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Effect of PVP on the low temperature bonding process using polyol prepared Ag nanoparticle paste for electronic packaging application

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Abstract. There has been an increasing interest in developing low temperature interconnection process using metal nanoparticles. In this study the Ag nanoparticles (NPs) for this low temperature bonding process applications were prepared based on the polyol method using polyvinylpyrrolidone (PVP) as the protecting agent. The effect of PVP on the Ag nanoparticle size, nanoparticle solution viscosity and the bondability of the Ag nanoparticle paste were studied. The silver nanoparticle with diameter of 90 nm, 40 nm and 20 nm were synthesized by adjusting PVP concentration. The bonding processes using different kind of Ag nanoparticle paste were conducted. The joint with shear strength of 50 MPa were formed using Ag nanoparticle (NP) paste prepared with appropriate PVP concentration.

1. Introduction

Soldering technology based on tin/lead (Sn/Pb) solders has been playing an important role in electronic packaging. However, Pb and its compounds result in serious health threat to humans when depositing the Pb containing electronic devices in the environment. Emerging regulations have targeted the elimination of Pb usage in electronic assemblies in many countries [1, 2]. Particularly, the high temperature solders are still widely used due to no suitable alternative. Therefore, there is a strong drive to find Pb-free alternatives especially for high temperature applications.

As Pb-free electronic interconnection materials, the low temperature bonding technology using metal nanoparticles (Ag, Cu, etc) have attracted people's attention in the recent years [3-12]. As the size of metal nanoparticles is reduced, their surface energy increases, which lead to some special properties such as increase of diffusion coefficient and decrease of sintering temperature [13-16]. Due to the size effect the metal nanoparticles can be used as the low temperature bonding materials. After the bonding is completed, the nanoparticles are changed into microscaled or bulk materials. Consequently, the apparent melting point of bonding materials increases to that of the bulk materials.

Therefore, the metal nanoparticle paste, which can be sintered at low temperature, has the potential to be a lead-free, high-performance interconnect material[17]. Based on this principle, the bonding technique using metal nanoparticles (Ag, Cu, etc) has been studied by several research groups [3-12]. Usually the metal nanoparticle paste was prepared by mixing the organic components to the commercial nanoparticles in order to prevent the self-cohesion. However, the added organic components will bring detrimental effect to the sintering and the bonding process. Recently, our group has developed a new method to prepare metal nanoparticle paste, which contains low organic component, based on the polyol method. This new Ag nanoparticle paste was prepared through the polyol synthesis of Ag nanoparticles and the subsequent concentration without a further addition of organic component. Thus the organic content in this new nanoparticle paste is significantly lower than that in the conventional Ag nanoparticle paste [7, 9-12]. During our Ag nanoparticle preparation, polyvinylpyrrolidone (PVP) was used as the protecting agent to prevent the self-cohesion of the chemical reduction created Ag nanoparticles. In this study, the effect of the added polyvinylpyrrolidone (PVP) concentration on the Ag nanoparticle size, the Ag solution viscosity and the bondability of Ag nanoparticle paste were studied.

2. Experimental procedure

Different kinds of silver nanoparticle solutions were synthesized by the modified polyol process in this study[18]. First, silver nitrite was dissolved into ethylene glycol (EG) to form a solution with an AgNO_3 concentration of 0.15 M. On the other hand, the EG solution of polyvinylpyrrolidone (PVP-K30, with viscosity about 2.5mPa.s) with a given PVP concentration such as 0.045 M (mol/L), 0.45 M, 1.35 M, were prepared. After the two kinds of mentioned solutions were heated to the chemical-reaction temperature of 160 °C, at a constant heating rate of 20 °C/min. The PVP solution was injected into the silver nitrite solution at a constant rate. The color of the solution changed from the colorless to gray, indicating the precipitation of Ag NPs. When the reaction was completed, the solution was rapidly cooled by adding chilled deionized (DI) water. Three kinds of Ag NP pastes (A, B and C) were prepared by directly condensing the chemically reduced Ag NP solutions using different PVP concentration (0.045 M, 0.45 M, 1.35 M) without a further addition of organic component.

The bondability of Ag nanoparticle pastes (A, B and C) prepared with different PVP concentrations were investigated by bonding the silver plated Cu discs, which simulate the metal-coated semiconductor chip and substrate respectively, in air. The shape of Cu specimens used for the bonding experiment is show in Figure 1. The Ag nanoparticle pastes were applied on the faying surfaces of Cu discs. Then the samples were dried at 80 °C on the hotplate to further remove the low boiling point components in the paste. Afterwards, put the smaller Cu disc on the bigger Cu disc stage. These prepared bonding specimens were heated up to the bonding temperature under assistant pressure of 5 MPa for 30 min in air atmosphere. The bonding strength was evaluated as shear strength measured using the Thermal-Mechanical Simulator Gleeble 1500D with a displacement speed of 5 mm /min under room temperature. Three samples were tested for the same bonding parameters.

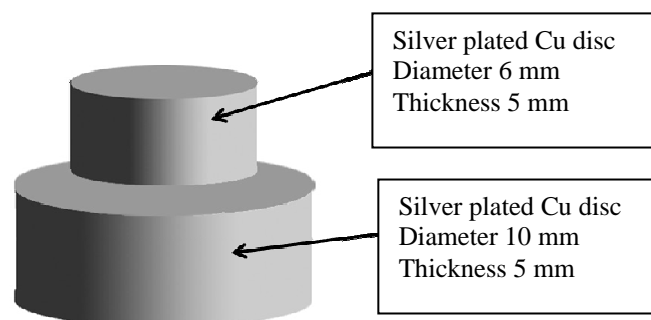


Figure 1. Schematic illustration of the bonding specimens.

3. Results and discussion

3.1. Effect of PVP concentration on the characteristics of Ag nanoparticle paste and the joint strength

The PVP concentration had a significant influence on the particle size distribution of the synthesized Ag NPs. The added PVP has a function to prevent the chemically generated Ag nanoparticles from aggregation. Figure 2 shows SEM images of Ag nanoparticles obtained when using different PVP concentration. As the PVP concentration was low (0.045 M), the PVP was not sufficient to completely cover the surface of Ag NPs. The initially generated Ag nanoparticles tended to merge into larger particles. Therefore, the generated Ag nanoparticles had a larger diameter size of about 90 nm. With increasing PVP concentration (0.45 M), more of the generated Ag nanoparticles were covered by the PVP opportunely. The diameter of Ag nanoparticles is of about 40 nm. When the PVP concentration was increased to (1.35 M), the corresponding Ag nanoparticles had a smaller diameter of 20 nm.

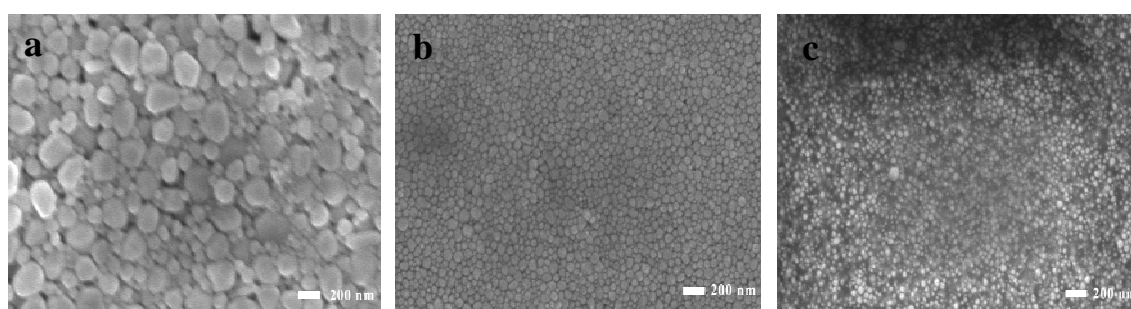


Figure 2. SEM images of Ag nanoparticles synthesized with different PVP concentration (a) 0.045 M, (b) 0.45 M, (c) 1.35M.

The viscosities of the Ag nanoparticle solutions before the condensing, which were detected using a Rheometer, increased with PVP concentration increasing. Ag nanoparticle solution synthesized with the PVP concentration of 0.045 M has a viscosity of 4.2 cP (mPa.s). As the concentration of PVP increased to 0.45 M, the corresponding viscosity of Ag nanoparticle solution slightly increased to 4.4 cP. When further increasing PVP concentration to 1.35 M, the viscosity increased to 6.0 cP. It seems that the viscosity of the solvent is strongly depended on PVP at high concentrations. The viscosity of solution is higher, when the PVP concentration increases. Since the PVP concentration will affect the viscosity of the Ag nanoparticle solutions, it is reasonable to deduce that the PVP concentration has a significant effect on the viscosity of the concentrated Ag nanoparticle paste.

The bond characteristics for Ag nanoparticle pastes (A, B and C) were evaluated at bonding pressure of 5 MPa in air for 30 min. Three bonded samples were made for each level. The PVP has a great effect on the bondability of the Ag nanoparticle paste. As shown in Table 1, the shear strengths of the joints using Ag nanoparticle pastes (A, B and C) are 26 MPa, 50 MPa and 5.0 MPa, respectively. Based on the above analysis, it can be seen that the PVP concentration affects the generated Ag nanoparticle sizes, solution viscosities and the bondability of the Ag nanoparticle paste, as shown in Table 1.

Table 1. Properties of Ag nanoparticle pastes prepared with different PVP concentrations.

Ag nanoparticle paste	PVP concentration (M)	Size diameter (nm)	Viscosity (cP)	Average shear Strength (MPa)
A	0.045	90	4.2	26
B	0.45	40	4.4	50
C	1.35	20	6.0	5.0

3.2. Microstructures of the joints using different Ag nanoparticle paste

Figure 3 displays the fracture appearance photographs of copper disc joints using Ag nanoparticle pastes (A, B and C). Figures 4 display the corresponding SEM images of the fracture appearances of the joints using Ag nanoparticle pastes (A, B and C). For the joint using Ag nanoparticle paste A (Figure 4a), the fracture appearance is coarse and many pit-cracks in the sintered Ag layers are observed. It is attributed to the low viscosity of the Ag nanoparticle paste prepared with low PVP concentration. Due to the existence of cracking in the sintered Ag layer, the average joint strength using Ag nanoparticle paste A is about 26 MPa. As shown in Figure 3b and Figure 4b, smooth and dense fracture surfaces were observed when using the Ag nanoparticle paste B and C as the bonding materials. The dimple structures are obvious which indicate the good joints were formed under these conditions. The PVP in the Ag nanoparticle paste has a function to adjust viscosity and to prevent the cracking of the sintered Ag layer. The joint strength using Ag nanoparticle paste B is significantly increased to 50 MPa since the cracking of the Ag paste was effectively prevented. This demonstrated that the Ag nanoparticle paste prepared with the PVP concentration of 0.45 M has a better bondability. The Figure 3c and Figure 4c display the smooth and dense fracture surfaces of the joints using Ag nanoparticle paste C. Although obvious fracture traces are observed in Figure 4c, the joints strength using Ag nanoparticle paste is as low as only 5 MPa. The results of qualitative analyses by EDX of three areas of the joints using different Ag nanoparticle pastes are given in Figure 5. As displayed in Figure 5a and Figure 5b, only pure Ag elements were detected, confirming that the bonding layer was consisted of only silver and no organic materials remained in those areas. However, in Figure 5c, a large carbon peak and a smaller oxygen peak were detected in addition to the silver peaks. This result indicates that organic materials remained in this area. The organic materials bring negative effects on the joint formation, because they prevent surface diffusion, lattice diffusion from the surface and grain boundary diffusion of nanoparticles during the sintering process, leading to low strength bonding between the sintered layer and Ag coating. In this case, the corresponding joint strength decreased significantly. This result demonstrated that, besides preventing the aggregation of the generated Ag nanoparticles, the PVP has the additional function of preventing cracking of the dried Ag paste during bonding process. When the PVP concentration is low, the cracking of the Ag nanoparticle paste is likely to happen. As the PVP concentration in the Ag nanoparticle paste is high, the remained organic components may reduce the joint quality. The optimization of PVP concentration is critical to the low temperature bonding process quality using polyol synthesized nanoparticle Ag paste.

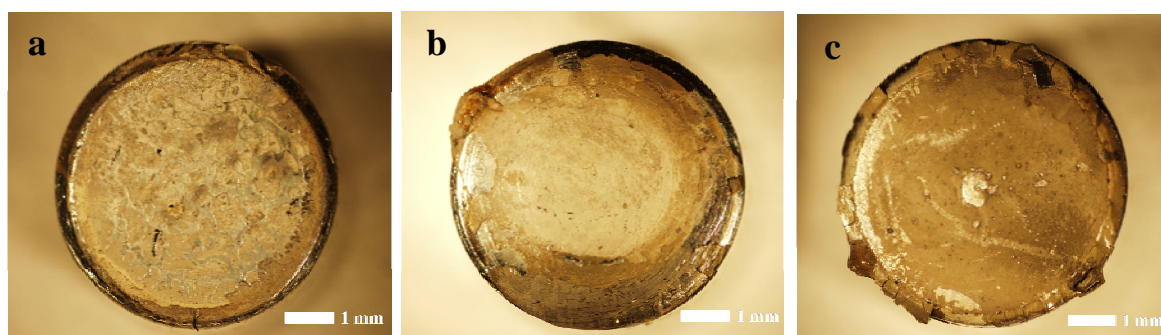


Figure 3. Photographs of the fractured joints bonded using different Ag nanoparticle paste (a) Ag nanoparticle paste A; (b) Ag nanoparticle paste B; (c) Ag nanoparticle paste C.

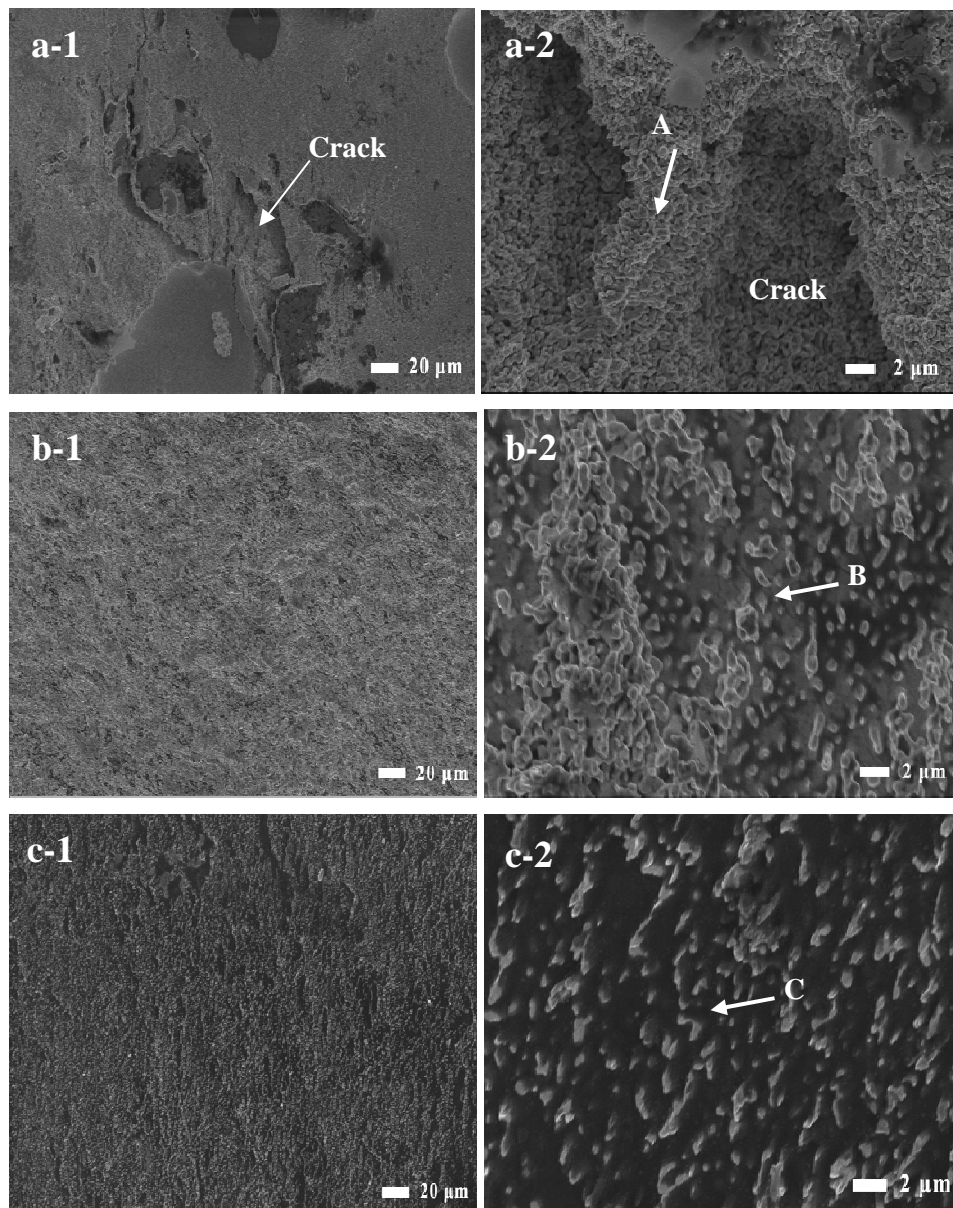


Figure 4. SEM images of microstructures of the joints using different Ag nanoparticle paste (a) Ag nanoparticle paste A, (b) Ag nanoparticle paste B, (c) Ag nanoparticle paste C.

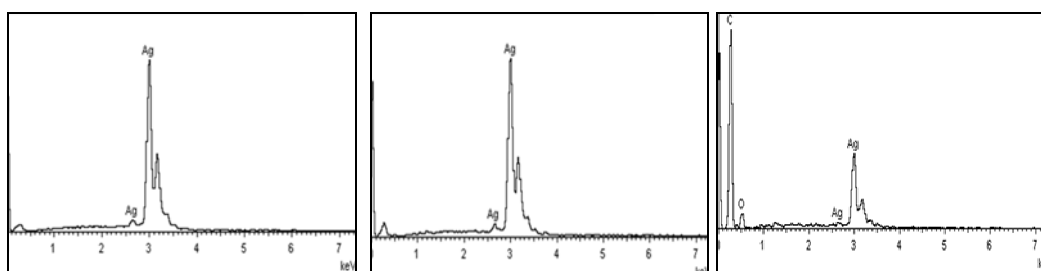


Figure 5. EDX spectra of different areas in Figure .4 (a) area A, (b) area B, (c) area C.

4. Conclusions

The low temperature bonding process using Ag nanoparticle pastes prepared through polyol method with different PVP concentration was studied. The PVP concentration has a significant influence on the size and solution viscosity of Ag nanoparticles and the bondability of Ag nanoparticle paste. The low PVP concentration (0.045M) would lead to cracking of the sintered Ag layer. As the PVP concentration in the Ag nanoparticle paste is much high, the remained organic components would reduce the joint quality. The strong joint with shear strength of 50 MPa was formed using Ag NP paste prepared with appropriate PVP concentration under the sintering conditions of 250 °C bonding for 30 min at 5 MPa.

Acknowledgements

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