JMEPEG (2012) 21:353–357
DOI: 10.1007/s11665-011-9918-z

1059-9495/$19.00

Easy and Large Scale Synthesis Silver Nanodendrites: Highly Effective Filler for Isotropic Conductive Adhesives

Kai Dai, Guangping Zhu, Luhua Lu, and Graham Dawson

(Submitted October 25, 2010; in revised form March 11, 2011)

Dendritic silver (Ag) nanoparticles have been successfully prepared by an easy and large scale liquid-phase reduction method. Transmission electron microscope (TEM), scanning electron microscope (SEM), and x-ray diffraction (XRD) have shown that the Ag particles prepared by this method are pure and with uniform dendritic morphology. The bulk resistivity and bonding strength of isotropic conductive adhesives (ICAs) filled with Ag nanodendrite and micrometer-sized Ag have been measured. The results show that the dendritic morphology of Ag nanoparticles has a strong effect for improving the reinforcement of the composite electrical performance. ICA filled with small amounts of Ag nanodendrites exhibits lower bulk resistivity and higher bonding strength than ICA filled with micrometer-sized Ag. When ICA is filled with 50 wt.% micrometer-sized Ag and 10 wt.% Ag nanodendrites, the bulk resistivity is 1.3×10^{-4} Ω cm, and the bonding strength reaches 18.9 MPa.

Keywords bonding strength, bulk resistivity, conductive adhesive, silver nanodendrite

1. Introduction

Solders are crucially important for electronics industry manufacturing. Tin-lead alloys, which have ever been widely used as conductive solder to interconnect circuit elements (Ref 1-4), have been banned in many countries for the actual harm of the lead to the health of people. As their main alternatives, lead-free alloys and isotropic conductive adhesives (ICAs) have been developed (Ref 5). Owing to high melting temperatures of many lead-free alloys, their use has been somewhat limited (Ref 6, 7). As a result, environmentally friendly ICA, which is easy to prepare and has advantages, such as low working stress on the substrates, short distances between the electrical lines in circuits, low processing temperature, and low cost, are now the most promising alternative to tin-lead solder under mild processing conditions (Ref 8-11).

ICA is prepared by dispersing conductive filler in polymeric resin that provides its mechanical properties. Among the various conductive particles, such as gold, palladium, nickel, copper, graphite, and carbon fiber, silver (Ag) is the most common filler for its excellent conductivity, and thermal and chemical durabilities (Ref 12-16). To understand the relationship of filler state and composite conductivity, the formation of conductive network of particles in polymer matrix has been studied (Ref 12, 17). Though high weight fraction could provide better conductivity, too many conductive particles may cause lower bonding strength during the processing of the composite materials (Ref 18-20). Thus, the most important issue for ICA is that it should ensure effective dispersion and connection of conductive filler to obtain highly conductive composite at low filler weight fraction, which preserves the important mechanical performance of solder.

To solve similar problem that micrometer-sized Ag particle systems encountered, dendritic Ag nanoparticles have been synthesized. The dendritic Ag nanoparticles are prepared by an extremely easy method that is amenable to large-scale production. The effects of substituting micrometer-sized Ag particles with Ag nanodendrites are tested in polymeric system.

Kai Dai and **Guangping Zhu**, College of Physics and Electronic Information, Huaibei Normal University, Huaibei 235000, People's Republic of China; and **Luhua Lu** and **Graham Dawson**, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, People's Republic of China. Contact e-mail: daikai940@163.com.

2. Experimental

2.1 Synthesizing of Ag Nanodendrite

In typical synthesis, 3 g $AgNO_3$ and 1 g polyvinylpyrrolidone (PVP) are put into 200 mL double distilled water, refluxed at 50 °C for 60 min, into which 20 mL ethyl alcohol absolution and 20 mL hydrazine hydrate are injected at 50 °C at a rate of 0.3 mL/min. After the injection, the reaction mixture is further refluxed at 50 °C for 60 min. Magnetic stirring is continuously applied throughout the entire process of reduction and nanodendritic growth. The mixtures are washed several times with double distilled water on a sintered glass filter until the washings show no acidity. Finally, Ag nanodendrites are obtained after drying in a vacuum oven at 80 °C for 4 h.

2.2 Preparation and Measurements of ICA

Epoxy resin (E-51), cure agent (Dibutylphthalate), hardener (Triethanolamine), and solvent (dimethylbenzene) are mixed, and then conductive filler is added and stirred for 30 min. Finally, the ICA sample is prepared after the mixture has been ultrasonicated for 10 min.

The schematic drawing of bulk resistivity is shown in Fig. 1(a). The bulk resistivity (ρ_v) can be calculated from Eq 1:

$$\rho_v = \frac{S \cdot R}{L} = \frac{b \cdot c \cdot V}{a \cdot I} \quad \text{(Eq 1)}$$

where R is resistance, and a, b, and c are the length, width, and thickness of the sample, respectively. It is necessary that a/b is more than 200.

With copper as testing electrode, bonding-strength test samples are prepared by coating ICA on two pieces of electrodes. The schematic drawing of the testing samples is shown in Fig. 1(b). The bonding strength (σ) can be calculated from Eq 2:

$$\sigma = \frac{f}{s} \quad \text{(Eq 2)}$$

where f is a force applied to break off the banded, and s is the area of bonding part on the sample.

2.3 Analytical and Testing Instruments

The morphology of synthesized Ag nanoparticles is observed on a JEM 200CX transmission electron microscope (TEM). The samples are prepared by dropping the Ag nanoparticles suspension on the carbon-coated Cu grids and observed at 100 kV.

The as-synthesized Ag nano-particles being distributed in polymeric matrix and the morphology of synthesized Ag nanodendrites are observed using a JSM-6700F field emission scanning electron microscope (SEM).

X-ray diffraction (XRD) data of Ag nanodendrites are collected using a Rigaku D/MAX 24000 diffractometer with Cu Kα radiation.

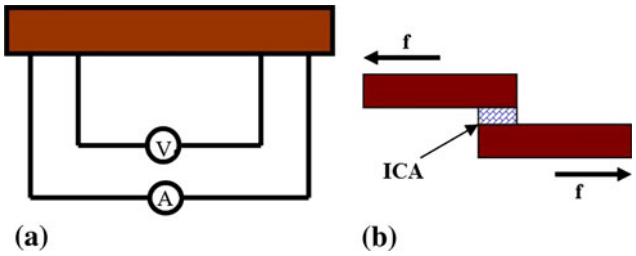

Fig. 1 Measurements of ICA. (a) Bulk resistivity test and (b) bonding strength test

Viscosities of ICA are tested using DV-I viscosity meter.

The resistant test is processed on Four Points ZL-5 Intelligent LCR Measurement.

The bonding strength of ICA is processed on Reger 3010 electric multiple-use test apparatus.

The life of ICA is tested using LP/DHS-225 constant temperature and humidity test chamber.

3. Results and Discussion

3.1 Characterization of Ag Nanoparticles

Figure 2 shows TEM and SEM images of the Ag nanodendrites. This sample is essentially composed of Ag nanodendrites with diameter from 30 to 100 nm and a length up to ca. 450 nm. This kind of particle has many branches, and the branches of Ag nanodendrites can be easily connected with each other, and we also found that Ag nanodendrites could not be obtained in the absence of PVP.

Figure 3 shows the XRD pattern of as-product, The peaks at 38.12°, 44.32°, 64.46°, 77.40°, and 81.54° can be assigned to (111), (200), (220), (311), and (222) reflections of the

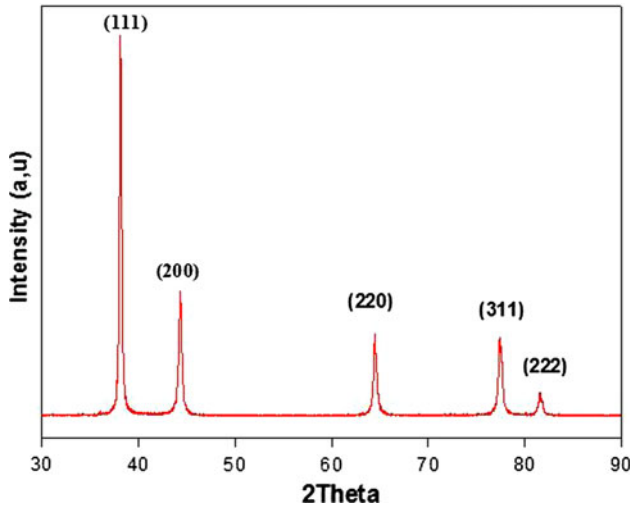

Fig. 3 XRD pattern of Ag nanodendrites

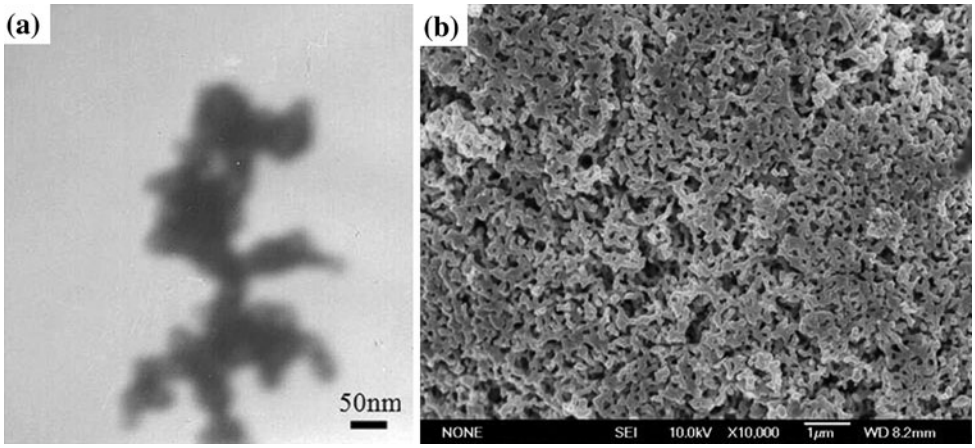

Fig. 2 TEM (a) and SEM (b) images of Ag nanodendrites

face-centered lattice of Ag. The lattice constant calculated from this XRD pattern is 4.090 Å, which is very close to Powder Diffraction Standards ($\alpha = 4.086$ Å, JCPDS File No. 04-0783).

3.2 Electrical Property Study of ICA

The current carrying capability is the most important property for ICA to connect electronic components. Table 1 shows bulk resistivity of ICA filled with different conductive fillers, where Nano-Ag are the Ag nanodendrites, and micro-Ag is micrometer-sized, which is bought from Sinopharm Chemical Reagent Co. Ltd, the size is 50-70 μm. As indicated in Table 1, when the fillers are micrometer-sized Ag particles, such as the samples A, B, C, and G, the more the content of Ag particles, the lower the bulk resistivity of ICA. The bulk resistivity attains to 1.7×10^{-4} (Ω cm) when the content of fillers reaches 75 wt.%. However, ICA with the mixture of micrometer-size of Ag and Ag nanodendrite can easily get such bulk resistivity with lower Ag content. When the contents of the micrometer-sized Ag and Ag nanodendrites are 50 wt.% and 10 wt.%, respectively, the minimum bulk resistivity is 1.3×10^{-4} (Ω cm), and Ag can be saved for 15 wt.%. However, more than 10% Ag nanodendrites cannot operate well with bulk resistivity.

Although contact between metallic particles seems necessary to achieve electrical conductivity, it has been observed that some conductivity could be obtained in systems where the particles are not in contact (Ref 21, 22). A carrier tunneling mechanism is proposed for this phenomenon. Hence, the bulk resistivity of ICA can be calculated as per Eq 3:

$$R = R_0 + R_i + R_t = R_0 + \frac{\rho_i}{d} + \frac{\rho_t \cdot L}{a} \quad \text{(Eq 3)}$$

where R_0 is the intrinsic filler resistivity; R_i is the contact resistance between Ag particles; R_t is the tunneling resistance between Ag particles, especially nanometer-sized Ag particles; ρ_i is the intrinsic filler resistivity; d is the diameter of the contact spot; ρ_t is the tunnelling resistivity; L is the length of the adhesive; and a is the contact area.

As compared to R_i and R_t, R_0 is much smaller so that it can be neglected for the total resistance (Ref 23). When the fillers are micrometer-sized Ag particles, such as the samples A, B, C, and G, the chances for direct contact and the diameter of the contact spot are relatively larger, thus the conductivity is dominated by R_i; R_t can be neglected, and so the bulk resistance of ICA is decreased by adding more of the micrometer-sized Ag particles. Whenever a part of micrometer-sized particles are replaced by Ag nanodendrite, the diameter of the contact spot between small and big particles becomes extremely small, and quantum-mechanical tunneling will occur, resulting in lower bulk resistivity. On comparison of the Samples C, D. and E, we observe that when the content of Ag nanodendrite reaches 10%, the bulk resistivity of ICA attains the lowest value. When more particles of Ag nanodendrites are added, the viscosity of ICA will increase, and so the bulk resistivity of ICA cannot be improved.

3.3 Bonding Strength Study of ICA

Viscosity is an important parameter for the ICA processability; the viscosities of the samples are shown in Table 2. As indicated in Table 2, the viscosity of ICA increased with more fillers, and incorporation of nano fillers in epoxy tends to increase the viscosity. The ability to connect things effectively is a critical property for electronic components. Most microelectronic commercial ICA have poor impact strength because of too many fillers, and the bonding strength of ICA may be increased by decreasing the filler loading (Ref 5). Lower joint strength is a critical limitation for application of ICA. Table 2 also shows bonding strength of ICA filled with different conductive fillers. As indicated in Table 2 for the samples C, D, and E, ICA filled with Ag nanodendrites and micrometer-sized Ag have higher bonding strength and resistance than the traditional ICA filled with the micrometer-sized Ag particles when they have the same total content of Ag. When the fillers have nanometer-sized dimensions, the specific surface area of the filler becomes larger, the nanodendrites have higher activity during curing of the matrix resin, and they might more easily contact the resin, as compared with the micrometer-sized Ag particles. As a result, the bonding strengths of the samples C,

Table 2 Bonding strength of ICA filled with different conductive fillers

Samples	Total Ag, wt.%	Micro-Ag, wt.%	Nano-Ag, wt.%	Bonding strength(a), MPa
O	0	0	0	32.4
B	50	50	0	20.5
C	60	60	0	17.7
D	60	55	5	18.7
E	60	50	10	18.9
F	60	45	15	19.1
G	75	75	0	14.9

(a) Average of five measurements for each sample

Table 1 Viscosity and bulk resistivity of ICA filled with different conductive fillers

Samples	Total Ag, wt.%	Micro-Ag, wt.%	Nano-Ag, wt.%	Viscosity(a), mPa s	Bulk resistivity(a), Ω cm
A	35	35	0	7100	3.5×10^{-3}
B	50	50	0	7650	9.3×10^{-4}
C	60	60	0	8020	5.1×10^{-4}
D	60	55	5	8260	2.0×10^{-4}
E	60	50	10	8310	1.3×10^{-4}
F	60	45	15	8340	1.6×10^{-4}
G	75	75	0	8930	1.7×10^{-4}

(a) Average of five measurements for each sample

D, E increase. When the sample E is compared with the sample G, the bulk resistivity of the former is lower than that of the latter, but the bonding strength of the latter is much higher than that of the latter, and thus a large quantity of Ag particles are saved. Hence, the sample E satisfies the requirements for the application of ICA to microelectrical packaging.

3.4 Life study of Conductive Adhesive

Figure 4 shows SEM image of sectional view of the sample E. In this sample, the fillers of Ag nanodendrites and the micrometer-sized Ag particles can be dispersed in E51 uniformly. As a tin-lead alloy replacement, ICA must have stable properties between finished components during aging at elevated temperature and relative humidity. The shift of bulk resistivity and bonding strength of the sample E in 85 °C/85% relative humidity environment is illustrated in Fig. 5. From Fig. 5, we can find that the shift of bulk resistivity of the sample E is less than 15% after 1000 h of aging. The change of bonding strength is less than 13%.

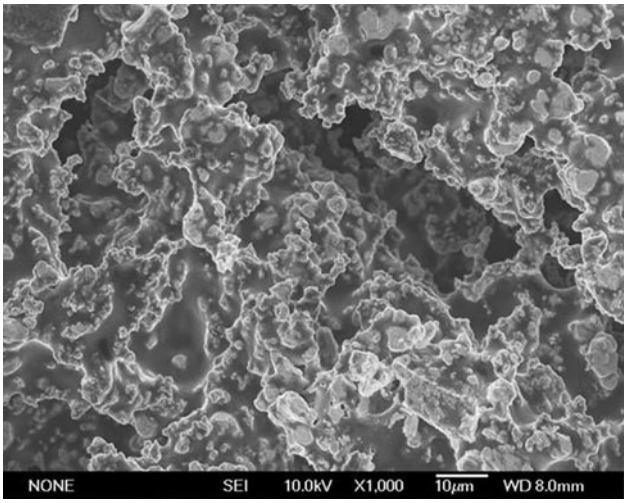

Fig. 4 SEM image of sectional view of the sample E

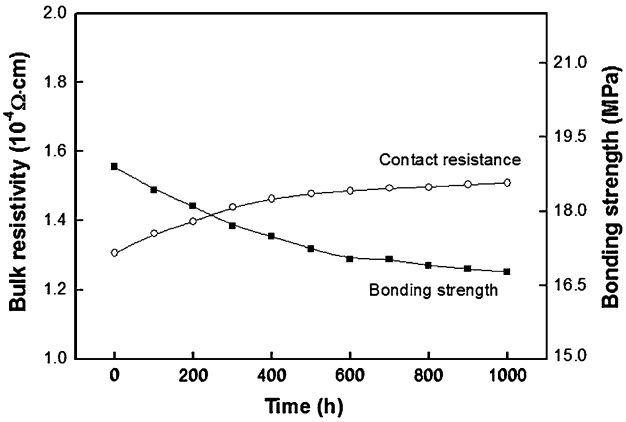

Fig. 5 Bulk resistivity and bonding strength of the sample E with hygrothermal aging time

4. Conclusion

In this study, Silver (Ag) nanoparticles have been successfully prepared with dendritic appearance. Our preliminary results demonstrate that the ICA exhibits lower bulk resistivity (down to 1.3×10^{-4} Ω cm) and higher bonding strength (up to 18.9 MPa) at lower filler content than those of the traditional ICA filled with the micrometer-sized Ag particles. In this way, large quantities of Ag particles can be saved. The developed ICA materials filled with Ag nanodendrites and the micrometer-sized Ag particles satisfy the requirements for the application of ICA to microelectrical packaging, which might be utilized as a replacement of traditional tin-lead alloys.

Acknowledgment

The authors acknowledge the supports of Natural Science Foundation of Jiangsu Province (BK2010258).

References

1. C.W. Anderson, Determination of Antimony in White Metals, A Volumetric Semimicromethod, *Ind. Eng. Chem. Anal. Ed.*, 1939, **11**, p 224–225
2. K. Carva and I. Turek, Ab Initio Theory of Spin-Transfer Torques, *J. Magn. Magn. Mater.*, 2007, **316**, p e926–e929
3. X.D. Wang, P. Petitpas, C. Garnier, J.P. Paulin, and Y. Fautrelle, A Quasi Two-Dimensional Benchmark Experiment for the Solidification of a Tin-Lead Binary Alloy, *Compt. Rendus Méc.*, 2007, **335**, p 336–341
4. V. Bhattacharya and K. Chattopadhyay, Melting of Multiphase Nano-Scaled Particles Embedded in Al Matrix, Case of Pb-Sn and Bi-Sn Alloys, *Mater. Sci. Eng. A*, 2007, **449–451**, p 1003–1008
5. Y. Li, K.S. Moon, and C.P. Wong, Electronics Without Lead, *Science*, 2005, **308**, p 1419–1450
6. D. Suraski and K. Seelig, The Current Status of Lead-Free Solder Alloys, Electronics Packaging Manufacturing, *IEEE Trans. Electron. Packag. Manuf., Part C*, 2001, **24**, p 244–248
7. M.J. Yim, H.J. Kim, and K.W. Paik, Anisotropic Conductive Adhesives with Enhanced Thermal Conductivity for Flip Chip Applications, *J. Electron. Mater.*, 2005, **34**, p 1165–1171
8. H. Zhao, T. Liang, and B. Liu, Synthesis and Properties of Copper Conductive Adhesives Modified by SiO_2 Nanoparticles, *Int. J. Adhes. Adhes.*, 2007, **27**, p 429–433
9. D. Lu and C.P. Wong, High Performance Conductive Adhesives, *IEEE Trans. Electron. Packag. Manuf.*, 1999, **22**, p 324–330
10. Y. Li, K.S. Moon, and C.P. Wong, Electrical Property Improvement of Electrically Conductive Adhesives Through In-Situ Replacement by Short-Chain Difunctional Acids, *IEEE Compon. Packag. Technol.*, 2006, **29**, p 173–178
11. T. Fałat, A. Wymysłowski, and J. Kolbe, Numerical Approach to Characterization of Thermally Conductive Adhesives, *Microelectron. Rel.*, 2007, **47**, p 342–346
12. Y. Li and C.P. Wong, Recent Advances of Conductive Adhesives as a Lead-Free Alternative in Electronic Packaging, Materials, Processing, Reliability and Applications, *Mater. Sci. Eng. R*, 2006, **51**, p 1–35
13. A.E. Pap, K. Kordás, H. Jantunen, E. Haapaniemi, and S. Leppävuori, Copper Plating on and Electrical Investigation of a Low-Permittivity Cycloolefin-Copolymer, *Polym. Test.*, 2003, **22**, p 657–661
14. I. Krupa, G. Miková, I. Novák, I. Janigová, Z. Nógellová, F. Lednický, and J. Prokeš, Electrically Conductive Composites of Polyethylene Filled with Polyamide Particles Coated with Silver, *Eur. Polym. J.*, 2007, **43**, p 2401–2413
15. L. Jing and J.K. Lumpp, Electrical and Mechanical Characterization of Carbon Nanotube Filled Conductive Adhesive, *Aerospace Conference, 2006 IEEE*, Vol 4-1, 2006, p 1–6
16. C.F. Goh, H. Yu, S.S. Yong, S.G. Mhaisalkar, F.Y.C. Boey, and P.S. Teo, The Effect of Annealing on the Morphologies and Conductivities

of Sub-Micrometer Sized Nickel Particles Used for Electrically Conductive Adhesive, *Thin Solid Films*, 2006, **504**, p 416–420

17. C.F. Goh, H. Yu, S.S. Yong, S.G. Mhaisalkar, F.Y.C. Boey, and P.S. Teo, Synthesis and Cure Kinetics of Isotropic Conductive Adhesives Comprising Sub-Micrometer Sized Nickel Particles, *Mater. Sci. Eng. B*, 2005, **117**, p 153–158
18. H.H. Lee, K.S. Chou, and Z.W. Shih, Effect of Nano-Sized Silver Particles on the Resistivity of Polymeric Conductive Adhesives, *Int. J. Adhes. Adhes.*, 2005, **25**, p 437–441
19. M. Inoue, H. Muta, S. Yamanaka, and K. Suganuma, Electrical Properties of Isotropic Conductive Adhesives Composed of Silicone-Based Elastomer Binders Containing Ag Particles, *J. Electron. Mater.*, 2009, **38**, p 2013–2022
20. H. Jiang, K.S. Moon, Y. Li, and C.P. Wong, Surface Functionalized Silver Nanoparticles for Ultrahigh Conductive Polymer Composites, *Chem. Mater.*, 2006, **1**, p 2969–2973
21. L.H. Fang, S. Bin, J.M. Qing, and C.P. Wong, Effects of Nanometer-Sized Particles on Electrical and Thermal Conductivities of Polymer Composites, *Advanced Packaging Materials, Processes, Properties and Interfaces, 2004 Proceedings, Ninth Int. Symp.*, 2004, p 193–199
22. L. Ye, Z. Lai, L. Johan, and A. Tholen, Effect of Ag Particle Size on Electrical Conductivity of Isotropically Conductive Adhesives, *IEEE Trans. Electron. Packag. Manuf.*, 1999, **22**, p 299–302
23. S.G. Yu and B. Gates, Crystalline Silver Nanowires by Soft Solution Processing, *Nano Lett.*, 2002, **2**, p 165–168