A novel metal-to-metal bonding process through in-situ formation of Ag nanoparticles using Ag$_2$O microparticles

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Abstract. The metal-to-metal bonding has been successfully achieved via the bonding process using Ag metallo-organic nanoparticles at a bonding temperature of around 300 °C, which can be alternative to the current microsoldering in electronics assembly using high-temperature solders. However, further reduction of bonding temperature and/or bonding pressure is needed. In the present research, a novel bonding process through in-situ formation of Ag nanoparticles instead of the filler material of the Ag metallo-organic nanoparticles has been developed. The Ag nanoparticles can form by the reduction of Ag$_2$O particles. In this study, the Ag$_2$O particles were mixed with triethylene glycol as a reducing agent to form a paste for bonding. The Au coated cylindrical specimens were bonded using the paste. The Ag nanoparticles formed at around 130 °C to 160 °C through the reduction process of Ag$_2$O particles with triethylene glycol. The Au coated specimens were immediately sintered each other due to a great surface energy per volume. A transmission electron microscope observation revealed that the sintered Ag metallurgically bonded to the Au substrate at around 160 °C, and a dense Ag layer formed after further heating. The tensile strength of the joint bonded at 250 °C under a bonding pressure of 5MPa was around 60MPa

1. Introduction
A recent rise of working temperature of silicon devices for the use of automotive is driving the substitution of a new bonding process for conventional Pb-containing solders. Additionally, conventional solders are inapplicable to wide bandgap semiconductor devices such as silicon carbide because of a higher operation temperature than silicon semiconductors. There is a strong drive to develop a novel bonding technology for these high temperature electronic applications.

The authors have proposed a novel bonding process using Ag nanoparticles as a bonding material through the viewpoint of the rapid sintering property of nanoparticles at a relatively lower temperature [1, 2]. The Ag nanoparticle is composed of a core Ag nanoparticle and an organic shell protecting from self-consolidating. Rapid sintering of Ag nanoparticles occurs after the release of the organic elements from a bonding layer. The metal-to-metal bonding has been successfully achieved via the bonding process using Ag metallo-organic nanoparticles at a bonding temperature of around 300 °C under an applied pressure of 2.5 to 5MPa. However, further reduction of bonding temperature and/or bonding pressure is needed. In the bonding process using Ag metallo-organic nanoparticles the
decomposition and removal of the organic matter adhering to the nanoparticles are necessary to bring out the low-temperature sintering property of the nanoparticles. This is a bottleneck of the bonding process. In practical applications, a productive cost of Ag nanoparticles is problem as well.

For above problems, we focused on the Ag nanoparticles generated through the reduction reaction of low-cost silver oxide (Ag$_2$O) microparticles. In this paper, we discussed the in-situ formation of Ag nanoparticles through the reduction reaction of Ag$_2$O microparticles and the interfacial bonding mechanism between Ag layer with sintered Ag nanoparticles and Au substrate.

The Ag$_2$O microparticles were processed to a paste with triethylene glycol (TEG). We analyzed the thermal characteristics of Ag$_2$O paste and observed the particles heated up to various temperatures using a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM). We evaluated the tensile strengths of joints bonded with Ag$_2$O paste and observed an interfacial structure of the joints.

2. Experimental procedure

Figure 1 shows the SEM image of Ag$_2$O microparticles. The Ag$_2$O microparticles were processed to a paste with TEG as a reduction agent. We carried out a differential scanning calorimeter (DSC) and a thermogravimetry (TG) in air at the heating rate of 10°C/min to investigate the thermal characteristics of the reduction reaction of Ag$_2$O microparticles with TEG. We analyzed and observed the decomposition process of Ag$_2$O microparticles and the generation process of Ag nanoparticles using X-ray diffraction (XRD), FE-SEM and TEM. The observed samples were prepared by heating Ag$_2$O paste to each temperature and quenched with DSC.

Figure 2 shows the shape of a Au/Cu specimen for a bonding test. The thickness of Au layer is about 0.7µm with Ni buffer layer (approximately 2µm in thickness) on Cu specimen. We performed a tensile test of Cu/Au-to-Cu/Au joints using Ag$_2$O paste bonded at temperature ranging from 140°C to 400°C with a bonding pressure of 5MPa and quenched. We observed the interfacial structures of the Cu/Au-to-Cu/Au joints bonded at 160°C and 400°C using HR-TEM.

3. Results and discussion

3.1. In-situ formation of Ag nanoparticles from Ag$_2$O paste

Figure 3 shows the DSC and TG traces upon heating of the Ag$_2$O paste. An exothermic peak was detected at around 150°C in the DSC trace, and simultaneously a great weight reduction occurred in the TG trace. These results suggest that a reduction reaction of Ag$_2$O take place at this temperature range. The XRD analysis was, therefore, applied to the Ag$_2$O paste heated to various temperatures ranging from 110°C to 160°C as shown in Fig. 4. The strength of the peaks from Ag$_2$O crystal
decreased with increasing temperature and disappeared at 160 °C. Reversely, the peaks from Ag crystal appeared at 130 °C, and became stronger with temperature rise. Therefore, it can be concluded that the reduction of Ag₂O into Ag by TEG starts at 130 °C and finishes at 160 °C in the present case.

Figure 5 shows TEM images of the Ag₂O paste heated to 130 °C and quenched. It was confirmed from the selected area diffraction patterns (SADP) that Ag nanoparticles formed in the outer region of the Ag₂O particles. Such formed Ag nanoparticles were immediately sintered each other and became larger in size as shown in Fig. 6 presenting TEM images of the Ag₂O paste heated to 145 °C. After heated to 160 °C, the Ag₂O particles were completely reduced to Ag particles, which were several hundred nm in size as shown in Fig. 7. Thus, in-situ formation of Ag nanoparticles, which were sintered rapidly, through the reduction reaction of Ag₂O paste at a temperature ranging from 130 °C to 160 °C was confirmed. It can be utilized to a low-temperature bonding process using nanoparticles.
3.2. Relationship between joint strength and bonding temperature

The tensile strength of the Cu/Au-to-Cu/Au joints using Ag$_2$O paste was plotted against bonding temperature in Figure. 8(a). The joint strength monotonously increased with bonding temperature. A certain joint strength was attained at a bonding temperature above 160 $^\circ$C. The detailed interfacial microstructure of the joint bonded at 160 $^\circ$C was observed using TEM as shown in Fig. 9(a). At this bonding temperature, Ag$_2$O still remained in the bonding layer as indicated in SADP in Fig. 9(b) and (c). This is caused by a higher heating rate of 60 $^\circ$C/min in the bonding test compared with the DSC analyses in Fig. 3. However, Ag nanoparticles also formed at the outer layer of the Ag$_2$O particle. The TEM image of Fig. 9(a) clearly shows that such formed Ag nanoparticles connected to the Au substrate. This indicates an active nature of the nanoparticles resulting from their high surface energy.

Figure 10 shows the TEM image of the interface of the joint bonded at 400 $^\circ$C. At this bonding temperature, fully sintered dense Ag layer was observed and the Ag layer successfully bonded to the Ag substrate. Thus, the metal-to-metal joint through the sintered Ag layer can be attained using the bonding process with Ag$_2$O paste. In this bonding experiment, the bonding specimen was heated to a bonding temperature followed by quenching without holding. The holding at a bonding temperature is thought to promote the sintering of the Ag nanoparticles, and thereby improve the joint strength. The strength of the joint bonded at 250 $^\circ$C is plotted against the holding time in Fig. 8(b). The joint strength was improved with holding time. The joint strength of approximately 60MPa was obtained after 5min holding. This joint strength is considered to be sufficient for an electronics assembly compared with conventional soldering using a Pb-rich high temperature solder [3].
Fig. 8  Relationship between bonding parameters and tensile strength of the Cu/Ni/Au-to-Cu/Ni/Au joint bonded using the Ag₂O paste at various bonding temperatures with a pressure of 5MPa.

Fig. 9  TEM image and diffraction patterns of the Ag/Au interface bonded using the Ag₂O paste at 160 ºC with a pressure of 5MPa and quenched.
4. Conclusions
In the present study, a new metal-to-metal bonding process through in-situ formation of Ag nanoparticles by reduction of Ag\(_2\)O particles. The main results obtained are as follows.

1) Ag\(_2\)O particles were reduced by triethylene glycol and Ag nanoparticles formed at temperature ranging from 130 \(\degree\)C to 160 \(\degree\)C. Such formed Ag nanoparticles were sintered rapidly.

2) A certain joint strength was attained at a bonding temperature above 160 \(\degree\)C with a bonding pressure of 5MPa. The joint strength increased with bonding temperature.

3) Interfacial bonding was achieved by the Ag nanoparticles reduced from Ag\(_2\)O particles at 160 \(\degree\)C. A dense bonded layer formed by sintering of the Ag nanoparticles at 400 \(\degree\)C.

4) The tensile strength of the joint bonded at 250 \(\degree\)C with a holding time of 5min under a bonding pressure of 5MPa was around 60MPa.

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