Advanced Materials Research Vol. 530 (2012) pp 52-55
Online available since 2012/Jun/04 at www.scientific.net

doi:10.4028/www.scientific.net/AMR.530.52

Effects of Reductant Amount and Capping Agent on Tin Nanoparticles Synthesis Using a Tin(II) 2-ethylhexanoate Precursor

Sang-Soo Chee[a] and Jong-Hyun Lee[b]

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

[a]gamdol2@daum.net, [b]pljh@snut.ac.kr

Keywords: tin nanoparticles, tin(II) 2-ethylhexanoate, reduction synthesis, reductant, capping agent.

Abstract. Tin nanoparticles were synthesized through compulsive reduction using a Tin(II) 2-ethylhexanoate precursor, and the effect of reductant (sodium borohydride) amount on the size distribution of the particles was surveyed. Issues caused by the absence of a capping agent (polyvinyl pyrrolidone) were similarly examined. An excessive amount of dissolved sodium borohydride caused variations in the tin nanoparticle sizes, from a few nanometers to several tens of nanometers. The formation of abnormally large particles was attributed to the vigorous coagulation among smaller tin particles. In the tin nanoparticles synthesized without polyvinyl pyrrolidone, an exceptionally wide size distribution was observed owing to irregularly coagulated and aggregated large particles.

Introduction

Solder paste, deposited in patterns through a screen printing process, is directly related to the implementation of fine pitch interconnection. Recent solder pastes with particles of several tens of microns in size cannot meet ultrafine patterns of several tens of microns in pitch [1,2]. Hence, a preparation method to achieve uniform nanoscale solder particles and replace atomization is an urgent technology. Furthermore, synthesizing solder or tin nanoparticles is directly related to producing low-cost conductive ink for jetting, a non-contact patterning process with the benefits of speed and simplicity [3-5].

The effects of process parameters should be scrupulously surveyed to effectively control the size of particles synthesized through a chemical method. The amount of reductant may be a crucial parameter in determining size distribution [6,7]. The influence of a capping agent, which is detrimental to electrical conductivity, will also be a major factor in size control [8,9]. This study elucidated the effects of reductant amount on the synthesis of fine tin particles and observed the resultant size distribution. In addition, an identical synthesis without capping agent was performed to clarify the synthesis trend.

Experimental

Tin(II) 2-ethylhexanoate ($[CH_3(CH_2)_3CH(C_2H_5)CO_2]_2Sn$) of ~95% (Aldrich Chemical Co.) is a common precursor agent for synthesizing tin nanoparticles. Diethylene-grycol (DEG) (99%, Sigma-Aldrich Chemical Co.) and polyvinyl pyrrolidone (PVP) (molecular weight: 1300000, Aldrich Chemical Co.) were used as a reaction medium and a capping agent, respectively. A sodium borohydride ($NaBH_4$) (99.99%, Aldrich Chemical Co.) was used as a reducing agent.

In a typical synthesis, 1 g PVP and 2 g sodium borohydride were completely dissolved in 100 ml DEG for 1 h. A 4 g sodium borohydride was dissolved in another synthesis to evaluate the influence of varied reductant amount. Stirring the DEG solution at room temperature, the tin(II) 2-ethylhexanoate was added using a dispenser with an injection rate of 4.5 ml/min. A holding step of 1 h by magnetic stirring completed the reaction. The DEG solutions containing Sn nanoparticles were dripped on copper grids coated with carbon film. The samples were analyzed using a high-resolution transmission electron microscope (HR-TEM) (Tecnai 20, FEI Co.).

The solution containing synthesized tin nanoparticles was enriched at low centrifugal speed of 6000 rpm to minimize agglomeration among nanoparticles. Drying with DEG is difficult due to its low volatility; thus, the medium was repetitively exchanged with methanol during centrifugation. The enriched methanol solution was dried at room temperature in a low vacuum chamber to elevate drying rate. The size and morphology of final Sn nanoparticles were observed using a field emission scanning electron microscope (FE-SEM).

Results and Discussion

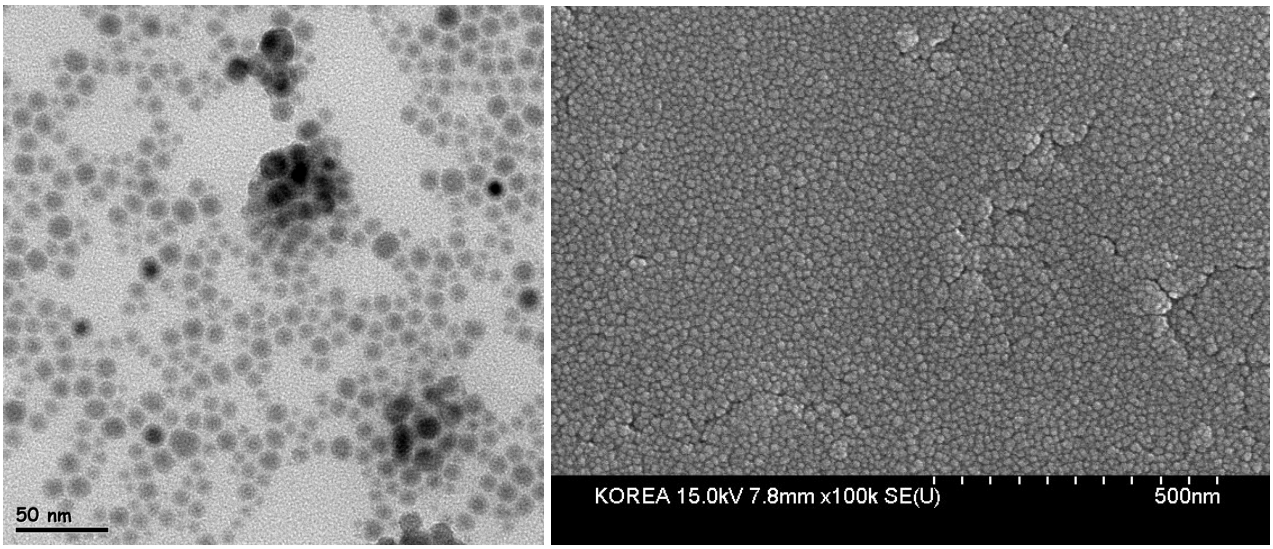
Effect of Reductant Amount

A reduction synthesis of tin using precursor and $NaBH_4$ in a DEG medium can be expressed as follows [10]:

$$BH_4^- + 8OH^- + 4Sn^{2+} \rightarrow B(OH)_4^- + 4H_2O + 4Sn$$

However, the reaction mechanism is not fully understood and has been reported as a complex reaction consisting of several reaction steps [10-12].

Figure 1 shows the TEM and SEM images of tin nanoparticles synthesized with 2 g of dissolved sodium borohydride. In Fig. 1(a), the nanoparticles demonstrate a fine formation with average nanoparticle diameters of <10 nm and high discreteness. However, a few nanoparticles have started to partially agglomerate. Moreover, severe coagulation among nanoparticles was rarely observed after drying, despite the occurrence of aggregation through sticky PVP capping [Fig. 1(b)].

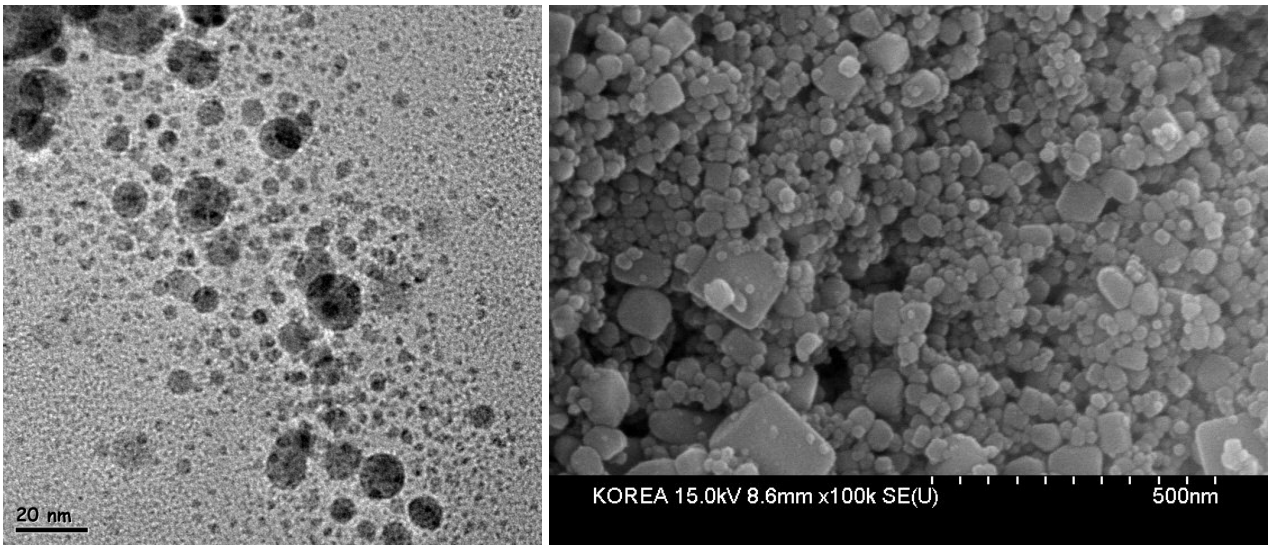


(a) (b)

Fig. 1. (a) TEM and (b) SEM images of tin nanoparticles synthesized in a DEG solution containing PVP with 2 g of dissolved sodium borohydride.

Figure 2 shows the TEM and SEM images of the tin nanoparticles synthesized with 4 g of dissolved sodium borohydride. The tin nanoparticle sizes varied from a few nanometers to several tens of nanometers, making the divergence in size appreciable [Fig. 2(a)]. Hence, excessive sodium borohydride caused a wide distribution in size. The reduction rate is enhanced with increasing reductant concentration, thus the number (or concentation) of precipitating metallic clusters abruptly increases at a higher nucleation rate. Hereafter, the nuclei generation steeply increases during the same nucleation period, causing the formation of smaller tin particles. The amount of metallic atoms for particle growth decreases with increasing nuclei number. However, excessive reaction at higher reductant concentration also forms large particles, mainly through coagulation among smaller tin particles by stirring DEG because excessive precipitation occurs only in restricted space. The burst

precipitation in short periods may inhibit the formation of complete PVP coverings surrounding the nanoparticles, which would thus allow coagulation to immediately occur after contact among nanoparticles due to the considerable diffusivity of tin.



(a) (b)

Fig. 2. (a) TEM and (b) SEM images of tin nanoparticles synthesized in a DEG solution containing PVP with 4 g of dissolved sodium borohydride.

The wide size distribution was significantly enhanced when the nanoparticles were reobserved after drying [Fig. 2(b)]. The biggest particles grew to several hundreds of nanometers, and the smallest particles retained their size. The growth in size was mainly estimated as caused by the coagulation during centrifugation. The probability and velocity of collision among particles are promoted with bigger particles. Therefore, the larger particles observed immediately after synthesis could absorb surrounding particles and further expand during centrifugation. The coagulation behavior of tin nanoparticles during centrifugation with PVP capping has been reported by authors [13].

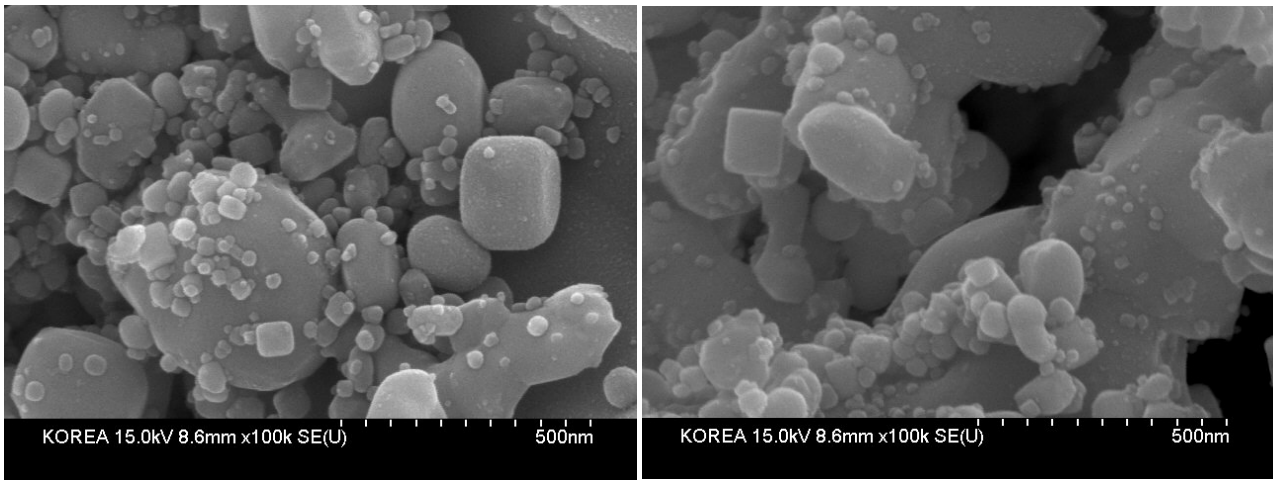


Fig. 3. SEM images of tin nanoparticles synthesized without PVP.

Effect of PVP Capping Agent

Jo et al. reported that the PVP encapsulating nanoparticles is a main reason for the low electrical conductivity of sintered tin ink [5]. They adopted a plasma ashing treatment with oxygen gas at different temperatures in a vacuum condition to reduce or eliminate the residual PVP polymer [5]. Therefore, the reduction synthesis of tin particles was attempted without PVP.

Figure 3 shows the SEM images of tin nanoparticles synthesized without PVP. The tremendous size increase of the tin particles prevented the use of TEM. Tin particles with a few tens of nanometer in size as well as coagulated and aggregated large particles were observed, showing an exceptionnally wide size distribution. The absence of capping agent adversely affected the preparation of tin particles with a uniform, small size. The absence of PVP can quickly accelerate coagulation and aggregation among particles upon nanoparticle contact during synthesis.

Summary

An excessive amount (4 g) of dissolved sodium borohydride caused size variations in tin nanoparticles, from a few nanometers to several tens of nanometers, resulting in a considerably wide size distribution. Although excessive sodium borohydride can cause the formation of smaller tin particles, the condition can also form abnormally large particles due to vigorous coagulation among smaller tin particles. Without PVP, an exceptionally wide size distribution was observed, including irregularly coagulated and aggregated large particles. Therefore, the absence of a capping agent adversely affected the preparation of tin particles with miniature and uniform sizes.

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) (2011-0009088).

References

[1] E.H. Amalu, W.K. Lau, N.N. Ekere, R.S. Bhatti, S. Mallik, K.C. Otiaba, and G. Takyi: Microelectron. Eng. Vol. 88 (2011), p. 1610.

[2] T.-N. Tsai: Robot. Comput. Integrated Manuf. Vol. 27 (2011), p. 808

[3] B.K. Park, D. Kim, S. Jeong, J. Moon and J.S. Kim: Thin Solid Films Vol. 515 (2007), p. 7706

[4] J. Choi, Y.-J. Kim, S. Lee, S.U. Son. H.S. Ko, V.D. Nguyen and D. Byun: Appl. Phys. Lett. Vol. 93 (2008), p. 193508

[5] Y.H. Jo, I. Jung, C.S. Choi, I. Kim and H.M. Lee: Nanotechnology Vol. 22 (2011), p. 225701

[6] J. Kasthuri, S. Veerapandian and N. Rajendiran: Colloid Surface B: Biointerf. Vol. 32 (2003), p. 117

[7] B.K. Park, S. Jeong, D. Kim, J. Moon, S. Lim and J.S. Kim: J. Colloid Interface Sci. Vol. 311 (2007), p. 417

[8] Y. Sun and Y. Xia: Science Vol. 298 (200), p. 2176

[9] Y. Li, E. Boone and M.A. El-Sayed: Langmuir Vol. 18 (2002), p. 4925

[10] C.Y. Lin, U.S. Mohanty, and J.H. Chou: J. Alloys Compd. Vol. 501 (2010), p. 204.

[11] L.-Y. Hsiao and J.-G. Duh: J. Electron. Mater. Vol. 35(9) (2006), p. 1755

[12] Y.H. Jo, J.C. Park, J.U. Band, H. Song, and H.M. Lee: J. Nanosci. Nanotecno. Vol. 11 (2011), p. 1037

[13] S.-S. Chee and J.-H. Lee: submitted to Transactions of Nonferrous Metals Society of China (2011)

Smart Technologies for Materials
10.4028/www.scientific.net/AMR.530

Effects of Reductant Amount and Capping Agent on Tin Nanoparticles Synthesis Using a Tin(II) 2-Ethylhexanoate Precursor

10.4028/www.scientific.net/AMR.530.52