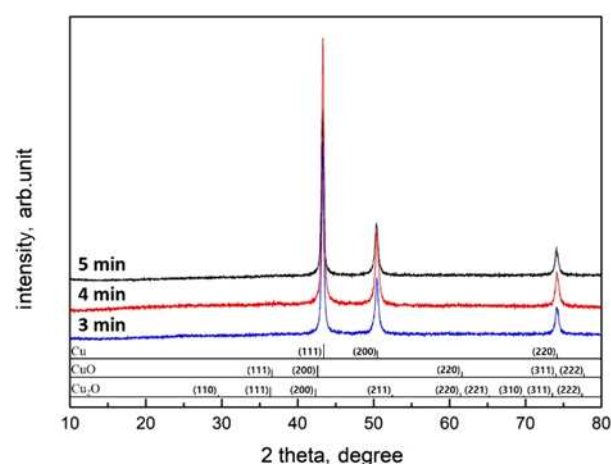


Fig. 9 XRD results of nanoparticles synthesised through microwave irradiation at different times with alcohol-type surfactant

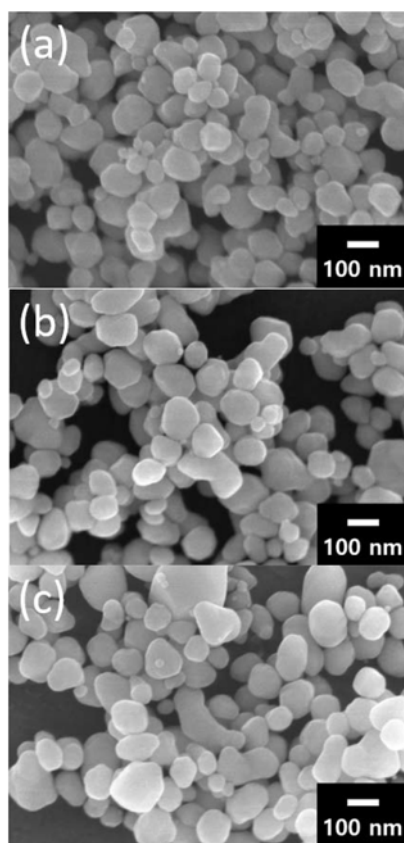


Fig. 8 SEM images of nanoparticles synthesised by microwave irradiation at different times with the addition of alcohol-type surfactant of 18.21 g
a 3 min
b 4 min
c 5 min

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 Cu 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.

5. Acknowledgments: This work was supported by the Materials & Components Technology Development Program (10080187) funded by the Ministry of Trade, Industry & Energy (MI, Korea).

6 References

- [1] Liu X., Nishikawa H.: 'Low-pressure Cu-Cu bonding using in-situ surface-modified microscale Cu particles for power device packaging', *Scr. Mater.*, 2016, **120**, pp. 80–84
- [2] Gao Y., Zhang H., Li W., *ET AL.*: 'Die bonding performance using bimodal Cu particle paste under different sintering atmospheres', *J. Electron. Mater.*, 2017, **46**, (7), pp. 4575–4581
- [3] Krishnan S., Haseeb A.S.M.A., Johan M.R.: 'Preparation and low-temperature sintering of Cu nanoparticles for high-power devices', *IEEE Trans. Compon. Packag. Manuf. Technol.*, 2012, **2**, (4), pp. 587–592
- [4] Jianfeng Y., Guisheng Z., Anming H., *ET AL.*: 'Preparation of PVP coated Cu NPs and the application for low-temperature bonding', *J. Mater. Chem.*, 2011, **21**, pp. 15981–15986
- [5] Ishizaki T., Watanabe R.: 'A new one-pot method for the synthesis of Cu nanoparticles for low temperature bonding', *J. Mater. Chem.*, 2012, **22**, pp. 25198–25206
- [6] Mou Y., Peng Y., Zhang Y., *ET AL.*: 'Cu-Cu bonding enhancement at low temperature by using carboxylic acid surface-modified Cu nanoparticles', *Mater. Lett.*, 2018, **227**, pp. 179–183
- [7] Gao Y., Li W., Chen C., *ET AL.*: 'Novel copper particle paste with self-reduction and self-protection characteristics for die attachment of power semiconductor under a nitrogen atmosphere', *Mater. Des.*, 2018, **160**, pp. 1265–1272

- [8] Grouchko M., Kamysny A., Magdassi S.: 'Formation of air-stable copper-silver core-shell nanoparticles for inkjet printing', *J. Mater. Chem.*, 2009, **19**, pp. 3057–3062
- [9] Jeong S., Woo K., Kim D., *ET AL.*: 'Controlling the thickness of the surface oxide layer on Cu nanoparticles for the fabrication of conductive structures by ink-jet printing', *Adv. Funct. Mater.*, 2008, **18**, pp. 679–686
- [10] Magdassi S., Grouchko M., Kamysny A.: 'Copper nanoparticles for printed electronics: routes towards achieving oxidation stability', *Materials (Basel)*, 2010, **3**, pp. 4626–4638
- [11] Deng D., Jin Y., Cheng Y., *ET AL.*: 'Copper nanoparticles: aqueous phase synthesis and conductive films fabrication at low sintering temperature', *ACS Appl. Mater. Interfaces*, 2013, **5**, pp. 3839–3846
- [12] Zenou M., Ermak O., Saar A., *ET AL.*: 'Laser sintering of copper nanoparticles', *J. Phys. D: Appl. Phys.*, 2014, **47**, p. 025501
- [13] Kim C.K., Lee G.-J., Lee M.K., *ET AL.*: 'A novel method to prepare Cu@Ag core-shell nanoparticles for printed flexible electronics', *Powder Technol.*, 2014, **263**, pp. 1–6
- [14] Woo K., Kim Y., Lee B., *ET AL.*: 'Effect of carboxylic acid on sintering of inkjet-printed copper nanoparticulate films', *ACS Appl. Mater. Interfaces*, 2011, **3**, pp. 2377–2382
- [15] Lee Y., Choi J.-R., Lee K.J., *ET AL.*: 'Large-scale synthesis of copper nanoparticles by chemically controlled reduction for applications of inkjet-printed electronics', *Nanotechnology*, 2008, **19**, p. 415604
- [16] Stewart I.E., Ye S., Chen Z., *ET AL.*: 'Synthesis of Cu–Ag, Cu–Au, and Cu–Pt core-shell nanowires and their use in transparent conducting films', *Chem. Mater.*, 2015, **27**, pp. 7788–7794
- [17] Sastry A.B.S., Aamanchi R.B.K., Prasad C.S.R.L., *ET AL.*: 'Large-scale green synthesis of Cu nanoparticles', *Environ. Chem. Lett.*, 2013, **11**, pp. 183–187
- [18] Yu X., Li J., Shi T., *ET AL.*: 'A green approach of synthesizing of Cu-Ag core-shell nanoparticles and their sintering behavior for printed electronics', *J. Alloys. Compd.*, 2017, **724**, pp. 365–372
- [19] Ko W.-Y., Chen W.-H., Cheng C.-Y., *ET AL.*: 'Architectural growth of Cu nanoparticles through electrodeposition', *Nanoscale Res. Lett.*, 2009, **4**, pp. 1481–1485
- [20] Takeda Y., Ito T.: 'Light trapping for silicon photovoltaic cells illuminated by solar-pumped lasers emitting at 1064 nm', *Jpn. J. Appl. Phys.*, 2015, **54**, p. 08KD13
- [21] Jeong S., Song H.C., Lee W.W., *ET AL.*: 'Stable aqueous based Cu nanoparticle ink for printing well-defined highly conductive features on a plastic substrate', *Langmuir*, 2011, **27**, pp. 3144–3149
- [22] Lu J., Lu Z., Peng C., *ET AL.*: 'Influence of particle size on sinterability, crystallization kinetics and flexural strength of wollastonite glass-ceramics from waste glass and fly ash', *Mater. Chem. Phys.*, 2014, **148**, pp. 449–456
- [23] Seo D.S., Park S.H., Lee J.K.: 'Sinterability and conductivity of silver paste with Pb-free frit', *Curr. Appl. Phys.*, 2009, **9**, pp. S72–S74
- [24] Balantrapu K., McMurran M., Goia D.V.: 'Inkjet printable silver dispersions: effect of bimodal particle-size distribution on film formation and electrical conductivity', *J. Mater. Res.*, 2010, **25**, (5), pp. 821–827
- [25] Yu M.-H., Joo S.-J., Kim H.-S.: 'Multi-pulse flash light sintering of bimodal Cu nanoparticle-ink for highly conductive printed Cu electrodes', *Nanotechnology*, 2017, **28**, p. 205205
- [26] Liu Z., Ji H., Wang S., *ET AL.*: 'Enhanced electrical and mechanical properties of a printed bimodal silver nanoparticle ink for flexible electronics', *Phys. Status. Solidi. A.*, 2018, **215**, p. 180007
- [27] Woo K., Kim D., Kim J. S., *ET AL.*: 'Ink-jet printing of Cu–Ag based highly conductive tracks on a transparent substrate', *Langmuir*, 2009, **25**, pp. 429–433
- [28] Zhang Y., Zhu P., Li G., *ET AL.*: 'Facile preparation of monodisperse, impurity-free, and antioxidation copper nanoparticles on a large scale for application in conductive ink', *ACS Appl. Mater. Interfaces*, 2014, **6**, pp. 560–567
- [29] Park B.K., Jeong S.J., Kim D., *ET AL.*: 'Synthesis and size control of monodisperse copper nanoparticles by polyol method', *J. Colloid. Interface. Sci.*, 2007, **311**, pp. 417–424
- [30] Carroll K.J., Reveles J.U., Shultz M.D., *ET AL.*: 'Preparation of elemental Cu and Ni nanoparticles by the polyol method: an experimental and theoretical approach', *J. Phys. Chem. C*, 2011, **115**, pp. 2656–2664
- [31] Liu X., Nishikawa H.: 'Pressureless sintering bonding using hybrid microscale Cu particle paste on ENIG, pure Cu and pre-oxidized Cu substrate by an oxidation-reduction process', *J. Mater. Sci.: Mater. Electron.*, 2017, **28**, pp. 5554–5561
- [32] Puckett W., Agbim K., Graham S.: 'Cooling of power electronics by integrating sintered Cu particle wick onto a direct-bond copper substrate'. 16th, IEEE Intersociety Conf. on Thermal and Thermomechanical Phenomena in Electronic Systems (ITherm), Orlando, 2017, pp. 547–553
- [33] Yoshikawa H., Nagao S., Sakae T., *ET AL.*: 'Cu paste sinter joining for die-attach of high T_j power devices realized by PEG solvent optimization'. Int. Exhibition and Conf. for Power Electronics, Intelligent Motion, Renewable Energy and Energy Management (PCIM), Shanghai, 2016, pp. 66–71
- [34] Lo S.H.Y., Wang Y.-Y., Wan C.-C.: 'Synthesis of PVP stabilized Cu/Pd nanoparticles with citrate complexing agent and its application as an activator for electroless copper deposition', *J. Colloid. Interface. Sci.*, 2007, **310**, pp. 190–195
- [35] Xiong J., Wang Y., Xue Q., *ET AL.*: 'Synthesis of highly dispersions of nanosized copper particles using L-ascorbic acid', *Green Chem.*, 2011, **13**, pp. 900–904
- [36] Zou H.-T., Zhang C.-Y., Yin Y.-S.: 'Rapid synthesis of copper nanoparticles by sodium hypophosphite reduction in ethylene glycol under microwave irradiation', *J. Cryst. Growth*, 2004, **270**, pp. 722–728
- [37] Blosi M., Albonetti S., Dondi M., *ET AL.*: 'Microwave-assisted polyol synthesis of Cu nanoparticles', *J. Nanopart. Res.*, 2011, **13**, pp. 127–138
- [38] Benaskar F., Patil N. G., Engels V., *ET AL.*: 'Microwave-assisted Cu-catalyzed Ullmann ether synthesis in a continuous-flow milliprep', *Chem. Eng. J.*, 2012, **207–208**, pp. 426–439
- [39] Chin S.F., Iyer K.S., Raston C.L.: 'Fabrication of carbon nano-tubes decorated with ultra fine superparamagnetic nano-particles under continuous flow conditions', *Lab. Chip.*, 2008, **8**, pp. 439–442
- [40] Corradi A.B., Bondioli F., Ferrari A.M., *ET AL.*: 'Synthesis of silica nanoparticles in a continuous-flow microwave reactor', *Powder Technol.*, 2006, **167**, pp. 45–48
- [41] Albuquerque G.H., Squire K., Wang A.X., *ET AL.*: 'Continuous synthesis of monodisperse Ag nanocubes', *Cryst. Growth Des.*, 2018, **18**, pp. 119–125
- [42] Han W.-S., Hong J.-M., Kim H.-S., *ET AL.*: 'Multi-pulsed white light sintering of printed Cu nanoinks', *Nanotechnology*, 2011, **22**, p. 395705
- [43] Dharmadasa R., Jha M., Amos D.A., *ET AL.*: 'Room temperature synthesis of a copper ink for the intense pulsed light sintering of conductive copper films', *ACS Appl. Mater. Interfaces*, 2013, **5**, pp. 13227–13234
- [44] Ryu C.-H., Joo S.-J., Kim H.-S.: 'Intense pulsed light sintering of Cu nano particles/micro particles-ink assisted with heating and vacuum holding of substrate for warpage free printed electronic circuit', *Thin Solid Films*, 2019, **675**, pp. 23–33