Pressureless bonding process using Ag nanoparticle paste for flexible electronics packaging

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We have developed a new method for preparing a paste containing a high concentration of Ag nanoparticles for pressureless bonding. A nanoscale layer of polyvinylpyrrolidone coated on the nanoparticles prevents the coalescence of Ag nanoparticles. After heating in air, sintering and bonding occur after the decomposition of polyvinylpyrrolidone. Joint strengths were increased significantly using this new Ag nanoparticle paste as bonding material. Robust joints with shear strength above 20 MPa were formed even without additional bonding pressure.

Metallic nanoparticles (NPs) have received much attention in recent years because of their attractive properties, such as high diffusion coefficient and low melting temperature, which differ significantly from those of bulk materials [1–5]. These size effect properties can be used to prepare NPs for low-temperature lead-free interconnect applications. Metal NPs have been shown to be capable of sintering and bonding at low temperatures [6]. This promising low-temperature interconnection process has potential application for flexible electronics, including flat-panel displays, organic electronics, and low-cost disposable microelectronic devices on plastic substrates [7–10].

In order to prevent the self-cohesion of metal NPs, most metal NP pastes are prepared by mixing NPs and organic components [11–15]. It is worth noting that the added organic component is detrimental to the sintering process of metal NPs. Generally, in order to remove the organic molecules from the metal NPs, bonding is usually performed in the annealing temperature range of 250–350 °C and with a pressure of 1–20 MPa [7,11–18]. However, the use of pressure restricts the application of the technology, especially for the flexible electronics.

Therefore, it is necessary to study pressureless bonding process using a paste of metal NPs.

In the present work, we developed a new method to prepare metal NP paste that can be used as bonding materials without additional pressure. The paste was prepared by the chemical reduction method and subsequent concentration without further addition of organic component. The new paste consisted of a high concentration of Ag NPs with a thin layer of polyvinylpyrrolidone (PVP) coated on the surfaces. Thus the organic content in this new Ag NP is much lower than that of conventional Ag metallo-organic compound pastes. Heating in air causes the organic component to volatilize and decompose. After that, the surface reactivity reappears due to the high specific surface area of NPs. Thus, the bonding is formed by sintering of Ag NPs through neck growth and atomic diffusion between the Ag NPs and clean Ag-plated substrate. This new technique can be used to fabricate joints for flexible applications, since it can fabricate joints without additional pressure.

The new NP paste was prepared by chemical reduction and subsequent concentration. Firstly the Ag solutions are synthesized based on the modified polyol method [19]. 10 ml of ethylene glycol (EG) solution of silver nitrite (0.15 M) in a conical flask and 40 ml of EG solution

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of polyvinylpyrrolidone (PVP.K30) (0.45 M) in a beaker were prepared. These solutions were then heated to the reaction temperature of 160 °C, at a constant heating rate of 20 °C min^{-1}. The solution of PVP was injected into the silver nitrite solution at a constant rate of 0.3 ml s^{-1} using a syringe pump. The color of the solution changed from colorless to gray after 30 min, indicating the precipitation of Ag NPs. When the reaction was completed, the solution was rapidly cooled by adding chilled deionized (DI) water. This new Ag NP paste is prepared by condensing Ag NP solution with a centrifuge at 7000 rpm for 20 min without addition of organic component. The highly concentrated Ag NP paste was used for all the experiments in this work.

The sizes and morphologies of the Ag NPs were determined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermogravimetric analysis (TGA) was also conducted to measure the organic content in the dried paste in air with a temperature increase rate of 10.00 °C min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed to analyze the organic substances adsorbed on the Ag NPs. The surfaces of the Ag-plated Cu discs (Cu disc sizes: 10 mm diameter × 5 mm height and 6 mm diameter × 5 mm height) were cleaned in ultrasonic bath with acetone and alcohol prior to bonding. The Ag NP paste was then coated on the surfaces of the two Ag-plated Cu discs. The specimens were dried at 80 °C to remove the low boiling point component in the paste. The smaller specimen was placed on top of the bigger specimen when enough Ag NP paste had been gathered. The bonding of Ag-plated Cu discs was conducted at different curing temperatures under pressures of 0 and 5 MPa for 5 and 30 min. TEM was performed to analyze the cross-sectional interface between the sintered Ag layer and the Ag-plated Cu substrate. The bonding strength was evaluated as shear strength measured using a Gleeble 1500D thermomechanical simulator with a displacement speed of 5 mm min^{-1} at room temperature.

The typical SEM image of as-prepared Ag NPs shown in Figure 1a indicates that these Ag NPs are mainly spherical in shape, with a mean diameter of about 40 nm. Figure 1b displays a TEM image of the synthesized Ag NPs. A clear organic shell 1–2 nm thick is visible on the surface of the particles. It is believed that this shell prevents the coalescence of Ag NPs. The inset in Figure 1b shows a diffraction pattern that was obtained by aligning the electron beam perpendicularly to an individual NP. The electron diffraction patterns confirm the single-crystalline structure of these Ag NPs. Figure 1c presents an SEM image of Ag NPs after annealing in air at 250 °C for 30 min. It is clear that grain growth and sintering of particles occurs without external pressure, and may be attributed to the capillary pressure between contacting NPs. These particles are connected through their surface rather than completely melting to generate a denser connected structure. It is believed that this sintering process is important for the application of these Ag NPs to bonding. In order to investigate the bonding mechanism at the interface using this new Ag NP paste, TEM observation of the bonding interface between sintered Ag layer and plated Ag layer interface bonded at 250 °C under 5 MPa was performed. As shown in Figure 1d, the TEM image illustrates that direct metallic bonding is achieved using this new Ag NP paste as bonding material.

The organic content in the Ag NP paste is determined by TGA, as shown in Figure 2. The weight of the dried paste gradually decreases as the temperature is increased from 40 to 400 °C. The weight loss can be attributed to
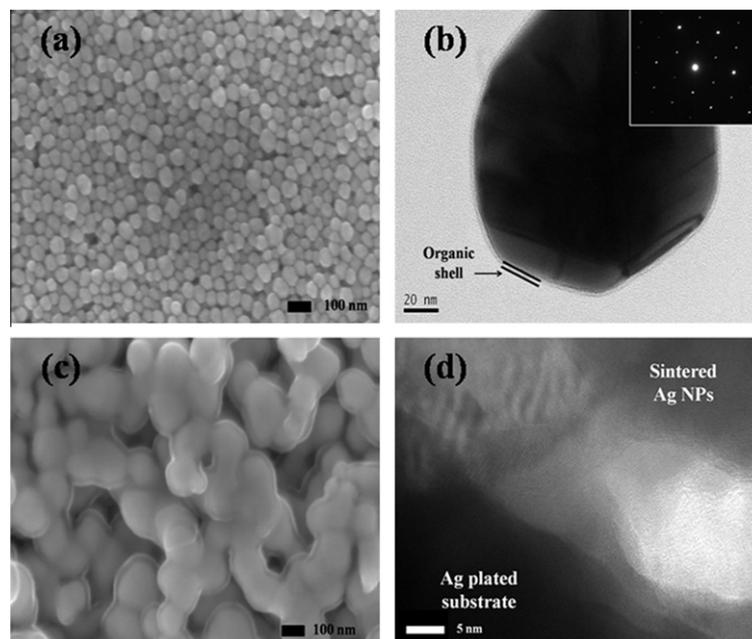

Figure 1. (a) SEM image of Ag NPs. (b) TEM image of a typical Ag NP. The inset shows the corresponding electron diffraction patterns. (c) SEM image of Ag NP paste annealed at 250 °C for 30 min. (d) TEM image of the bonding interfaces between sintered Ag layer and Ag-plated substrate of the joint bonded at 250 °C under 5 MPa.
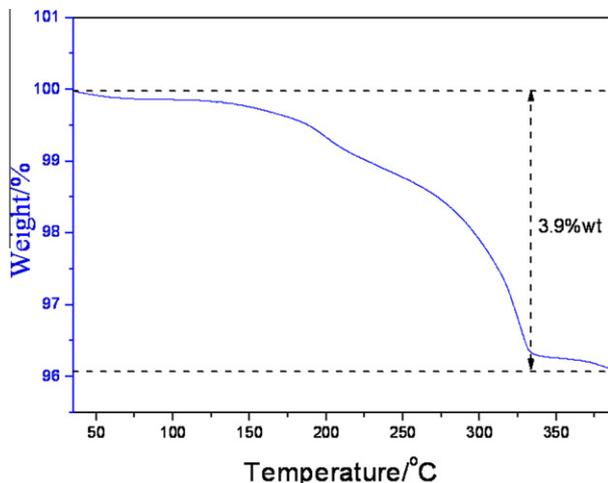
Figure 2. Traces of TGA for the Ag NP paste in air (temperature increasing at 10.00 °C min^{-1}).

Figure 4. Shear strength with Ag NPs as a function of sintering temperatures with additional pressure of 0 and 5 MPa with holding times of 5 and 30 min. The inset shows the bonding of a chip to a flexible circuit board using the Ag NP paste.

vaporization and decomposition of the organic components contained in the Ag NP paste. From these results, it is found that the content of organic component of the new paste is only about 3.9 mass%, which is significantly lower than the 15 mass% found in conventional Ag NP paste [11]. Thus, the Ag content (96.1 mass%) in this new Ag NP paste is remarkably more than that in conventional Ag NP paste. It is reasonable to deduce that the improvement of bondability can be attributed to this decrease in the organic component, since organic material has a detrimental effect on the sintering process.

Surface chemical analysis was performed using XPS to elaborate the state of the organic substances adsorbed on the Ag NPs in the paste. The XPS results for C1s and O1s of the Ag NP paste after drying at 80 °C in air for 30 min are shown in Figure 3. Through curve fitting it can be seen that the C1s spectrum is composed of four peaks. The bonding energy of the peaks are determined to be at 284.2 eV (C—H bonding), 285.5 eV (C—C bonding), 288 eV (C=O bonding) and 291 eV (C—N bonding). These four bonding energies can be attributed to the four types of C atom in the PVP molecule. Curve fitting in the O1s region led to two peaks, at 535 and 533.5 eV, coming from carboxyl (C=O bonding) and hydroxyl (C—OH bonding) oxygen, respectively. Compared with pure PVP, the O1s peak from the

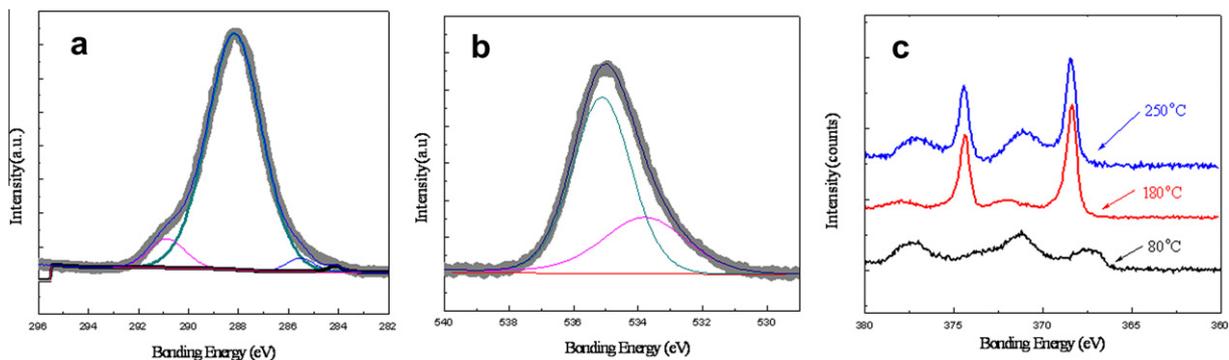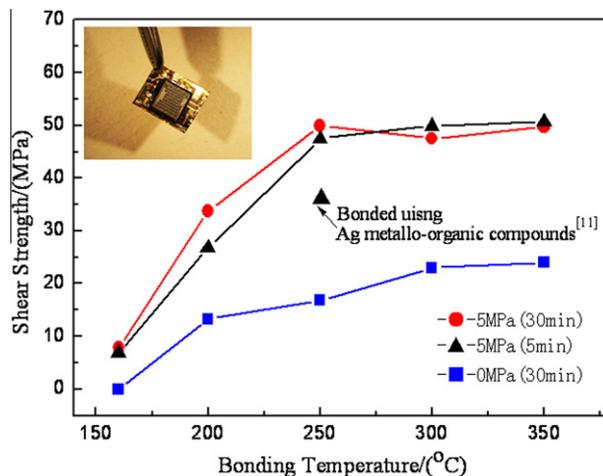carboxyl (C=O bonding) oxygen atom shifts to higher binding energy. Based on the above results, it is clearly demonstrated that a strong interaction exists between the carboxyl oxygen atom (C=O bonding) of PVP and the Ag NP surface.

Based on the spectrum of Ag 3d, the peak of Ag NP paste after drying at 80 °C was found to be 367.5 eV. However, after annealing at 180 and 250 °C the peak is significantly increased to 368.3 eV. This result confirms that PVP is adsorbed to Ag NPs, which will induce an image dipole on the particle surface. After annealing at 180 and 250 °C, the volatilization and decomposition of organic component occurs. Thus the corresponding Ag 3d peak shifts to 368.3 eV, which is the value for Ag metal.

Figure 4 shows the shear strength of bonded Ag-plated Cu bulk samples as a function of sintering temperature under a pressure of 0 and 5 MPa for 5 and 30 min. When bonded with a pressure of 5 MPa, strong joints with a shear strength above 30 MPa were formed even at 200 °C with holding times of 5 or 30 min. The shear strength is increased to 50 MPa at 250 °C, clearly demonstrating better mechanical behavior than that obtained using conventional Ag metallo-organic compounds [11]. It should be noted that this new paste can be used

Figure 3. XPS of Ag NP paste: (a) C1s and (b) O1s of Ag NP paste after drying at 80 °C; (c) Ag 3d spectra of Ag NP paste after drying at 80 °C, and annealing at 180 and 250 °C.

to form the bonding even without pressure as shown in Figure 4. Robust joints with shear strengths of about 10 MPa were formed at a bonding temperature of 200 °C even without added bonding pressure. A bonding temperature of 300 °C increases the shear strength to more than 20 MPa. These results confirm that a reduction of organic component can improve the bondability of Ag NP paste. The inset in Figure 4 illustrates the bonding of a chip to a flexible circuit board using Ag NP paste at a low bonding temperature of 200 °C without additional bonding pressure. All these characteristics indicate the potential value of this new Ag NP paste in future electronics packing applications. Our results demonstrate that reduction of the organic component in the metal NP paste was beneficial to achieving pressureless bonding process using this paste. Further study into the mechanism of this pressureless bonding process using Ag NP paste is needed in the future.

In summary, a new method to prepare paste containing a high concentration of Ag NPs for pressureless bonding was developed. Strong joints with shear strengths of 50 MPa under 5 MPa of pressure and 20 MPa without additional pressure were formed using this new NP paste, respectively. Our results demonstrate that reducing the organic component in the metal NP paste resulted in a pressureless bonding process. The new paste has potential application for flexible electronics packaging, since it can be performed without additional pressure.

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