

Preparation and reflow soldering characteristics of solder paste containing submicron Sn powders synthesised via chemical reduction

Sang-Soo Chee · Jong-Hyun Lee

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Abstract Sn nanoparticles (NPs) were synthesised via chemical reduction. Trisodium citrate dihydrate and mixtures of trisodium citrate dihydrate and 1,10-phenanthroline monohydrate were used as capping agents for the synthesis. When a specific amount of trisodium citrate dihydrate (3.4×10^{-1} mM) was solely added, very fine particle sizes and excellent suppression of aggregation were achieved in the dried samples. When 5 mM of 1,10-phenanthroline monohydrate was used in combination with trisodium citrate dihydrate (at the optimum concentration of 3.4×10^{-2} mM), the particle refining and the suppression of aggregation were further improved. The nano-solder paste prepared by mixing the synthesised Sn NPs with a commercial flux exhibited stable reflow soldering characteristics. The formation of an intermetallic layer, similar to that observed when commercial solder pastes containing micron-sized powders were used, was seen when soldering was carried out with the solder paste containing the synthesised Sn NPs.

Keywords Solder paste · Submicron Sn · Chemical reduction · Capping agent · Reflow soldering

Introduction

Solder is the most typical interconnection material used in the assembly of electronic products. Over the past few decades, the technical aspects of using Pb-free solders have been established; however, there is a continuing demand for solder materials which are capable of being applied to finer pitch interconnections. For example, recent research has focused on fabrication techniques to reduce the solder

S.-S. Chee · J.-H. Lee (✉)

Department of Materials Science & Engineering, Seoul National University of Science and Technology, 232 Gongneung-ro, Nowon-gu, Seoul 139-743, Korea
e-mail: pljh@snu.ac.kr

ball sizes from several hundred microns to the sub-100 micron range [1]. However, in the case of solder paste, which is deposited in patterns by screen printing processes, the research on developing processes aimed at producing type-7 materials (with at least 80 % of the particles exhibiting sizes in the range of 2–11 μm) is at its beginning stages [2, 3]. Therefore, the synthesis of submicron solder particles is necessary and their application as solder pastes in future fine-pitch interconnections is indispensable.

Some physical methods of fabricating solder nanoparticles (NPs), such as the spark erosion or arc discharge methods, have been studied in recent years [4–6]. However, chemical reduction might be a more promising fabrication technique, considering the advantages the method offers such as uniform-sized products and zero investment on building of special facilities [7–14].

The chemical reduction process comprises the decomposition of a precursor and the reduction of metal ions in a solvent. In conventional chemical reduction processes used for synthesising metal NPs, a capping agent such as polyvinyl pyrrolidone (PVP) has usually been used to suppress the agglomeration or coagulation of the reduced metal clusters [10, 12–16]. In addition to forming an oxidation-resistant layer in the reduced metal NPs, the capping agent also promotes nucleation of metal ions [15, 16]. Nevertheless, our preliminary study revealed that PVP, which disrupts the subsequent reflow soldering, is a problematic substance when used in association with solder NPs. Hence, an appropriate chemical reduction synthesis of solder NPs without PVP is necessary. In this study, the synthesis of Sn NPs via chemical reduction was performed. Trisodium citrate dihydrate and 1,10-phenanthroline monohydrate were used as capping agents during the synthesis. The variations in the size and dispersibility of the Sn NPs with the type and amounts of the capping agent(s) added were investigated after the reduction reaction. Finally, the soldering characteristics of a paste containing the synthesised Sn NPs were evaluated.

Materials and methods

Tin(II) 2-ethylhexanoate ($[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2]_2\text{Sn}$, ~95 %) and diethylene glycol (DEG, $[\text{HOCH}_2\text{CH}_2]_2\text{O}$, 99 %) were used as the precursor agent and solvent, respectively, for synthesising the Sn NPs. Trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) was added, which simultaneously acted as the reducing and capping agent. 1,10-phenanthroline monohydrate ($\text{C}_{12}\text{H}_8\text{N}_2 \cdot \text{H}_2\text{O}$) was used as an additional capping agent. All the chemicals were purchased from Sigma-Aldrich and used as received without further processing or purification.

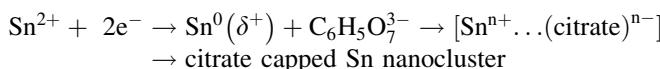
Trisodium citrate dihydrate was dissolved completely in 100 mL of DEG for 2 h. In another synthesis batch, 1,10-phenanthroline monohydrate was additionally dissolved in the DEG solution. Then, tin(II) 2-ethylhexanoate was injected into the DEG solution containing the capping agent(s) under magnetic stirring at room temperature. During and after the immediate initiation of the reduction reaction, the solution was continued to be stirred for 1 h to complete the reaction.

The size and morphology of the Sn NPs synthesised were characterized by high-resolution transmission electron microscopy (HRTEM, Tecnai 20; FEI). The samples for analysis by HRTEM were prepared by adding a few drops of the DEG solution containing the Sn NPs to carbon-coated copper grids. The remaining solution containing the Sn NPs was enriched by centrifugation at low speeds (of 4,000 rpm) to minimize agglomeration between the NPs. The DEG was repetitively exchanged with methanol during the centrifugation to achieve effective drying later, because the removal of DEG is very time consuming owing to its low volatility. The solutions enriched with methanol were dried in a low-vacuum chamber at room temperature. The dried Sn NPs were analyzed with a field-emission scanning electron microscope (FE-SEM, S-4800; Hitachi). The composition of the dried NPs was confirmed by X-ray diffraction studies (XRD, X'pert PRO-MPD; PANalytical) with specific focus on identification of any surface oxides.

In addition, the methanol solution containing Sn NPs was mixed with a commercial flux (CVP520; Cookson Electronics) and a homogenizer (PRO200; Pro Scientific) to prepare the solder paste. The mixture was then dried in a low-vacuum chamber at room temperature to achieve an appropriate viscosity.

Results and discussion

The reduction of Sn ions supplied from the precursor can be represented by the reaction given below [17–19]:



The $\text{C}_6\text{H}_5\text{O}_7^{3-}$ radicals, formed at the DEG solution with trisodium citrate dehydrate, might form a complex with the Sn seeds due to charge attraction. As the citrate complex grows slowly through further agglomeration, it reaches the citrate-capped Sn nanocluster of specific sizes at which stage the citrate layer prevents further agglomeration [17].

Figure 1 shows the SEM images of the dried Sn powders obtained from reaction mixtures containing different amounts of trisodium citrate dihydrate. In the amounts ranging from 1.4×10^{-2} to 1.7×10^{-1} mM, coarse powders of a few hundreds of microns in diameter were frequently observed together with fine powders of diameters of a few hundred nanometers. However, coarse powders almost disappeared when a citrate content of 3.4×10^{-1} mM was used in the synthesis, which resulted in the formation of relatively well-dispersed fine powders with submicron-sized particles. When the citrate content in the reaction mixture was increased to 3.4 mM, the powder size marginally increased in proportion, and coarse particles occurred randomly in the samples. This implies that an optimum amount of trisodium citrate dehydrate was required to obtain well-dispersed powders made of submicron-sized Sn particles. Henglein et al. [20] reported that the citrate concentration has a strong influence on the size of Ag NPs in the γ -radiolytic reduction of Ag^+ ions in solution. They suggested the existence of different growth mechanisms in the various ranges of the citrate concentration.

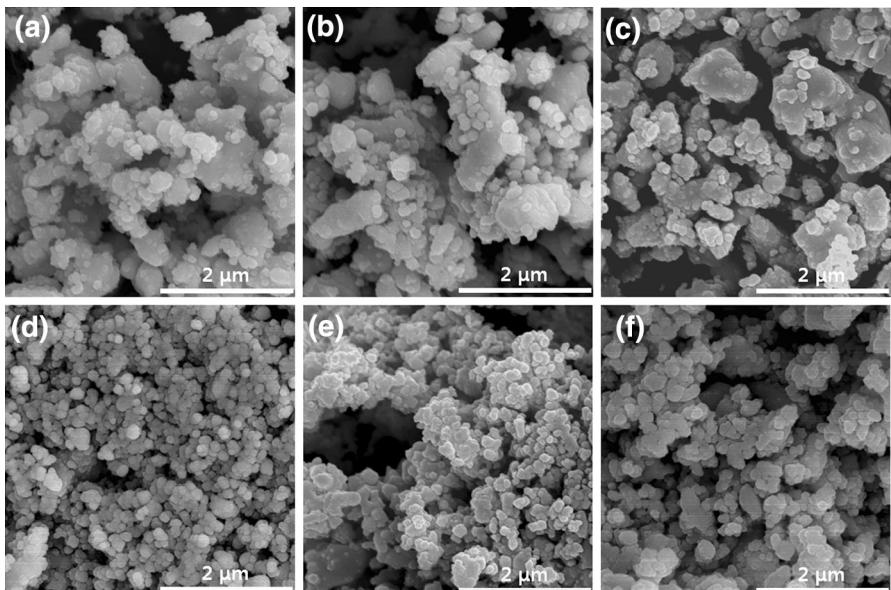


Fig. 1 Variation in the morphology of dried Sn powders obtained from reaction mixtures with a trisodium citrate dihydrate content of **a** 1.4×10^{-2} , **b** 3.4×10^{-2} , **c** 1.7×10^{-1} , **d** 3.4×10^{-1} , **e** 1.7, and **f** 3.4 mM

Considerable aggregation of the Sn NPs can be observed in Fig. 1, including in Fig. 1d, which was the best result obtained. The aggregation was mainly caused by the contact between Sn powder particles, which occurred during drying. Hence, 1,10-phenanthroline monohydrate, another strong capping agent, was additionally added during the synthesis. In our investigation, we used varying amounts of 1,10-phenanthroline monohydrate along with 3.4×10^{-1} mM of trisodium citrate dihydrate to reduce the degree of aggregation.

Figure 2 shows the SEM images of dried Sn powders obtained from reaction mixtures containing various amounts of 1,10-phenanthroline monohydrate, which was added additionally to trisodium citrate dihydrate. Although no reduction in the aggregation could be observed in most cases, because of the compatibility of the two capping agents, the product obtained with reaction mixtures containing 5.0 mM (Fig. 2d, e) of 1,10-phenanthroline monohydrate were distinctively different from the others.

To confirm that the aggregation and coalescence of the as-synthesised Sn NPs observed in Figs. 1 and 2 were due to drying, HRTEM analysis was carried out. Fig. 3a shows the TEM image of the as-synthesised Sn NPs. Most of the Sn NPs were elongated spheres less than 10 nm in diameter, although some NPs with diameters of a few tens of nanometers were also observed. Considering that the apparent size of the particles observed in Fig. 2e was in the range of 50–200 nm, the enormous size discrepancy in particles observed in Figs. 2e and 3a needs explanation. This discrepancy suggested that the coalescence of the as-synthesised

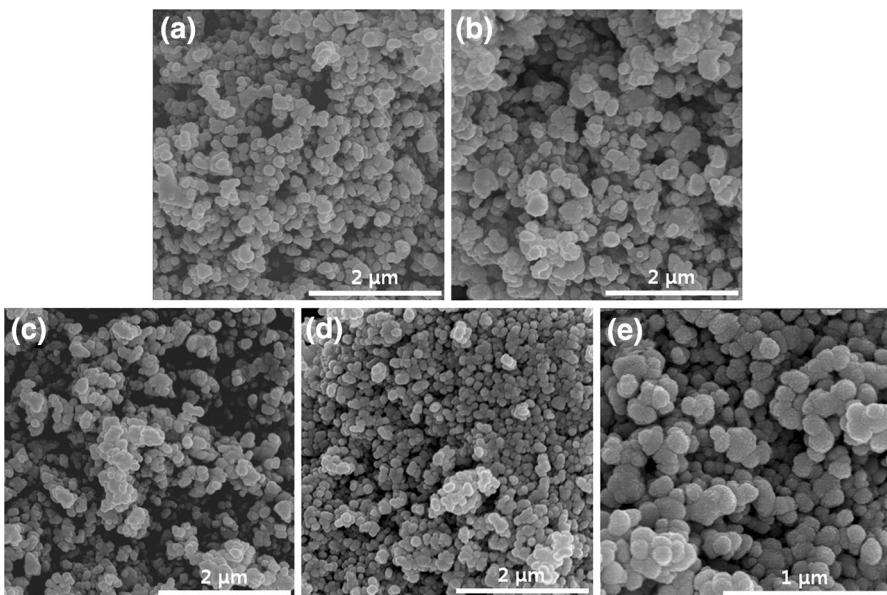


Fig. 2 Variation in the morphology of dried Sn powders obtained from reaction mixtures containing 3.4×10^{-1} mM of trisodium citrate dihydrate along with **a** 7.6×10^{-1} , **b** 1.5, **c** 3.0, **d** 5.0, and **e** 5.0 mM (high magnification) of 1,10-phenanthroline monohydrate

Sn NPs occurred in addition to the aggregation during drying. The fast Fourier transformation (FFT) pattern (Fig. 3b), which corresponded to the specific area of Fig. 3a, confirmed the formation of crystalline β -Sn. The observable ring fringes indicated that (200) and (220) growth planes were present in the NPs.

In addition, another drying process was carried out to suppress the aggregation and coalescence of the Sn NPs. Fig. 4 represents the microstructure of the composite samples, which were obtained by adding an epoxy formulation to the DEG solution containing the as-synthesised Sn NPs, followed by drying and curing. Although some Sn NPs of a few tens of nanometers in diameter were observed in the composite, most Sn NPs were found to be elongated spheres of less than 10 nm in diameter, similar to those observed in Fig. 3a. Therefore, Figs. 3 and 4 indirectly support our assumption that the coalescence and aggregation of Sn NP occurred during drying. From the results presented in Figs. 1, 2, 3 and 4, it can be concluded that, to prepare a solder paste containing submicron particles, the flux should be mixed after drying the NP solution, and to prepare a solder paste containing NPs, the flux should be mixed with the NP solution itself.

XRD patterns obtained from the dried Sn powders synthesised by chemical reduction with or without 1,10-phenanthroline monohydrate are shown in Fig. 5. Irrespective of the addition of 1,10-phenanthroline monohydrate to the reaction mixture, similar results were obtained. Peaks corresponding to tin oxide were absent because there was hardly any formation of the surface oxide layer during the synthesis and drying process. However, the peak intensities were generally reduced

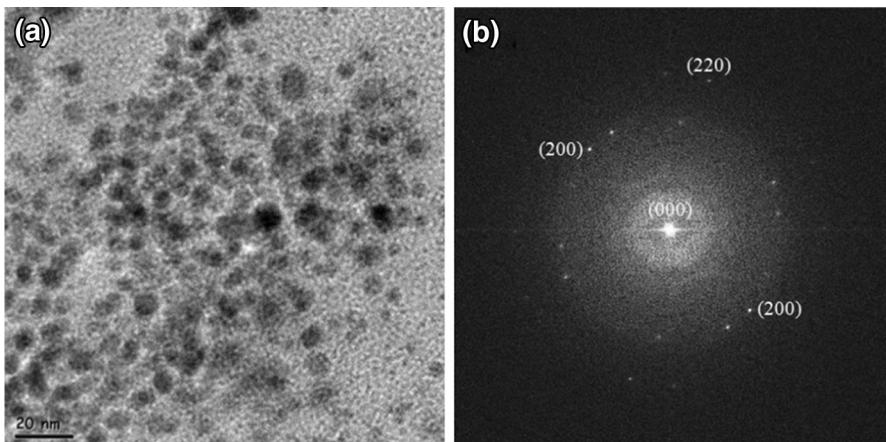
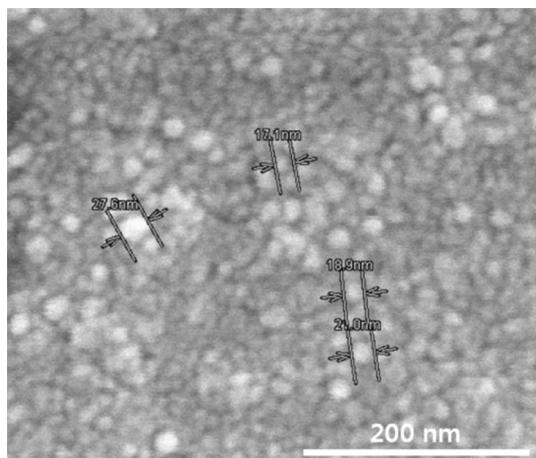


Fig. 3 **a** TEM image of Sn NPs synthesised by chemical reduction when 3.4×10^{-1} mM trisodium citrate dehydrate and 5.0 mM 1,10-phenanthroline monohydrate were used in the reaction mixture; **b** FFT pattern of the Sn NPs

Fig. 4 SEM micrograph of the composite obtained by adding an epoxy formulation to the DEG solution containing the as-synthesised Sn NPs, followed by drying and curing



in samples obtained from reaction mixtures containing 1,10-phenanthroline monohydrate. This observation was interpreted as the result of the presence of a barrier as in the case of Sn NPs capped by 1,10-phenanthroline, implying that the thickness of the capping layer was considerable.

Figure 6 shows a cross-sectional image of the interface obtained after reflow soldering (peak temperature: 240 °C) was carried out on a Cu plate with a solder paste containing the Sn NPs that were synthesised by chemical reduction from reaction mixtures containing both trisodium citrate dihydrate and 1,10-phenanthroline monohydrate. A Cu₆Sn₅ intermetallic layer of a few microns in thickness was clearly observed, which was identical to the results obtained by reflow soldering with a commercial solder paste containing micron-sized solder powders [21].

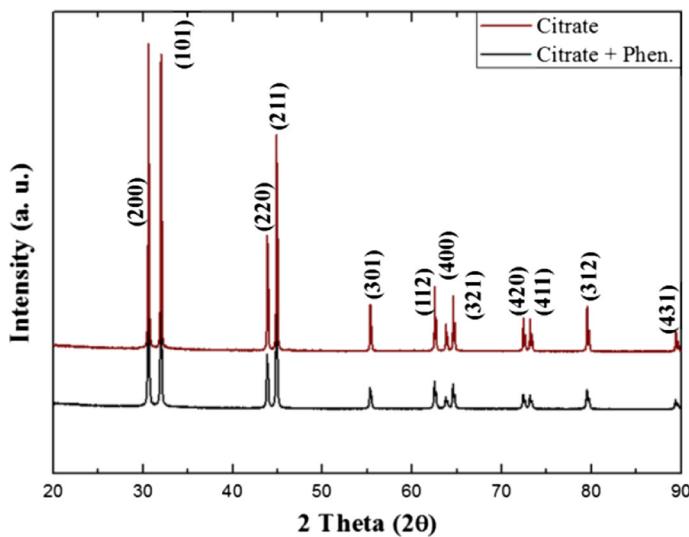


Fig. 5 XRD profiles of dried Sn powders synthesised by chemical reduction

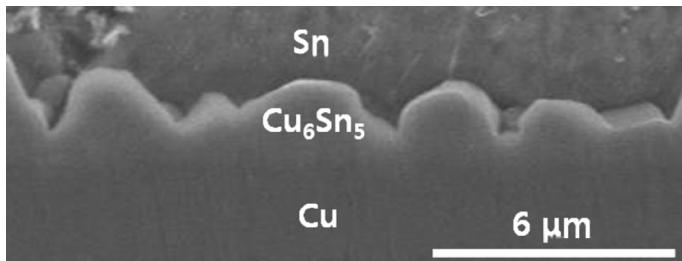


Fig. 6 SEM micrograph of the interfacial microstructure obtained after conducting reflow soldering on a Cu plate using a solder paste containing Sn NPs synthesized by chemical reduction

The results obtained by reflow soldering with a solder paste containing Sn NPs synthesized using only trisodium citrate dihydrate as the capping agent were also identical to the aforementioned observations. Therefore, our study demonstrated the feasibility of a solder paste containing nanometer-sized solder particles.

Conclusions

Synthesis of Sn NPs was performed by chemical reduction reactions using trisodium citrate dihydrate or a mixture of trisodium citrate dihydrate and 1,10-phenanthroline monohydrate (instead of PVP) as capping agents. When only trisodium citrate dihydrate was used in the reaction mixture, minimum particle size and excellent aggregation suppression were achieved in samples obtained after drying,

specifically when the amount of trisodium citrate dihydrate in the reaction mixture was maintained at 3.4×10^{-1} mM. When 5 mM of 1,10-phenanthroline monohydrate was additionally added along with 3.4×10^{-1} mM of trisodium citrate dihydrate, the particle refining and suppression of aggregation were further improved. The results of the reflow soldering experiments carried out using a solder paste containing the synthesized Sn NPs were identical to those obtained when reflow soldering was carried out with a commercial solder paste containing micron-sized solder powders. Hence, we have demonstrated the feasibility of solder pastes containing nanometer-sized solder particles for application in fine-pitch interconnections.

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