Development of low temperature sintered nano silver pastes using MO technology and resin reinforcing technology

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Abstract

Traditional thick film technology is widely used in various electronics products. There are two type of paste based on thick film technology. Typically, over 400^{o}C is required for high temperature sintering type which contains glass for adhesion function. It shows high electrical and thermal performance. On the other hand, 150-300^{o}C range process is used for low temperature process type as silver epoxy. In last decade, nano silver technology shows amazing progress to address low temperature operation by low temperature sintering.

This paper will discuss the results on fundamental study of newly developed nano silver pastes with unique approach which uses MO (Metallo-organic) technology and resin reinforcing technology.

Nano silver pastes contain several types of dispersant as surface coating to prevent agglomeration of the particles. Various coating technique has been reported to optimize sintering performance and stability. MO technology provides low temperature sintering capability by minimizing the coating material. The nano silver pastes show high electrical and thermal performance. However, degradation of die shear strength has been found by thermal cycling test due to the fragility of porous sintered structure. To improve the mechanical property, resin reinforcing technology has been developed. By adding special resin to the pastes, the porous area is filled with the resin and the sintered structure is reinforced. Degradation of die shear strength was not found by thermal cycling test to 1000 cycles.

Nano silver pastes using MO technology and resin reinforcing technology will meet lots of requirement on various thick film applications.

Introduction

Traditional thick film technology is widely studied in electronics products such as electrode for flat panel display, electrode for Photovoltaic, module for automotive, power module, passive components, EMI shielding, bio-sensors, RFID, die attach materials and so on.[1],[2],[3],[4] Among those applications, the heat generated from power semiconductor devices or light emitting diode applications has especially been a significant problem. For example, light emitting diodes with higher electrical power and further intensified working current would produce increased heat and became overheated. As a result, it adversely affected its performance. Therefore, die attach materials for the applications require high thermal conductive performance and high reliability.

Generally, sintering type silver paste or curing type silver paste is used as thick film material. Sintering type silver paste shows high electrical and thermal performance due to its dense silver structure. But high temperature (over 400^{o}C) is required for the sintering process. On the other hand, curing type silver paste shows low temperature (150-200^{o}C) process capability to meet the requirement of lower stress and fewer heat damage. However, the electrical and thermal conductivity is limited due to its cured structure of silver which is fixed in the epoxy resin.

The latest nano silver technology has potential to take over existing technology.[5] To use nano silver particles on conductive paste, there is a difficult problem which is agglomeration of silver particles. Various surface treatment techniques have been reported to prevent agglomeration issue. Also this surface treatment agent has lots of negative impact for silver sintering behavior. To address the balance of nano silver behavior, MO technology has been developed.

In addition, we proposed resin reinforcing technology. The porous sintered silver structure was reinforced by the resin system, and the reliability was improved.

This paper will discuss the result on fundamental study of newly developed low temperature sintered nano silver paste with unique approach which uses the MO technology and the resin reinforcing technology.

Experimental Procedure

A. Sample preparation

Two nano silver particle pastes, A and B, were prepared. Paste A consisted of nano silver particles synthesized by MO technology and solvent without resin reinforcing system. Paste B consisted of the nano silver particles, solvent and resin reinforcing system as shown in Table 1

Table 1. Nano silver particle pastes for the experiments

Paste	Filler type	Resin type	Silver content (wt%)
A	Nano silver particles synthesized by MO technology	—	85
B	Nano silver particles synthesized by MO technology	Liquid epoxy resin with hardener (Resin reinforcing system)	85

Fig.1 shows Scanning electron microscopy (SEM) image of the nano silver particles. The diameter is approximately 100 nm.

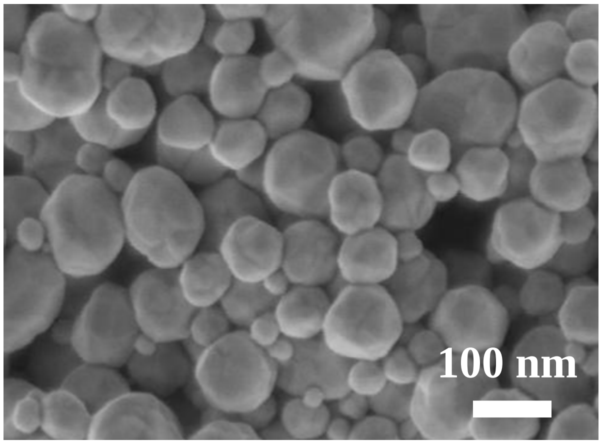


Figure 1. SEM image of nano silver particles synthesized by MO technology.

B. Measurement and evaluation

To study the sintered structure, scanning electron microscopy (SEM) was performed for the surface or cross sectional observation. 200degC for 60 minutes was used as sintering condition. The formulated pastes were printed on the glass slide. Sintered sample was etched with Ar ions using ion milling device for the cross sectional observation.

To investigate the electrical performance, electrical resistivity was evaluated. The formulated pastes were printed on the glass slide. Electrical resistance *R* of the sintered film was measured with typical four-probe method using digital multimeter. The thickness was measured with micrometer. Electrical resistivity ρ was conducted by following equation.

$$\rho = R\frac{wt}{l}$$

ρ : electrical resistivity, R : electrical resistance,
w : width, t : thickness, l : length

To investigate the thermal performance, thermal conductivity was evaluated by laser flash method. The formulated pastes were printed on the glass slide. 200degC for 60 minutes was used as sintering condition. The thermal conductivity of sintered sample was measured by laser flash analyzer.

To investigate the adhesion behavior, die shear strength was evaluated. The test coupon were prepared using 2 x 2mm size Si chip (backside: Au) and Ag plated Al2O3 substrate. The formulated pastes were dispensed on the substrate and the Si chip was mounted. 200degC for 60 min was used as sintering condition. The bond line thickness was controlled to approximately 20µm. Die shear strength (at 25degC and 260degC) was measured by die shear tester. The schematic illustration for die shear test is shown in Fig. 2.

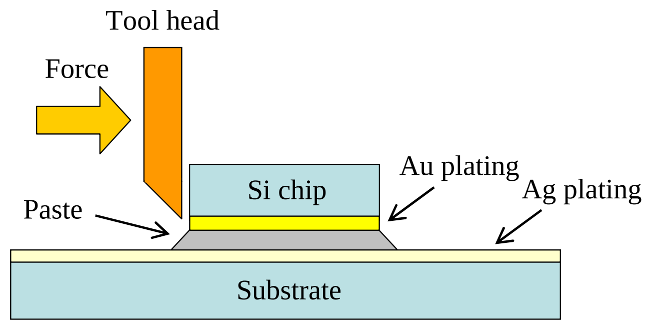


Figure 2. Schematic illustration of die shear test.

Thermal cycle test(-55degC (30min) to +150degC (30min) for 1000 cycles) was conducted as the reliability test. Die shear test samples were used for the reliability test. Die shear test and C-SAM (Scaning Acoustic Microscrope) observation were conducted for the evaluation of die shear strength and delamination, respectively.

Results and Discussion

A. Design of the low temperature sinterable nano silver paste

MO technology and resin reinforcing technology have been developed for the design of the new nano silver particle paste.

A-1. MO technology

Fig. 3 shows the schematic view for synthesizing nano silver particles using MO technology.

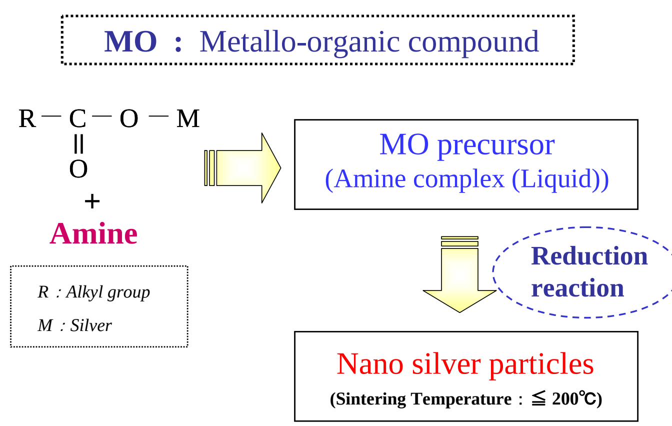


Figure 3. Schematic view for synthesizing nano silver particles using MO technology.

MO precursor (amine complex) was obtained by the reaction between silver carboxylate and amine. The nano silver particles were synthesized by reduction reaction of the MO precursor. During the reaction, the particles were coated by the amine. To obtain low temperature sinterable nano silver particles, the amine which can be decomposed at low temperature was used for the reaction. In addition, the amine for coating the particles was minimized by the MO technology.

Fig. 4 shows the comparison of Thermal Gravimetric(TG) behavior with the MO nano silver paste and conventional nano silver paste.

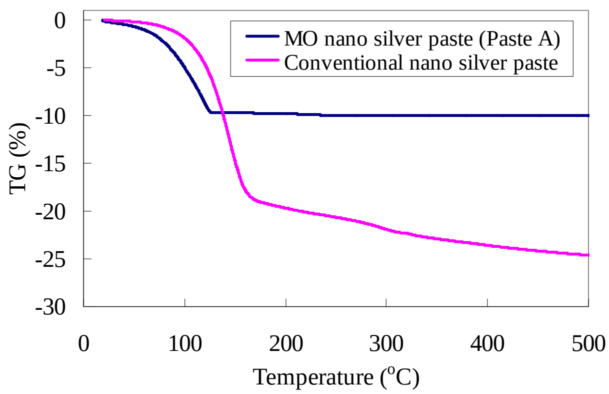


Figure 4. TG chart of the MO nano silver paste and conventional nano silver paste.

TG of conventional nano silver paste gradually decreased from 180 °C to 500°C. On the other hand, nano silver paste prepared by MO technology showed simple reduction at low temperature and had no change from 130°C to 500 °C. This indicates that the coating material of MO nano silver particles was easily decomposed and the paste could be sintered at low temperature. SEM images and thermal conductivity of MO nano silver paste (Paste A) after sintering are shown in Fig. 5 and Fig. 6, respectively. With the rise of heating temperature, the particles were well sintered, and show high thermal conductivity.

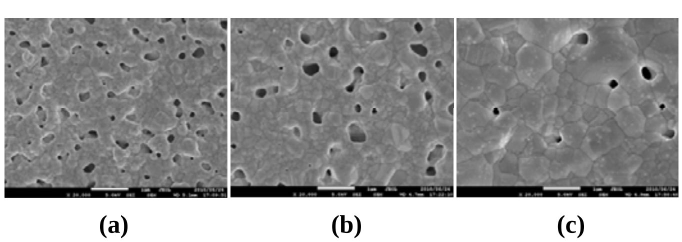


Figure 5. SEM images of MO nano silver paste (Paste A) after sintering at (a)150°C, (b)200 °C and (c)300 °C.

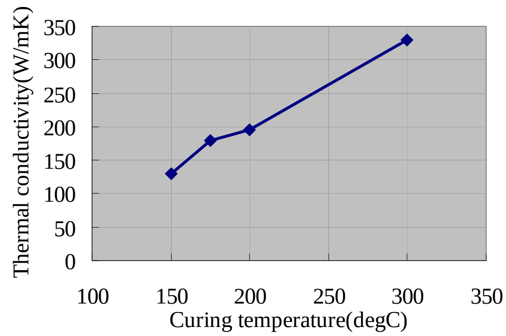


Figure 6. Thermal conductivity of MO nano silver paste (Paste A) after sintering.

Fig. 7 shows the schematic illustration for the mechanism of sintering behavior. With the rise of temperature, the amine is decomposed, and then the silver particles are sintered. Because the coating material can be decomposed at low temperature and minimized by MO technology, the particles are low temperature sinterable.

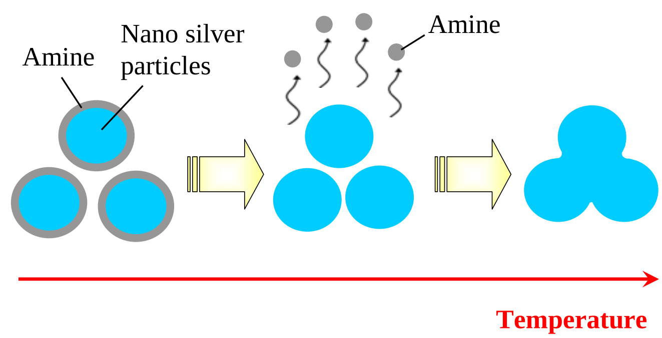


Figure 7. Schematic illustration for the mechanism of sintering behavior.

A-2. Resin reinforcing technology

To reinforce the porous sintered silver structure, Resin reinforcing technology has been introduced. The schematic illustration for the mechanism of forming the reinforced structure is indicated in fig. 8.

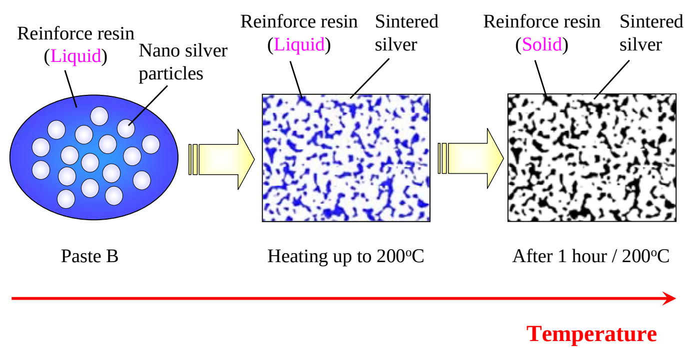
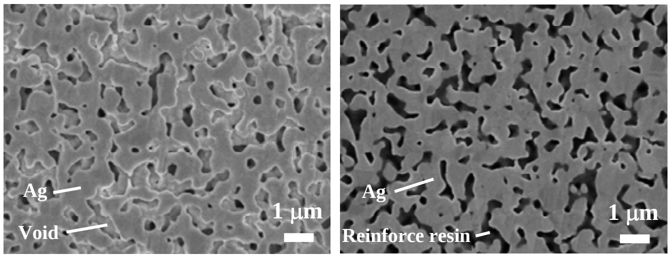


Figure 8. Schematic illustration for the mechanism of forming the reinforced structure while heating.

First, nano silver particles should be sintered in the liquid resin, and then the resin has to be cured. Fig. 9 shows the cross sectional SEM image of Paste A and B.



(a) (b)

Figure 9. Cross sectional SEM images of (a) paste A and (b) paste B after cure at 200 ^{o}C

Sintering structures of the nano silver particles were almost the same. The porous area of Paste B was well filled with reinforce resin. If the resin was cured faster than the sintering of nano silver particles, the particles were fixed in the cured resin. As a result, sintering of the nano silver particles were hindered as shown in Fig. 10. Therefore, timings on sintering of the silver particles and curing of the resin are significant factor for forming the reinforced structure.

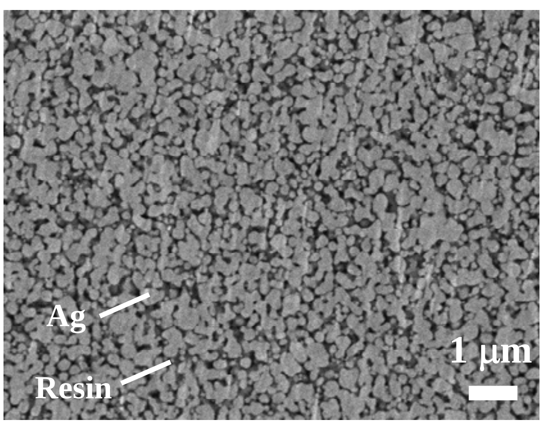


Figure 10. Cross sectional SEM image. When the resin was cured faster than the sintering of nano silver particles, sintering of the particles was hindered.

B. Results of the measurement and evaluation

B-1. Fundamental properties

Table 2 shows electrical resistivity, thermal conductivity and die shear strength of nano silver pastes with or without resin reinforcing system. Those properties were almost the same. The pastes show high electrical and thermal performance. Die shear strengths were also very high.

Table 2. Fundamental properties of paste A and B

	Electrical resistivity (μΩcm)	Thermal conductivity (W/mK)	Die shear strength (MPa)	
			@25^{o}C	@260^{o}C
Paste A	3	182	33	27
Paste B	3	186	35	31

Conventional nano silver pastes need pressure while curing process to obtain high die shear strength. On the other hand, the nano silver particles synthesized by MO technology do not require pressure. Fig. 11 shows cross sectional SEM image of the interface of die shear test samples with reinforced resin.

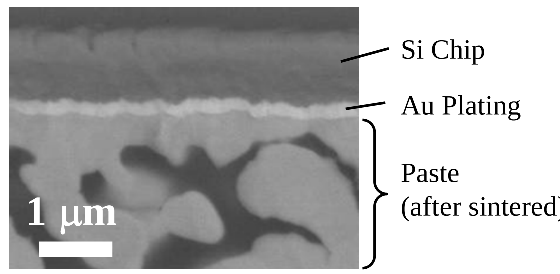
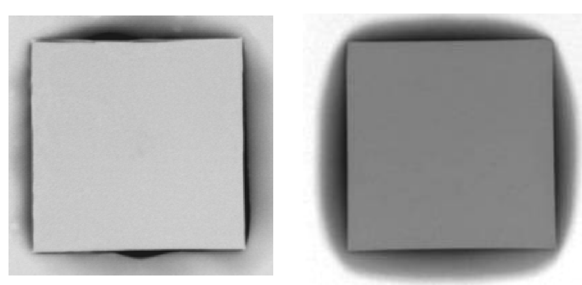


Figure 11. Cross sectional SEM image of the interface of die shear test samples with reinforce resin

Strong adhesion to Au plating was observed. In addition, die shear strengths at 260^{o}C were almost the same compared with the value at room temperature. This indicated that metallurgical connection was formed between the sintered silver and Au or Ag plating.

Fig. 12 shows X-ray images of the die shear test samples. No voids were observed from the X-ray observation.



(a) **(b)**

Figure 12. X-ray images of die shear test samples of (a) paste A and (b) paste B.

B-2. Reliability

To investigate the reliability, thermal cycle test was conducted. Fig. 13 shows the reliability test results of paste A and B.

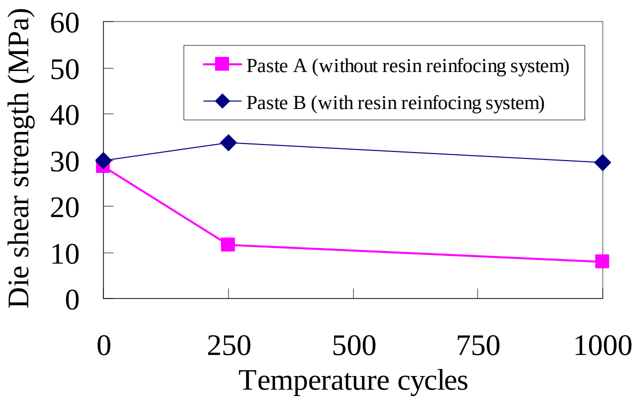


Figure 13. Results of thermal cycle test (Die shear strength)

Die shear strength of nano silver pastes without reinforce resin gradually decreased. The cross sectional structure of the paste A after 250 cycles is shown in Fig. 14. Cracks were observed in the sintered silver paste.

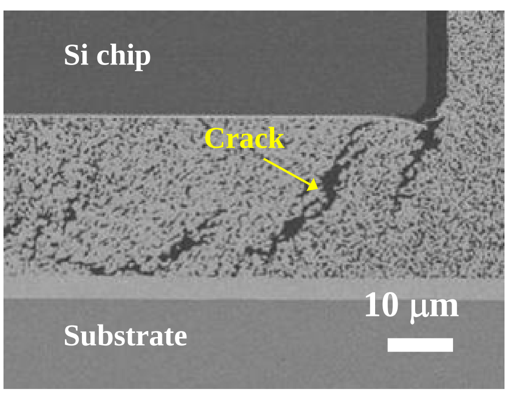


Figure 14. Cross-sectional structure of paste A after thermal cycle test.

On the other hand, die shear strength of nano silver pastes with reinforce resin was stable to 1000 cycles.

To evaluate the delamination, C-SAM observation was also conducted. The images of the samples are shown in Fig. 15. Delamination was observed from Paste A after the thermal cycle test. On the other hand, no delamination was confirmed.

The results indicated that the reinforce resin in the porous sintered silver structure prevented the cracks. Reliability of nano silver pastes was improved by the resin reinforcing technology.

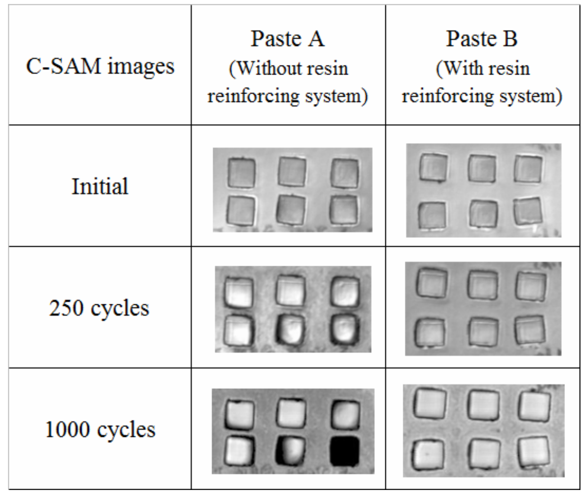


Figure 15. Results of thermal cycle test (C-SAM through scan images.) Black area indicates delamination. No delamination was confirmed in the test samples of paste B after 1000 cycles.

Conclusions

We have been developing low temperature sinterable nano silver pastes using MO technology for thick film application. The paste showed high electrical and thermal performance. Strong adhesion to metalized die and substrates was confirmed from the results of die shear test and cross sectional observation. In addition, the paste does not require pressure while curing.

Furthermore, resin reinforcing technology has been introduced to improve the reliability. The porous sintered structure of the nano silver particles was reinforced by the resin system without spoiling its high thermal conductivity. Properties of the paste with the reinforce resin system were stable to 1000 thermal cycles.

We expect this technology will migrate to various electric devices and printed electronics applications.

Acknowledgement

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