Electronic packaging is a technology of manufacturing electronic products that is composed of integrated circuit (IC) chips and electronic devices. It provides the medium for electronic interconnections, as well as the mechanical support. Solder provides the electrical and mechanical connections between the silicon die and the bonding pad in electronic packaging. Material selections for solder alloys are thus critical and play key roles in joint reliability of assemblies in electronic packaging. The most widely used solders for electronic packaging are based on lead-tin alloys, which are low cost, high ductility, low surface tension, and low eutectic temperature. However, with the toxicity of lead and the pollution of the environment, the investigation of replaceable Pb-free solder becomes critical. Many Pb-free solder alloys have been proposed, such as Sn-Zn, Sn-Sb, Sn-Bi, Sn-Ag, Sn-Ag-Bi, and Sn-Ag-Cu. The near-eutectic Sn-Ag-Cu system has received growing interest due to virtues such as low eutectic temperature, good solderability, high strength, a low wetting angle, and reliability.

There are many methods to produce solder alloys, such as mechanical alloying (MA) technique and screen-printing technique, yet those methods produce relatively large size solders. Owing to the continuing reduction in size of electronic devices, those methods with serious limitations as the size/pitch of solder bumps decreases in microelectronic packaging. To meet the requirements for future electronic packaging technology predicted by technology roadmaps, an ultrasmall solder bump of less than 100 μm pitch is a tendency. Therefore, as the size of solder bumps reduces with that of electronic devices, fine grain in solder paste is critical for fine pitch bumping. The aim of this research was to investigate SnAgCu alloy nanopowders for lead-free bumping applications. There are many methods to produce nanoparticles, such as chemical vapor deposition (CVD), laser ablation, microemulsion, sol-gel, and chemical reduction. Most of these synthesis techniques are faced with some problems when being scaled up for industrial application. The CVD and laser ablation methods have problems related to high-temperature processing, high cost, and low production efficiency. The microemulsion and sol-gel methods with organic solvents also exhibit some problems, such as pollution of the environment and impurity. Among these, chemical reduction is the most suitable method for industrial manufacture. It is a low-temperature process with relatively low production cost and high yield. Furthermore, compositions of the nanoparticles prepared by this method can be precisely controlled by carefully adjusting the synthesis parameters, such as pH value and temperature.

In this study, SnAgCu alloy nanoparticles with different Cu contents were successfully synthesized via a chemical reduction method. The SnAgCu alloy nanopowders were characterized by field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), and related techniques. The wettability of the SnAgCu alloy nanopowders with Cu substrate was also investigated.

**Experimental**

The Sn-3.5Ag-xCu (x = 0.2, 0.5, 1.0) alloy nanopowders were synthesized by precipitation with NaBH4 in aqueous solutions at room temperature. The total weight of the precipitated powder was fixed to 5 g, while the amount of Cu was varied from 0.2 to 1.0 wt %, SnSO4, AgNO3, and Cu(NO3)2·2.5H2O (98%) were from Riedel-deHaën (St. Louis, MO, USA), while the other chemicals were of analytical grade. SnSO4, AgNO3, and Cu(NO3)2·2.5H2O in stoichiometric amounts were dissolved in aqueous solutions as the precursors. A solution of appropriate metal precursors was rapidly added to a NaBH4/NaOH solution under strong stirring. Quintuple the amount of the NaBH4 solution was used to ensure complete reduction of the metal ions. After mixing these two solutions under strong stirring, black precipitates were formed by the chemical reduction method in this study can be used as appropriate solder powders in electronic packaging.

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**Synthesis and Characterization of Lead-Free Solders with Sn-3.5Ag-xCu (x = 0.2, 0.5, 1.0) Alloy Nanoparticles by the Chemical Reduction Method**

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Due to the concerns of human health and the natural environment, the investigation of an alternative Pb-free solder is necessary. Currently, near-eutectic SnAgCu alloys are being developed as a lead-free solder. In this study, lead-free solders with Sn-3.5Ag-xCu (x = 0.2, 0.5, 1.0) nanoparticles were synthesized by chemical precipitation with NaBH4. The X-ray diffraction (XRD) patterns revealed that the Ag3Sn was formed due to the alloying process. From the XRD patterns, only Cu6Sn5 was formed when Cu concentration was as high as 1.0 wt % in the derived nanopowders. The formation of Ag3Sn and Cu6Sn5 gave strong evidence that the nanoparticles were mixed homogeneously. From transmission electron microscopy observation, the isolated nanoparticles were close to spherical shape and the particle sizes of powders were about 5 nm. The field emission scanning electron microscopy morphology of SnAgCu nanoparticles indicates that the major particle size of SnAgCu nanoparticles is in the range of 40 nm. It was evidenced from the differential scanning calorimetry profile that the SnAgCu nanopowders could be melted successfully. In the wettability test, good metallurgical bonding was revealed between soldered and substrates after reflow. Thus, the nanoparticles derived by the chemical reduction method in this study can be used as appropriate solder powders in electronic packaging.

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observed immediately. The black precipitates were washed with distilled water and filtered until the pH of the filtrate was the same as that of the distilled water. The precipitates were then dried at room temperature.

The nanopowders were characterized with an X-ray diffractometer (XRD, LabX XRD-6000, Shimadzu, Japan) using a wavelength of Cu Kα (λ = 1.5406 Å). The particle size, shape, and morphology of nanopowders were observed with a field emission

Figure 2. FE-SEM image showing the morphology of nanoparticles: (a) Sn3.5Ag0.2Cu, (b) Sn3.5Ag0.5Cu, and (c) Sn3.5Ag1.0Cu.

Figure 3. Transmission electron micrographs of (a) Sn3.5Ag0.2Cu, (b) Sn3.5Ag0.5Cu, and (c) Sn3.5Ag1.0Cu nanoparticles.
Ag$_3$Sn indicated successful alloying after precipitation. Only the phase was exhibited in the XRD patterns and the formation of nanoparticles was investigated by XRD measurements. Figure 1 shows XRD patterns of the nanopowders with different Cu concentrations. The Ag$_3$Sn phase was exhibited in the XRD patterns and the formation of Ag$_3$Sn indicated successful alloying after precipitation. Only the Cu$_6$Sn$_5$ phase was observed from the XRD patterns shown in Fig. 1c when the concentration of Cu was as high as 1.0 wt% in the alloy powders. During the test, nanopowders were heated at the rate of 10°C/min under the N$_2$ atmosphere. A dynamic contact angle analyzer system (FTA200, first ten angstroms, USA) was introduced to measure the contact angle of the solder pastes on Cu substrate. The Cu substrate with solder pastes was put into the heated environment chamber. During the melting process, live images were continuously captured by the grabber and transferred to the user screen. From the live images, the contact angle can be drawn and measured.

### Results and Discussion

**Characterization of SnAgCu nanoparticles by XRD analysis.**—The crystal structure of the Sn-3.5Ag-0.5Cu alloy nanoparticles was investigated by XRD measurements. Figure 1 shows XRD patterns of the nanopowders with different Cu concentrations. The Ag$_3$Sn phase was exhibited in the XRD patterns and the formation of Ag$_3$Sn indicated successful alloying after precipitation. Only the Cu$_6$Sn$_5$ phase was observed from the XRD patterns shown in Fig. 1c when the concentration of Cu was as high as 1.0 wt% in the alloy nanopowders. The XRD patterns reveal that the Cu$_6$Sn$_5$ was formed due to the alloying process. The formation of Ag$_3$Sn and Cu$_6$Sn$_5$ gives strong evidence that the nanoparticles were mixed homogeneously.

**Scanning electron microscopy observation.**—In order to produce a broader visual image showing the morphology of SnAgCu nanoparticles, plan-view FE-SEMs were obtained. Figure 2 depicts the shape and morphology of nanoparticles for (a) Sn3.5Ag0.2Cu, (b) Sn3.5Ag0.5Cu, and (c) Sn3.5Ag1.0Cu. FE-SEM analysis revealed that the particles exhibited equiaxed morphology with all particles smaller than 100 nm. The average particle size, which was determined using the line intercept method, on more than 100 particles, was estimated to be around 40 nm.

**Transmission electron microscopy evaluation.**—TEM micrographs of SnAgCu alloy nanoparticles with different Cu contents are shown in Fig. 3. It is observed that the isolated particles appear to be close to a spherical shape and the particle sizes of SnAgCu powders are about 5 nm. The average particle size from SEM and TEM analysis is listed in Table I. There exist some size discrepancies between SEM and TEM analysis. This discrepancy may be attributed to the nucleation and particle growth in the related process. In the literature, the mechanism of formation for nanoparticles was proposed by Goia. The formation of metal atoms after mixing two solutions under strong stirring is caused by the transfer of electrons from the reducing agent (NaBH$_4$) to the metallic ions. As the nuclei generated in the solution, they undergo rapid diffusional growth at the expense of the remaining atoms in solution and form nanosize primary particles. As more metal atoms are generated in the system, the primary particles may aggregate to form polycrystalline particles with larger sizes, as shown in Fig. 4a. The typical TEM image, as shown in Fig. 4b, clearly reveals that the morphology of the Sn3.5Ag0.2Cu randomly oriented polycrystalline particles by aggregation of primary particles. Region A in Fig. 4b is magnified in Fig. 4c and reveals the fringes of the Sn3.5Ag0.2Cu primary powder around 5 nm. This is in good agreement with iso-

<table>
<thead>
<tr>
<th>Solder composition</th>
<th>Average size from SEM observation (nm)</th>
<th>Average size of isolated particles from TEM analysis (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn3.5Ag0.2Cu</td>
<td>41.5</td>
<td>4.7</td>
</tr>
<tr>
<td>Sn3.5Ag0.5Cu</td>
<td>42.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Sn3.5Ag1.0Cu</td>
<td>45.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>
lated particles, as shown in Fig. 3a. The size of polycrystalline particle, as shown in Fig. 4b, was 40 nm, which was identical to the SEM analysis.

Quantitative analysis with ICP-AES.—The composition of the SnAgCu solder with nanoparticles was quantitatively measured with ICP-AES. The Ag and Cu concentrations are listed in Table II. The ICP-AES derived concentration of the as-precipitated solder powders by chemical reduction was fairly close to the nominal one. To ensure accurate measurement, each powder composition was measured by ICP-AES several times and the average results were obtained. It was revealed that the contents of Ag and Cu in solder alloy were well controlled.

Melt point measured with DSC.—Figure 5 displays the DSC curves of SnAgCu alloy nanoparticles. As the temperature increases, the DSC curves exhibit only one endothermic peak at 215°C, corresponding to the melting of SnAgCu nanoparticles. In the DSC curve, no other endothermic peaks were found, indicating the complete melting of nanopowders below 240°C reflow. The evaluated melting point of SnAgCu nanoparticles was 215°C. Thus, nanopowders derived from the chemical reduction method could be employed as solder materials for the subsequent reflow process along with the wettability test.

Wettability.—The SnAgCu solder paste was produced by adding the RMA flux (TACFLUX, Indium Corporation of America) directly into nanopowders at room temperature and mixed by hand on a glass plate with a plastic spatula until uniform covering of flux on the surface of the nanopowders was achieved. The contact angles of SnAgCu solders on the Cu substrate are listed in Table III. It appears that SnAgCu nanopowders showed good wettability with contact angles less than 30°. The contact angle of the commercial solder pastes on the Cu substrate was between 30 and 40°. In addition, the wettability of the SnAgCu solder paste with nanoparticles decreased with the Cu content. Nevertheless, the contact angle of the SnAgCu solder with nanoparticles ensured good wettability. Therefore, the lead-free solder paste with SnAgCu nanoparticles synthesized by chemical reduction exhibited favorable wettability.

Conclusion

Lead-free solders with Sn-3.5Ag-xCu (x = 0.2, 0.5, 1.0) alloy nanoparticles were successfully synthesized by the chemical reduction method, and the contents of Ag and Cu in the solder alloy could be well-controlled. TEM images revealed that the size of the isolated and polycrystalline particles is about 5 and 40 nm, respectively. The polycrystalline particles analyzed by TEM were in good agreement with the results from SEM observation. In addition, the melting point of SnAgCu nanopowders was reduced to 215°C. Thus, nanopowders derived from the chemical reduction method could be employed as solder materials for the subsequent reflow process along with the wettability test.

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References


| Table II. ICP-AES results of Sn3.5AgxCu nanopowders by the chemical reduction method. |
|----------------------------------|----------------|----------------|
| Solder composition | Ag concentration (wt %) measured by ICP-AES | Cu concentration (wt %) measured by ICP-AES |
| Sn3.5Ag0.2Cu | 3.48 | 0.197 |
| Sn3.5Ag0.5Cu | 3.47 | 0.499 |
| Sn3.5Ag1.0Cu | 3.49 | 1.010 |

| Table III. Contact angles of SnAgCu solder joints on Cu substrate at 240°C. |
|----------------------------------|----------------|
| Solder composition | Contact angle (degree) |
| Sn3.5Ag0.2Cu | 28 |
| Sn3.5Ag0.5Cu | 24 |
| Sn3.5Ag1.0Cu | 22 |