Effect of Sintering Environment on Silver-Copper Die-Attach Nanopaste

Kim Seah Tan * and Kuan Yew Cheong **
*Electronic Materials Research Group, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Penang, Malaysia
**E-mail: scheong@usm.my; Tel.: +604-5995259; Fax: +604-5941011

Abstract

In this work, a silver-copper (Ag-Cu) nanopaste that designed for high-temperature die-attach applications has been reported. This nanopaste was prepared by mixing Ag and Cu nanoparticles with an organic binder system, in which the weight ratio of nanoparticles and organic binder system was fixed at 87:23. The prepared nanopaste was then sintered at 380°C with a dwell time of 30 min and ramp rate of 5°C/min. A different sintering environment, namely open air, nitrogen and argon, was employed during the sintering process, which aimed to study its effect on the physical and electrical properties of sintered Ag-Cu nanopaste. X-ray diffraction analysis detected the formation of Ag9Cu, Ag,Cu99 and CuO compounds in the sintered nanopaste, irrespective of its sintering environment. A larger grain, revealed by scanning electron microscopy, was formed as the sintering was done in open air. The electrical study indicated that the nanopaste sintered in open air has higher electrical conductivity than other sintering environment. This study concluded that open air environment was the optimum sintering environment for Ag-Cu nanopaste.

1. Introduction

Advances of technology over the years, alongside with silicon carbide devices, has driven a need of high-temperature die-attach material. The traditional tin (Sn)-based solder alloys (lead-bearing and lead-free) although have been extensively used in silicon devices [1], yet it is primary designed for low-temperature range of applications (< 300°C) [2]. Various solder alloys that based on gold (Au) [2, 3], bismuth (Bi) [4, 5], and zinc (Zn) [6, 7] are subsequently introduced as alternative solutions, but these solder alloys have generally fallen into the low-temperature (< 300°C) and medium-temperature (300-400°C) ranges of applications [2]. There are some exceptional die-attach materials which fall into high-temperature range (> 400°C), such as inter-diffusion bonding of Au-indium (In) film [8] and Ag-In film [9]. Nonetheless, creating a firm joint from this bonding technique is a rather lengthy process due to the need of annealing up to 26 h [8, 9]. Hence, there is still a need to seek for an alternative solution.

In recent years, a strategy of employing nano-sized materials has brought to the development of a new die-attach solutions. In particular, Ag nanopaste has emerged as a forefront candidate of this strategy [10, 11]. This nanopaste utilized nanoparticles in its formulation, where the high surface energy associated with nanoparticles could offer a lower processing temperature. Besides, the nanopaste utilized sintering technique to set the joint can also avoid occurs of die-shifting issue that associated with solder reflow technique. Ag nanopaste, however, is limited to its high cost associated with Ag nanoparticle. Therefore, aluminum (Al) and copper (Cu) nanoparticles, with cheaper cost, were respectively introduced to replace a portion of Ag nanoparticle in the nanopaste formulations [12-14]. Of these, Ag-Cu nanopaste has demonstrated a better electrical and thermal conductivity than Ag-Al nanopaste [13, 14]. This is due to the excellent electrical and thermal conductivity that associated with Cu if compared to Al. In this work, the effect of sintering environment on Ag-Cu nanopaste has been investigated. The physical and electrical properties after sintering were carefully examined, which aim to determine an optimum sintering environment for Ag-Cu nanopaste.

2. Experimental details

Ag and Cu nanoparticles were acquired commercially from MTI Corp., Richmond, USA, with average sizes of 40 ± 10 nm and 50 ± 10 nm, respectively. The nanopaste was prepared by mixing 87 weight percent (wt%) of nanoparticles with an organic binder and solvent system, which constituted of resins binder (V006 from Heraeus, Inc.), terpineol (RV372 from Heraeus, Inc.) and ethylene glycol (MW 40,000 from Merck). The nanopaste content was consisted of 80 wt% Ag and 20 wt% Cu combined. Soda lime glass was used as substrate throughout the study, and it was cleaned by using distilled water and ethanol. Then, the prepared nanopaste was stencil-printed onto the pre-cleaned soda lime glass substrate with stencil thickness of 50.8 µm and area of 1.0 x 1.0 cm². A Lenton horizontal tube furnace was used to sinter the printed nanopaste at 380°C with a ramp rate of 5°C/min and dwell time of 30 min. Whilst, the sintering was carried out in either open air, nitrogen gas or argon gas environments. The flow rate of those gases was controlled at 150 mL/min. After sintering, the furnace was naturally cooled down to room temperature, followed by switching off the gas flow. Finally, the sintered nanopaste was being withdrawn from the furnace for characterization.

X-ray diffraction (XRD) (D500 Siemens Diffractometer) was carried out to identify phases presented in the sintered nanopaste with radiation of Cu kα (wavelength = 1.5406 Å). The measurements were scanned over a 20 range from 10 to 90°, using a step time of 71.60 s and a step size of 0.034°. Carbon-hydrogen-nitrogen-sulfur (CHNS) elemental analyzer (Perkin Elmer 2400) was used to determine the carbon content in the sintered nanopaste. Field emission scanning electron microscope (FE-SEM) (Zeiss Leo Supra 50VP) was used to characterize the surface morphology of sintered nanopaste. For electrical conductivity measurement, co-linear four-point probe system (Changmin Tech CMT-SR2000N) was used to measure electrical resistivity of the sintered nanopaste. A total of 10 measurements was performed on each sample at different locations, and its electrical conductivity was calculated with the reciprocal of the measured electrical resistivity.
3. Results and Discussion

Fig. 1 shows the XRD diffractogram of sintered Ag-Cu nanopaste, where Ag$_{97}$Cu$_3$, Ag$_{1}$Cu$_{99}$ and CuO compounds were detected in the sintered nanopaste, irrespective of its sintering environment. It has been revealed that the CuO compound has not been reduced significantly if the sintering environment was changed from open air to argon and nitrogen ambient.

Fig. 1: XRD diffractogram of sintered Ag-Cu nanopaste with various sintering environments

In addition, Fig. 2 shows the CHNS analysis on carbon content in sintered Ag-Cu nanopaste with various sintering environments. The CHNS analysis shows lower weight percent of carbon was detected in the nanopaste that sintered in open air (0.56 wt%) if compared with nitrogen (0.75 wt%) and argon (0.78 wt%) ambient. This indicates that the nanopaste is favored to be sintered in an open air environment. Sintering in an open air environment shows that it is able to assist organic binder burn-off from the nanopaste, and thus, it could induce better solid-state fusion between the nanoparticles.

Fig. 2: CHNS analysis on carbon content in sintered Ag-Cu nanopaste with various sintering environments

This finding was supported by FE-SEM micrographs, where microstructure with larger grains and better densification was observed for the nanopaste that sintered in an open air ambient [Fig. 3(a)]. For nanopaste that sintered in nitrogen and argon ambient, although large grains also can be observed in the micrographs, but their microstructures are less densification and having larger amount of porous [Fig. 3(b) and (c)]. This may attribute to insufficient burn-off of organic binder upon sintering the nanopaste in nitrogen and argon ambient; whereby, the residue organic binder could impede the efficiency of solid-state fusion to be occurred between the nanoparticles. Thus, a cluster of nanoparticles that cannot be well coalescence is also noticeable in the micrographs [marked by white arrows in Fig. 3(b) and (c)].

Fig. 3: FE-SEM micrographs of Ag-Cu nanopaste that sintered in (a) open air, (b) nitrogen and (c) argon ambient

Fig. 4 shows the electrical conductivity of sintered Ag-Cu nanopaste with various sintering environments. The electrical study showed the nanopaste that sintered in open air \(2.27 \times 10^5\, (\Omega\cdot\text{cm})^{-1}\) has higher electrical conductivity than other sintering environments \([1.78-1.85 \times 10^5\, (\Omega\cdot\text{cm})^{-1}]\). Table 1 compares the electrical conductivity of the sintered Ag-Cu nanopaste with other die-attach systems. Of these, the electrical conductivity of sintered Ag-Cu nanopaste is higher than most of the die-attach systems, but it is slightly lower than the Ag nanopaste. Overall, the Ag-Cu nanopaste that sintered in an open air environment provides the best physical and electrical attributes, hence, it could be considered as the optimum sintering environment for Ag-Cu nanopaste.

Fig. 4: Electrical conductivity of sintered Ag-Cu nanopaste with various sintering environments
Table 1: Electrical conductivity of Ag-Cu nanopaste versus typical die-attach systems

<table>
<thead>
<tr>
<th>Die-attach system</th>
<th>Electrical conductivity, $\times 10^3$ ((\Omega \cdot \text{cm}))</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag nanopaste</td>
<td>2.50-2.60</td>
<td>[10, 11]</td>
</tr>
<tr>
<td>Ag-Cu nanopaste</td>
<td>2.27</td>
<td>This work</td>
</tr>
<tr>
<td>Ag-Al nanopaste</td>
<td>1.01</td>
<td>[12]</td>
</tr>
<tr>
<td>Sn solder alloys</td>
<td>0.50-0.90</td>
<td>[1]</td>
</tr>
<tr>
<td>Conductive glass</td>
<td>0.70-0.80</td>
<td>[15]</td>
</tr>
<tr>
<td>Au solder alloys</td>
<td>0.20-0.40</td>
<td>[2, 3]</td>
</tr>
<tr>
<td>Bi solder alloys</td>
<td>0.05-0.10</td>
<td>[4, 5]</td>
</tr>
</tbody>
</table>

4. Conclusions

In this work, the effect of sintering environment on Ag-Cu nanopaste was systematically investigated. After sintering, \(\text{Ag}_{30}, \text{Cu}_{30}\), \(\text{Ag}_{50}, \text{Cu}_{50}\), and \(\text{CuO}\) compounds were formed in the sintered nanopaste, irrespective of its sintering environment. For microstructure and electrical study, the nanopaste that sintered in open air has demonstrated larger grain, better densification and better electrical conductivity if compared to nitrogen and argon ambient. Hence, this work concluded open air environment was the optimum sintering environment for Ag-Cu nanopaste.

Acknowledgments

This work was supported by Universiti Sains Malaysia RU-PRGS grant no 8045012 and eScience Fund Cycle 2/2014. One of the authors (K.S.T.) would like to acknowledge MyPhD scholarship support given by Ministry of Education Malaysia.

References