Effect of Polyethylene Glycols with Different Polymer Chain Lengths on the Bonding Process Involving In Situ Formation of Silver Nanoparticles from Ag₂O

Tomohiro Yagishita, Tomo Ogura* and Akio Hirose

Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan

The need for lead-free alternatives to conventional solders for metal-bonding processes has prompted the development of processes based on metal nanoparticles. In this study, the low-temperature bondability of silver oxide (Ag₂O) pastes containing polyethylene glycols (PEGs) with different polymer chain lengths was investigated. Bonding was achieved because of the low-temperature sinterability of silver nanoparticles that form in situ through redox reactions between Ag₂O and PEGs. It was found that PEGs with shorter chain length provide superior bondability at low bonding temperatures. Thermogravimetric-differential thermal analysis and thermomechanical analysis showed that shorter PEGs resulted in less residual organic material in the sintered silver layer and contributed to form a larger amount of silver nanoparticles. Therefore, pastes with shorter PEGs afforded well-sintered, high-density silver joints and exhibited superior bondability even at lower temperatures. Using ethylene glycol, which has the shortest chain length, the tensile strength achieved was 11 MPa for bonding at 150°C.

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1. Introduction

Soldering is a widely used bonding process that is fundamental to modern electronics packaging and various other applications. However, conventional solder contains lead, which is harmful to the environment and human body; the use of lead is subject to considerable government regulation. Nevertheless, lead-rich high-melting-point solders are currently used because of the lack of effective alternatives. To resolve this problem, for example, Au–Sn solders have good mechanical properties at high temperatures and finds use in power electronics and light-emitting devices; however, it is expensive, which prevents its widespread application.

To resolve this problem, we previously proposed the use of silver nanoparticles in a new joining process. Metal nanoparticles exhibit quantum size effects and surface plasmon resonance and have a much larger surface energy than does the bulk material. These unique properties have been exploited in wiring for flexible electronic circuits, multifunctional catalysts and sensors. We applied metal nanoparticles to bonding, where the large surface energy led to low-temperature sinterability. In this process, silver nanoparticles are coated with organic materials to prevent aggregation. The combustion and discharge of the organic material at low temperature triggers sintering of silver at the interface of joints. Thus, metal-to-metal bonding could be successfully achieved at 300°C.

This bonding method has since been studied extensively and is recognized as the most promising alternative to soldering. However, although silver nanoparticles have superior low-temperature bondability, they are still expensive. Hence, we recently proposed a novel alternative involving in situ formation of silver nanoparticles. In this bonding process, microsized Ag₂O particles, which are much cheaper than nanoparticles, are used as a precursor for silver nanoparticles. The Ag₂O particles are mixed with triethylene glycol (TEG) as the reducing solvent to produce silver nanoparticles during the bonding process via a redox reaction. These Ag₂O-derived nanoparticles have the same high sinterability as that of conventional nanoparticles and achieve metal-to-metal bonding with a gold substrate at 250°C. Furthermore, the crystal orientation of the sintered silver corresponds to that of the gold substrate in the vicinity of the bonding interface. However, further reduction in the bonding temperature is required to reduce the residual thermal stress.

It is well known that the strength of a sintered material depends on its density, and in turn, the particle size: smaller particles afford a highly dense arrangement of the sintered layer, contributing to superior strength. For silver nanoparticles formed by the chemical reduction of AgNO₃, the particle size depends on the polymer chain length of the polyethylene glycol (PEG) used as the reducing solvent, as reported by Luo et al. Therefore, the optimum PEG chain length should be identified to obtain relatively smaller nanoparticles and higher bonding strength even at lower temperatures. However, the effects of PEG chain length on Ag₂O reduction are unclear. In addition, in the case of the proposed bonding process, the effects of any residual organic material on the bonding strength should also be clarified.

In this study, four types of PEGs—diethylene glycol (DEG), TEG, PEG200 and PEG400—were compared. The formation and sintering behavior of the Ag₂O-derived silver nanoparticles were evaluated on the basis of thermal analyses and scanning electron microscope (SEM) observations. Furthermore, the bonding strength achieved at 200 and 250°C and the microstructures of the joints were investigated. From these results, the effect of PEG chain length on bondability at different temperatures was evaluated. In addition, we tested the bondability of the paste formed with the monomer ethylene glycol (EG) and larger-sized Ag₂O particles.

*Corresponding author, E-mail: tomo.ogura@mapse.eng.osaka-u.ac.jp
2. Experimental Procedure

The Ag$_2$O pastes were produced by mixing 1 g of Ag$_2$O microparticles with 180 ml of the various PEGs. As shown in Fig. 1, we used two types of Ag$_2$O powders with different particle sizes. The molecular weight of each reducing solvent is listed in Table 1. PEG200 and PEG400 are composed of various PEGs of different polymer chain lengths and have average molecular weights of 200 and 400, respectively.

The thermal characteristics of the Ag$_2$O pastes were determined by thermogravimetric-differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), and thermomechanical analysis (TMA) in air at a heating rate of 0.167°C/s.

A field-emission SEM was used to observe the microstructure in the Ag$_2$O-DEG and Ag$_2$O-TEG pastes up to the formation temperature of the silver nanoparticles. To test the bondability of the used pastes, Cu specimens coated with Ni/Au were bonded as shown Fig. 2. A 50-µm-thick layer of each paste was printed on the surface of the lower substrate and the samples were preheated under the paste-specific optimum temperature to remove excess solvent. Next, the upper substrate was placed on the lower substrate and the samples were heated to 150, 200 and 250°C at 1°C/s and held at the target temperature for 300 s under an applied pressure of 5 MPa in an infrared heating furnace.

The joint strength was measured at a strain rate of 1.67 × 10$^{-5}$ l·s$^{-1}$ in the tensile test. A cross-section of each joint was prepared using a cross-section polisher and observed by SEM.

3. Results and Discussion

3.1 Characteristics of Ag$_2$O pastes

As previously mentioned, smaller particles result in a higher initial packing density. However, EG, the shortest PEG in the series, can reduce Ag$_2$O even at room temperature using the smaller Ag$_2$O particles. Therefore, EG cannot be used unless its reducing ability is curtailed; this point is discussed in a later section. In contrast, the other PEGs have no effect even on the smaller Ag$_2$O particles at room temperature. Figure 3 shows the TG-DTA traces of each Ag$_2$O paste composed of smaller Ag$_2$O particles and the PEGs (DEG, TEG, PEG200 and PEG400). Each paste exhibits an exothermal peak with large weight loss at low temperatures of 100–150°C. X-ray diffraction (XRD) analysis of the pastes above and below the reaction temperature (not shown) indicated that the Ag$_2$O particles indeed reduced to silver through the reaction. Therefore, every paste formed silver nanoparticles that began to sinter at or below 150°C. Furthermore, we found that the shorter-chain PEGs reacted at lower temperatures. The reactivity of the reducing agents with Ag$_2$O is considered to depend on the number of hydroxyl units in the reducing agent.

In addition, every paste exhibits smaller exothermal peaks at higher temperatures. The DEG, TEG and PEG200 pastes have peaks at approximately 250°C and PEG400 has two peaks at 165 and 265°C. The PEG200 and PEG400 pastes exhibit little decrease in weight after the reduction temperature of Ag$_2$O and exhibit a smaller exothermal peak temperature. The residual components of the pastes after the redox reaction are silver and some organic materials obtained as byproducts. Therefore, these smaller peaks are attributed to the reduction of the organic material. The amounts of residual organic materials are compared in Table 2. The value is identified as the amount of weight loss after the reduction of Ag$_2$O. Although the DEG and TEG pastes indeed exhibit a decrease in weight with the reduction of the residual organic materials at 250°C, the loss is...
considered to be so small that the amount is lower than the resolution of the TG apparatus. For either silver or copper nanoparticles, the residual organic materials in the joint layer inhibit sintering, which in turn decreases the bonding strength. Therefore, it is predicted that these residual organic materials inhibit the sintering of the in situ-formed silver nanoparticles, thereby decreasing the bonding strength. Therefore, the DEG and TEG pastes, which have the least amount of residual organic materials, have the potential to achieve superior joint strengths at low bonding temperatures.

3.2 Shrinkage of Ag₂O DEG paste and Ag₂O-TEG paste

Figure 4 shows the TMA and DSC traces for the DEG and TEG pastes. Each paste shrinks through three stages. First, the pastes shrink without a thermal reaction. The second shrinkage occurs along with the redox reaction. This is caused by the volume shrinkage associated with the conversion of Ag₂O to silver and sintering of the in situ-formed silver particles. Finally, the samples again begin to shrink via the combustion of the residual organic materials. This indicates that even a small amount of residual organic material can strongly inhibit sintering.

However, the DEG paste shrunk more than the TEG paste did. Figure 5 shows SEM images of the pastes as they were heated to just after the first shrinkage temperature (DEG: 110°C; TEG: 130°C). Each paste formed silver nanoparticles with diameters on the order of 10 nm, but the DEG paste formed a larger amount of silver nanoparticles. Although the organic materials in the samples evaporated before the observations, the pastes contained enough organic materials to prevent aggregation or sintering of the nanoparticles at the bonding temperature. Thus, the silver nanoparticles are considered to be dispersed and rearranged in the microscale interspaces between the residual Ag₂O particles. This is the most plausible mechanism for the first shrinkage. Thus, the DEG paste, which formed more nanoparticles by the reduction of the residual Ag₂O, achieved a higher density of arrangement than did the TEG paste. Therefore, a much stronger joint can be attained at low bonding temperatures using the DEG paste.

3.3 Tensile strength and cross-sectional microstructure

Figure 6 shows the tensile strength of the joints bonded at 200 and 250°C using each Ag₂O paste. Higher bonding strengths were attained using PEGs with shorter chain length. The DEG paste achieved the highest bonding strength. Furthermore, the difference in result between the DEG and TEG pastes was greater at 200°C than at 250°C. Figure 7 shows a cross-sectional image of each joint bonded at 200°C.

Table 2 Amounts of the residual organic materials after the redox reactions of Ag₂O pastes.

<table>
<thead>
<tr>
<th>Paste Type</th>
<th>Residual organic (mass%)</th>
</tr>
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<tbody>
<tr>
<td>DEG</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>TEG</td>
<td>&lt;0.7</td>
</tr>
<tr>
<td>PEG200</td>
<td>2.3</td>
</tr>
<tr>
<td>PEG400</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Fig. 3 TG-DTA traces of Ag₂O pastes.
It can be seen that the DEG and TEG pastes both afforded uniformly sintered joints. In addition, the DEG paste formed high-density sintered layer. In contrast, the PEG200 and PEG400 pastes formed sintered layers with larger voids, where PEG400 formed much larger voids between the two. The PEG200 and PEG400 pastes also left more residual organic materials in the sintered silver layer than did the DEG and TEG pastes. The residual organic materials inhibit sintering, and this explains the larger voids and lower bonding strength observed for PEG200 and PEG400. However, TMA analysis indicated that even the DEG and TEG pastes exhibited some inhibition of sintering along with volume shrinkage at 200°C. In the result, the joint strength was lower than that achieved at 250°C or higher, i.e., after the combustion of all organic materials. The DEG paste shrunk more than the TEG paste did, indicating that the silver particles derived from DEG paste achieved higher density packing. Thus, the difference in bonding strength at 200°C can be attributed mainly to the difference in density of sintered silver particles. In contrast, at 250°C and above, the joint strength increased along with the increase in density owing to the complete combustion of organic materials, and the joint strength mainly determined the bonding strength. Thus, the TEG paste attained almost the same strength as that of the DEG paste at 250°C. In conclusion, the DEG paste, which has a shorter chain length than that of the TEG paste, formed uniformly sintered high-density joints with superior strength, especially at 200°C.

### 3.4 Improvement in low-temperature bondability using EG

Figure 8 shows the XRD patterns of the EG pastes with the two Ag₂O powders. EG is a strong reducing agent for the smaller Ag₂O powder at room temperature. However, the larger Ag₂O powder is not as reactive with EG and remains as Ag₂O at room temperature. Therefore, the larger Ag₂O powder can be used with EG for this bonding process. Figure 9 shows the TG-DTA trace for this EG paste. Ag₂O...
reduced to silver at approximately 60°C and all residual organic materials combusted at approximately 160°C. These temperatures are lower than the corresponding values for the other pastes. Figure 10 compares the bonding strengths of the EG, DEG and TEG pastes bonded at 150°C for 5 min under the bonding pressure of 5 MPa. Although the DEG and TEG pastes did not achieve bonding, it can be seen that the EG paste achieved a bonding strength of 11 MPa on average. Furthermore, because the residual organic materials in the EG paste combusted at the much lower temperature of 160°C, the particles were sintered and bonding was achieved at 150°C.

Fig. 7 SEM images of cross-sections of Au-to-Au joints bonded at 200°C for 5 min with the bonding pressure of 5 MPa using Ag₂O pastes. (a) DEG, (b) TEG, (c) PEG200, (d) PEG400.

Fig. 8 X-ray diffraction patterns of Ag₂O-EG pastes prepared with larger or smaller Ag₂O particles.

Fig. 9 TG-DTA traces of the larger Ag₂O-EG paste.

Fig. 10 Tensile strengths of Au-to-Au joints bonded at 150°C for 5 min with the bonding pressure of 5 MPa using Ag₂O pastes.
4. Conclusions

The effect of PEG chain length on the bonding process involving the \textit{in situ} formation of silver nanoparticles from Ag$_2$O was evaluated. The PEGs with shorter chain length resulted in less residual organic material after the formation of the silver layers. The DEG paste shrunk more than the TEG paste did, which is considered to be a result of the rearrangement of silver nanoparticles between unreacted Ag$_2$O microparticles. Thus, the DEG paste formed the most uniformly sintered, densest and strongest joints observed in this study. The EG paste with larger Ag$_2$O particles attained bonding even at 150°C. This is because all of the residual organic material combusted at a much lower temperature than for any other paste.

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