Research Article

Low-Temperature Sintering Bonding Using Silver Nanoparticle Paste for Electronics Packaging

Wei Guo,¹ Zhi Zeng,² Xiaoying Zhang,¹ Peng Peng,³ and Shanping Tang¹

¹School of Mechanical Engineering and Automation, Beihang University, Beijing 100191, China

²School of Mechanical, Electronic, and Industrial Engineering, University of Electronic Science and Technology of China, Chengdu 611731, China

³Mechanical and Mechatronics Engineering, University of Waterloo, Waterloo, ON, Canada N2L 3G1

Correspondence should be addressed to Zhi Zeng; zhizeng@uestc.edu.cn

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Ag nanoparticles (NPs) with about 40 nm diameter covered with 5–8 nm organic shell were prepared by chemical reduction reaction. The thermal characteristics of Ag nanoparticle (NP) paste were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The low-temperature sintering bonding processes using Ag NP paste were carried out at the temperature range of 150–350°C for 5 min under the pressure of 3 MPa. The microstructures of the sintered joint and the fracture morphology were evaluated by scanning electron microscopy (SEM). The shear strength was used to evaluate the mechanical property of the sintered joint. TGA-DSC test showed that the Ag content is approximately 95.5 mass% in Ag NP paste. The average shear strength of the joint fabricated at 250°C for 5 min under the pressure of 3 MPa was about 28 MPa, which could meet the requirements of electronics packaging working at high temperature. The joint shear strength increased with the increase of the sintering temperature due to much denser sintered Ag NPs and more comprehensive metallurgical bonds formed in the joint.

1. Introduction

Microelectronic devices and large power devices interconnection to the substrate is essential for device packaging, which provides paths for increased high power density electrical interconnection and high-efficiency heat dissipation [1]. However, the traditional eutectic or near eutectic Sn-Pb, Sn-Ag, and Sn-Ag-Cu solders and conductive adhesive used in die attachment are not reliable for high power density and high temperature electronic applications [2–4]. The Pb-containing solder alloys (Sn-Pb) have been temporarily exempted from the Restriction of Hazardous Substances (RoHS) directive in the European Union due to serious health threat to human being and heavy pollution to environment [5, 6]. On the other hand, it is reported that the joint using Pb-containing solder and Pb-free eutectic or near eutectic Sn-Ag and Sn-Ag-Cu solders is not suitable for long-term usage at elevated temperature due to crack formation at the intermetallic (IMC) layer between the solder and the metallized substrate on the devices [7–9]. Thus, the new

lead-free interconnection materials as alternative for device packaging have attracted much attention.

When material size is reduced down to nanoscale, some special characteristics, such as lower melting point [10], much higher surface energy [11], and diffusion coefficient [12], are significantly different from their parent materials in bulk. Therefore, a new low-temperature Pb-free interconnection method is developed using the sintering of nanomaterial, in particular, nanoparticles (NPs) [13–18]. Among those NPs, silver (Ag) has been demonstrated as a candidate because of its excellent properties, such as high electrical conductivity, high thermal conductivity, and excellent high temperature service performance [15]. At present, low-temperature sintering of Ag NPs has been developed for bonding of semiconductor devices onto metallized substrate [16–21]. Unlike traditional liquid solder wetting, solid-liquid interfacial reaction, and solidification process, Ag NPs sintering bonding process is achieved under quite low temperatures, usually at 150–350°C, through atomic diffusion and NP consolidation.

Organic compounds are usually used to disperse and stabilize Ag NPs, which will be adsorbed on the surface of Ag NPs. During the sintering process, the removal of organic shell is a requisite by heating and thus being certain of the temperature is needed. After sintering process, the joint shows high melting point of pure Ag (about 960°C) and excellent electrical and thermal properties as that of bulk Ag. Thereby, these sintered Ag NP joints produced at relatively low temperatures (below 350°C) could be used at elevated temperatures (beyond 350°C) at which the conventional solder joints could fail. Furthermore, this promising low-temperature Ag NPs sintering process has wide potential applications in flexible electronics, including rapid prototyping [22], flat-panel printing [23], organic electronics [24], and low-cost disposable microelectronic devices on plastic substrates applications [25]. However, the microstructure evolution of the sintered joint during the sintering process is less studied. On the other hand, usually, the Ag NPs application is restricted by the long sintering times as it requires about 20–30 min [26].

In this paper, Ag NP paste was fabricated by chemical reduction method. The morphology and size distribution of Ag NPs have been observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to evaluate thermal characteristics of Ag NP paste. The rapid sintering experiment was performed in the furnace at air atmosphere. The mechanical property of the joint was evaluated using shear strength. The microstructure evolutions of the joint and the fracture surface morphology were also observed by SEM.

2. Materials and Methods

Ag NPs used in the experiment were prepared by modified reducing silver nitrate (AgNO_3) with ethylene glycol in the presence of polyvinylpyrrolidone (PVP) [27]. All of the chemical reagents were of analytical grade. First, 20 mL ethylene glycol solution of 0.3 M AgNO_3 and 40 mL solution of PVP (0.9 M, K30) were prepared, respectively. The ethylene glycol solution was then heated to the reaction temperature of 160°C. The PVP solution was injected into the silver nitrite solution at a constant rate of 0.3 mL s^{-1} . When the solution color changed from colorless to gray (indicating the chemical reaction is completed), the solution was cooled rapidly through adding deionized water into the hot solution. Then, the Ag NP paste was collected by condensing the solution in a centrifuge (TW16-WS) with 7000 rpm for 30 min.

TGA and DSC analyses (STA 449 F3) were performed in air with the increase rate of 10.00 K min^{-1} to determine the organic content and the thermal properties of Ag NP paste. The morphology of Ag NPs and their size distribution were observed by SEM (JEOL 1530) and TEM (JEM-2100).

The nickel (Ni) and Ag layers plated Copper (Cu) discs were adopted as the electronics packaging connection samples in this work. The upper and bottom sizes of Cu discs were Φ 6 mm $\times$ 5 mm and Φ 10 mm $\times$ 5 mm, respectively. Prior to bonding, the as-received Cu discs were ultrasonically

FIGURE 1: Schematic illustration of the sintering joint using Ag NP paste.

cleaned in acetone for 20 min to remove containments on the joining surface. Ag NP paste was blushed about 200 μm on the surface of Cu discs and dried at 70°C on the heating plate for 10 min. And Ag NP paste was sandwiched between upper and bottom Cu discs (shown in Figure 1). The sintering experiments were performed in the muffle furnace in air atmosphere from 150 to 350°C for 5 min under the pressure of 3 MPa. In detail, the furnace was heated to sintering temperature, holding for about 20 min for uniform temperature, and then the joining assembly was put into the furnace and put the pressure on the assembly. After sintering process, the assembly was taken out from the furnace.

The shear strengths of the sintered joints were evaluated using a Gleeble thermomechanical simulator (1500 D) with a displacement speed of 5 mm min^{-1} at room temperature. The interfacial microstructures of the joints and fracture surfaces were examined by SEM (CS3400 and JEOL 1530).

3. Results and Discussion

3.1. Morphologies of Ag NPs. Figure 2(a) shows the typical morphology of as-prepared Ag NPs. It can be seen that most of Ag NPs are polyhedron in shape. The distribution of Ag NP size was in the range of 20–80 nm (shown in Figure 3) and the average diameter of Ag NPs was about 40 nm. Transmission electron microscopy (TEM) image of Ag NPs is displayed in Figure 2(b). An organic shell with a thickness of 5–8 nm is observed on the surface of Ag NPs, which prevented the oxidation and aggregation of Ag NPs.

3.2. Thermal Characteristics of Ag NP Paste. Figure 4 shows the TGA and DSC results of Ag NP paste. Two exothermic peaks in DSC curve are recognized at around 350 and 400°C, respectively. When the temperature is above approximately 150°C, some organic compositions covered on Ag NP may start to vaporize, oxidize, or burn out by reacting with oxygen in air or being adsorbed on Cu disc surface [28]. As known, nanoparticles tend to aggregate because of much

FIGURE 2: SEM (a) and TEM (b) images of Ag NPs.

FIGURE 3: Ag NP size distribution.

FIGURE 4: TGA and DSC curves of Ag NP paste.

higher surface energy [18, 29]. The exothermic peak at around 350°C is mainly due to the decomposition of organic shell. The exothermic peak at ~400°C is possibly attributed to the oxidation of C derived from PVP [30]. As shown in TGA curve, the weight of the dried paste gradually decreases as

the temperature increases from room temperature to 450°C, which can be attributed to vaporization and decomposition of the organic compounds in the paste. The Ag content of Ag NP paste was approximately 95.5 mass%, which is significantly higher than 85 mass% in conventional Ag NP paste [13]. Since the bonding process is atom diffusion and sintering of Ag NPs with the vaporization and decomposition of the organic components. When the organic component reduces, Ag NPs aggregate and sinter together under the annealing temperature and pressure. Because of the much lower organic content of the Ag NP paste used in this research, it is reasonable to predict that it will have lower sintering temperature and shorter sintering time during bonding compared with the conventional Ag NP paste.

3.3. Microstructures of the Sintered Joint. Figures 5(a)–5(c) give the low magnification microstructures of the joint at the temperature of 150°C, 250°C, and 350°C, respectively. Macrocracks were observed between Ag coated layer and Ag NP sintered zone of the joint at 150°C as arrows indicated in Figure 5(a). Since only few organics vaporized and oxidized at the temperature of 150°C as shown in DSC curve in Figure 4, these cracks format the interlayer between Ag coated substrate and Ag NP sintered zone due to the residual organics in Ag NP paste. No significant macrocracks could be observed when the sintering temperature increased to 250°C and 350°C (see Figures 5(b)–5(c)), indicating that the joint strength would be increased. Meanwhile, a high magnification image of the connection areas of the joint is given in Figures 5(d)–5(f). It was found that the sintered zone of the joint at 150°C (Figure 5(d)) was composed of small size Ag NPs (several hundred nanometer diameter) with high percentage of pores. With the temperature increasing to 250°C, a uniform and denser Ag NP sintered layer was formed between the Ni/Ag plated Cu discs (Figure 5(e)). Since the more intense sintering happened at higher temperature, Ag NPs sintered and grew together causing the increase of material density and decrease of the porosity. As the sintering temperature reached 350°C, much better metallurgical combination of joining zone was attained as shown in Figure 5(f). Some submicron voids still existed in the sintered layer but the porosity of the joint

FIGURE 5: SEM images of interface microstructure of joints with different sintering temperatures: (a) low magnification at 150°C; (b) low magnification at 250°C; (c) low magnification at 350°C; (d) high magnification at 150°C; (e) high magnification at 250°C; (f) high magnification at 350°C.

FIGURE 6: Microstructure of the joint: (a) line scan; (b) element distribution.

decreased compared with that at 250°C. It is worth mentioning that the volume of the single pore increased with the sintering temperature from a few hundreds of nanometers to several microns. Benefiting from such porous structures, this sintered material could help relieve the thermomechanical stresses during operation. Moreover, the presence of such pores could balance the elastic modulus or other mechanical properties like strength and fatigue properties [31] of joints with the substrates, especially the plastic substrates. The chemical element distributions across the joining interface

are shown in Figure 6. It can be seen that Ag content drops much sharply at the edge of Ni coating, and Ni coating does well on impeding Ag diffusion due to much lower solution of Ag in Ni. No voids are discovered near the edge of Ni coating.

3.4. Mechanical Property of the Joints. Figure 7 shows the average shear strength of the sintered joints as a function of sintering temperature. The average strength of the joints at 150°C and 200°C was about 8 MPa and 10 MPa,

FIGURE 7: Average shear strength of sintered joints at different sintering temperatures.

FIGURE 8: The fracture surface morphology of the joints. (a) Macromorphology. (b) Fracture at 150°C. (c) Fracture at 250°C. (d) Fracture at 350°C.

respectively. When the sintering temperature increased to 250°C, the average shear strength of the joint significantly increased to 28 MPa, which is comparable to the traditional lead solder and lead-free solder, suggesting that it could meet the requirements of electronic packaging (24 MPa) in practical applications [13]. The average shear strength of 40 MPa was achieved at sintering temperature of 350°C. The higher temperatures are beneficial to the contact, diffusion, and sintering process between Ag NPs and substrate [32]. Therefore, higher sintering temperature could promote

the sintering between Ag NPs and also between Ag NPs and substrates, which results in a better strength of joint.

Figure 8(a) shows the macrofracture surface of the joint. The ring-like structure on the fracture surface of the sintered joint as observed by Rautio et al. [33] due to the coffee ring effect caused by the rheological property of Ag NP paste was not obvious because of a very high content of Ag NPs in the paste. Figures 8(b)–8(d) show the fracture morphology of sintered Ag NPs joint at different temperatures from 150 to 350°C. At low temperature of 150°C (Figure 8(b)),

the majority of the Ag NPs were sintered together with clear the edges and corners, indicating that the Ag NPs maintained the original shape and sintering was feeble at low temperature. When the sintering temperature is 250°C (Figure 8(c)), obvious neck growth and particle growth were observed and sintering densification occurred. At 350°C, the particle size grew further and large grain appeared resulting in a much denser sintering structure (see Figure 8(d)). The Ag NP size increased with the increase of the sintering temperature, as shown in Figures 8(b)–8(d). After measuring, it was found that Ag NPs on fracture surface sintered at 150°C, 250°C, and 350°C were about 150 nm, 0.8 μm , and 1.2 μm , respectively. The phenomenon can be explained by the fact that the organic shell covered on Ag NPs decomposed faster and more completely at higher temperature [33]. The diffusion rate increased with the increasing of the sintering temperature, which resulted in the rapid coarsening of Ag NPs. Moreover, at high temperatures such as 250 to 350°C in this work, the Ag NPs became rounded and the corners were tuned (Figures 8(c) and 8(d)), which suggested that the liquid phase might appear during sintering. The liquid involved sintering would have much higher sintering speed than that of solid state sintering. It is worth mentioning that this liquid might only present on the surface of Ag NPs, the so-called surface melting [34], because the sintering temperatures are below the melting temperature of Ag NPs.

4. Conclusions

Ag NP paste with an average diameter of about 40 nm covered with organic shell 5–8 nm thick was synthesized via chemical reduction reaction. The organic shell can prevent the oxidation and aggregation of Ag NPs. TGA-DSC curves showed that the silver content was approximately 95.5 mass% in Ag NP paste and the organic shell vaporized, oxidized, or decomposed by reacting with the oxygen during the heating process in air. The sintered joint with Ag NP paste was successfully achieved at different temperatures with a rapid sintering process. With the increase of the sintering temperature, the interfacial microstructure of joint became denser. The average shear strength of the joint fabricated at 250°C for 5 min under 3 MPa is 28 MPa because of metallurgical bond formed between the silver plated layer and the sintered Ag NP layer, which could meet the requirements of electronics packaging. It suggests that this Ag NP paste as an alternative low-temperature connection material is suitable for high power semiconductor devices packaging with a rapid sintering process, which could also be applied to flexible electronic packaging.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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