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Thermal characteristic of sintered Ag–Cu nanopaste for high-temperature die-attach application

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ABSTRACT

In this work, thermal characteristic of silver–copper (Ag–Cu) nanopaste that consists of a mixture of nano-sized Ag and Cu particles and organic compounds meant for high-temperature die-attach application is reported. The Ag–Cu nanopaste was sintered at 380 °C for 30 min without the need of applying external pressure and the effect of Cu loading (20–80 wt%) on the thermal properties was investigated in against of pure Ag nanopaste and pure Cu nanopaste. The results showed the specific heat of sintered Ag–Cu nanopaste was increased as the loading of Cu increased. For thermal conductivity and coefficient of thermal expansion (CTE) of sintered Ag–Cu nanopaste, a declining trend has been recorded with the increment of Cu loading. Overall, the sintered Ag–Cu nanopaste with 20 wt% of Cu loading has demonstrated the best combination of thermal conductivity (K) and CTE (α), which were 159 W/m K and 13×10^{-6}/K, respectively. It has proven that there was a strong correlation between the amount of pores and thermal properties of the nanopaste. The ratio of K/α is a performance index (M), which has shown a higher value (12.2×10^{6} W/m) than most of the commonly used die-attach systems. Finally, the Ag–Cu nanopaste has demonstrated a melting point of 955 °C, which can be proposed as an alternative high-temperature die-attach material.

1. Introduction

In recent years, electronic devices are continually improving for high-temperature applications, such as (i) brake and exhaust gas sensors for automotive (500–1000 °C) [1], (ii) turbine and gas sensors for aeronautic (~600 °C) [2], (iii) geothermal sensor for well-logging (~600 °C) [3], (iv) nuclear radiation detector and nuclear reactor for nuclear plant (700–1000 °C) [2,4], and (v) transmitter, antenna and electromechanical devices for space exploration (>500 °C) [5]. The challenge is thus driven to design an electronic packaging material, i.e. die-attach material, that is able to work in the aforementioned high-temperature conditions. The primary focus is therefore aimed to select a die-attach material that possesses melting point higher than 500 °C, which makes it suitable for high-temperature applications [6]. In addition, the die-attach material must also possess high thermal conductivity to dissipate the heat that originating from the die to the substrate [6], as well as, possess low coefficient of thermal expansion (CTE) to minimize the buildup strain that caused by temperature gradient [6]. To relate both thermal conductivity and CTE, performance index is thus being used to optimize the selection of a die-attach material. According to Fourier's Law for steady state one directional, x, heat flow from die to substrate [7]:

$$q = \frac{K}{x}\Delta T \tag{1}$$

where q is the heat input per unit area, K is the thermal conductivity, and ΔT is the change of temperature. The buildup strain, ε, in the die-attach material is related to the change of temperature by [7]:

$$\varepsilon = \alpha\Delta T \tag{2}$$

where α is the CTE. Eq. (3) is thereby derived by combining Eqs. (1) and (2) [7]:

$$q = \frac{\varepsilon}{x}\left(\frac{K}{\alpha}\right) \tag{3}$$

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Thus, for a given heat flow from the die, the buildup strain (ε) could be minimized by selecting a die-attach material with large value of K/α, which is defined as performance index, M [7]:

$$M = \frac{K}{\alpha} \tag{4}$$

The larger value of performance index indicates the die-attach material has higher efficiency in conducting thermal energy from the die to the substrate, making less thermal energy being absorbed and stored in the atoms of die-attach material. Less thermal energy being stored will eventually cause less displacement of the inter-atomic distance, which resulting less deformation of the die-attach material. With this idea in mind, the performance indices for various die-attach materials are being computed for later comparison (Table 1).

Table 1
Thermal conductivity, CTE and performance index for various die-attach systems.

Die-attach system	Thermal conductivity, K (W/m K) at 25 °C	CTE, α ($\times 10^{-6}$/K)	$M = K/\alpha$ ($\times 10^{6}$ W/m)	Ref.
Metal paste				
(i) Ag nanopaste	200–240	19–20	10.0–12.6	[33,34,36]
(ii) Ag–Cu nanopaste	159	13	12.2	This work
(iii) Ag–Al nanopaste	123	8	15.4	[41]
(iv) Ag hybrid paste	136–250	19.7*	6.9–12.7	[30,31]
(v) Cu micropaste	94	16.5*	5.7	[29]
(vi) Ag micropaste	80–220	19.7*	4.1–11.2	[28,32]
Metal film				
(i) Au	–	–	–	[25]
(ii) Au–In	–	–	–	[26]
(iii) Ag–In	–	–	–	[27]
Conductive glass	60–80	16–25	2.4–5.0	[15]
Solder alloy				
(i) Zn	77–110	20–30	3.7–3.9	[21–23]
(ii) Au	27–59	12–16	2.3–3.7	[15–17]
(iii) Sn				
(a) Pb-free	20–66	15–40	1.3–1.7	[11,12,14,16,36]
(b) Pb-bearing	23–53	19–30	1.2–1.8	[11,12,14,22,36]
(iv) Bi	7–11	–	–	[18,19]
Conductive adhesive	1–25	26–53	0.1–0.5	[8]

Symbol “–” means no reported value. Symbol “*” is theoretical value.

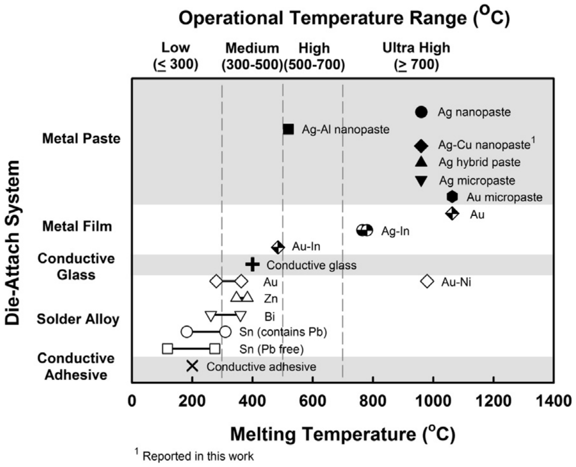

Fig. 1. Melting temperature of various die-attach systems and their operational temperature range [6,8–37,41].

In general, die-attach materials can be classified into five categories, which are conductive adhesive, solder alloy, conductive glass, metal film, and metal paste (Fig. 1). Nowadays, conductive adhesive [8–10] and tin (Sn) based solder alloys (lead-bearing and lead-free) [11–14] are most commonly used die-attach materials for level-1 interconnection, namely between the die and substrate, but these materials are having low value of M ($0.1–1.8 \times 10^{6}$ W/m) (Table 1) and low melting points (<250 °C), making them only suitable to be applied for low-temperature range (≤300 °C) of applications (Fig. 1) [6]. Conductive glass [15], gold (Au) [12,15–17], bismuth (Bi) [18–20], and zinc (Zn) [21–23] based solder alloys were subsequently introduced. But most of these materials are also displaying low value of M ($2.3–3.9 \times 10^{6}$ W/m) (Table 1) with maximum melting point at 400 °C, which limited to application at medium-temperature range (300–500 °C) (Fig. 1) [6]. Although Au-nickel (Ni) is an exceptional solder alloy that could be operated at high-temperature range (≥500 °C) but its high soldering temperature at 980 °C has become a drawback [24]. Metal film and metal paste systems are next being introduced, which aim to reduce the processing temperature, yet the entire system still able to operate at medium to ultra-high temperature ranges. Au–Au [25], Au-indium (In) [26], and silver (Ag)–In [27] are particular systems that form a joint by inter-diffusion bonding of metal films at temperature of 200–300 °C and pressure of 0.28–40 MPa. The joints formed by Au–Au and Ag–In films could be operated at ultra-high temperature range (≥700 °C), whereas the joint formed by Au–In film is only limited to medium-temperature range (300–500 °C) (Fig. 1). However, this inter-diffusion bonding technique requires additional long annealing duration (26–100 h) in order to increase its bonding strength [26,27]. Au [25], Ag [28] and copper (Cu) [29] micropastes are next sourcing as alternative solutions. These micropastes (i.e. a mixture of micro-sized metal particles and organic compounds) utilize sintering technique to form a joint at temperature of 700 °C; whilst application of external pressure (40 MPa) in assists of sintering process could further lower the sintering temperature down to 250 °C [25,28,29]. The joint formed by sintering of metal micropaste technique, with or without pressure assisted, has been proven suitable for ultra-high temperature range (≥700 °C) of applications with melting point higher than 960 °C (Fig. 1) [25,28,29]. But the application of external pressure during sintering tends to complicate the manufacturing process. Ag hybrid micro-nanopaste [30,31] (i.e. a mixture of micro- and nano-sized metal particles and organic compounds), Ag nanopaste [32–36] and Cu nanopaste [37] (i.e. a mixture of nano-sized metal particles and organic compounds) were then introduced to promote sintering at 250–380 °C without the need of external pressure in assisting the sintering process.

Ag, however, is limited to its high cost and low electrochemical migration resistance [38–40]; whereas Cu is limited to its complicated die-attach process, such as the requirement to preheat at vacuum atmosphere prior to sintering, and the sintering process must carry out in either H_2/N_2 or vacuum atmosphere [37]. The sintered Cu nanopaste even required additional 4 h annealing at N_2 atmosphere to minimize oxidation of Cu [37]. As a result, two alternative materials that could be used at high-temperature range, namely Ag–Al [41] and Ag–Cu [42,43] nanopastes, were introduced to surpass the preceding limitations of Ag and Cu nanopastes. These materials not only could tailor the cost to be cheaper than Ag nanopaste, yet it could also sinter in air atmosphere without assisting of external pressure and additional annealing step, hence making the die-attach process becomes much simpler. By comparing between Ag–Al and Ag–Cu nanopastes, Ag–Cu nanopaste that was studied in our previous works [42,43] has