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DIE ATTACHMENT METHOD ON A Cu FINISH BY PRESSURE-ASSISTED SINTER BONDING IN AIR USING Cu FORMATE PASTE

A paste containing Cu(II) formate rods was prepared, and characteristics of sinter bonding at 250°C under a pressure of 10 MPa were investigated to accomplish a high-speed die attachment for wide-bandgap power chips on Cu finish in air. Synthesis of the plate-type Cu formate particles from CuO was accomplished through a wet reaction for 180 min. Cu, formed in situ in the bondline by pyrolysis of the formate during heating for the attachment, was sufficiently active to lead high-speed sintering within a carbon dioxide-hydrogen atmosphere derived from the pyrolysis, and the oxide layer on the Cu finish was reduced by the hydrogen. As a result, sinter bonding for 10 min formed a robust bonding with a shear strength approaching 27 MPa.

Keywords: Die attach, Cu formate paste, Sinter bonding, Cu finish, Shear strength

1. Introduction

Wide-bandgap power devices, including SiC and GaN, are increasingly replacing current Si devices in power modules because they exhibit low switching loss and high efficiency. To achieve higher conversion efficiency and operating frequencies, the chip junction temperature should be eventually increased to as high as 300°C [1-5], which can be managed using bondline materials with high melting points and thermal conductivities. Hence, Pb-5Sn, commonly used as a high-temperature solder for the application, would be unsuitable as a bondline material due to mechanical instability at high operating temperatures [6,7].

Transient liquid-phase sinter bonding was developed as an alternative to soldering; however, the method involves long bonding times and can cause problems for automotive applications owing to reliability issues related to brittle intermetallics [4,5,8,9]. Therefore, another method to achieve a more robust bondline must be developed using a more suitable metal. The solid-state sinter bonding technique based on silver (Ag) particles, which exhibit a high melting point, high thermal conductivity, and ductile mechanical property, is promising in this respect [1,10,11]. However, the use of Ag paste as a bonding material is considered to have no practical use from the viewpoint of industrial competitiveness because of the high cost of Ag particles. In addition, longer bonding times require urgent alternatives for the improvement of production efficiency [11]. Hence, studies focused on copper-based pastes have been suggested, and methods to decrease the bonding time are still being conducted [12,13].

Copper (Cu) is easily oxidized in air, furthermore, the degree is accelerated with increasing temperature [14]. However, the native oxide layer and additionally oxidized surface during heating in air are crucial obstacles that interrupt the sinter bonding. For this reason, the in situ formation of active pure Cu during the heating and prompt sintering can be a strategy to accomplish an effective sinter bonding in air. Pioneering studies on the formation of pure Cu films by thermal decomposition in a copper-amine-complex paste have been reported by Yabuki et al. [15,16]. Lee et al. also reported the film fabrication using a single paste formulation containing Cu complexes [17-19]. These results indicate that sinter bonding using a Cu formate paste can be a novel method to form a bondline composed of Cu, even though fabricating the film by sintering requires a long process time, even in a nitrogen atmosphere. Therefore, the assistance of an external pressure during the sinter bonding is required to enhance the sintering speed and achieve a compact bondline structure.

Die attachment technology commonly demands an Ag finish on the chip and a direct bonded copper (DBC) substrate to obtain a robust bond by preventing oxidation of the Cu metallization. However, the additional Ag layer will increase the cost.

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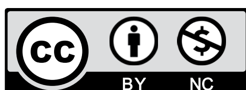

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Consequently, the die attachment process using a chip and DBC substrate with a Cu finish is a more developed process, although studies covering the die attachment on Cu finishes are rare. However, a previous study using a DBC substrate demonstrated that long bonding in air induced the oxidation of the Cu finish, leading to decreased bonding strength [20]. Therefore, in this study, a high-speed die bonding on a Cu finish was conducted with an external pressure of 10 MPa in air using a Cu formate paste.

2. Experimental

Small Cu formate particles, filler material for a sinter-bonding paste, were synthesized via a wet precipitation method. First, 50 g of copper(II) powder (CuO, 95%, Daejung Chemical Co., Ltd.) and 252 mL of formic acid (HCOOH, 85%, Daejung Chemical Co., Ltd.) were added to a 500 mL beaker. The ingredients were then stirred for 3 h using a magnetic bar at 250 rpm. The resultant slurry was separated using a filter and washed three times with ethanol. Finally, the washed Cu formate sludge was dried in a low-vacuum oven for 7 h.

Subsequently, the dried Cu formate particles were milled for 50 s using a blade-type mixer to transform them into finer and homogeneous particles that were more beneficial in preparing a paste, and the milling process was repeated five times. A paste containing the shredded Cu formate particles was prepared by mixing the Cu formate particles with α-terpineol (98.5%, Samchun Pure Chemical Co., Ltd.) at a weight ratio of 5.5:4.5 with a spatula.

The prepared paste was screen-printed on a Cu dummy substrate over an area of 3×3 mm using a 100 μm-thick stencil mask, followed by drying at 150°C for 3 min to sufficiently decrease the solvent in the printed pattern through evaporation. A 3×3×1 mm dummy Cu chip was laid to correspond to the pattern, resulting in the formation of a sandwich structure. For the die attachment, the sample was placed on a heating stage of a thermos-compression bonder set at 250°C and held for a specific time in air to heat the sample up to the set temperature. The sample was subsequently compressed for the whole bonding period by applying an external pressure of 10 MPa immediately after the placement, and then the bonding time was measured.

The microstructures, fracture surfaces of the bondlines, and the morphology and size of Cu formate particles were examined using high-resolution scanning electron microscopy (HR-SEM, SU8010, Hitachi High-Technologies Corp.). Phase transformations in the synthesized particles were verified by X-ray diffraction (XRD, DE/D8 Advance, Bruker).

The bonding strength of the bondline was measured using a Dage-4000 bond tester (Nordson Dage), which was defined as the maximum stress measured during shearing at a height of 200 μm using a tip moving at 200 μm/s. For each sinter-bonding time, the measurement was conducted five times, and average values were obtained.

3. Results and discussion

Figure 1 shows the morphologies of the initial CuO particles and the particle shape synthesized as a function of the immersion reaction time in formic acid. The CuO particles are the aggregates of irregular nanoscale particles. After a reaction time of only 5 min, particles with completely different shapes were observed. The nanoscale CuO particles nearly disappeared after a reaction time of 15 min, and the newly synthesized particles grew along the lateral plane with an increase in the reaction time. Eventually, plate-like particles were frequently observed after 90 min, and most of the synthesized particles exhibited plate-like morphologies after 180 min.

Figure 2 displays the XRD patterns of particles synthesized as a function of reaction time. The particles collected from a reaction time of 90 min clearly demonstrated the synthesis of Cu(II) formate, and hardly indicated the existence of any copper oxide, implying a sufficient reaction of the added CuO. Although

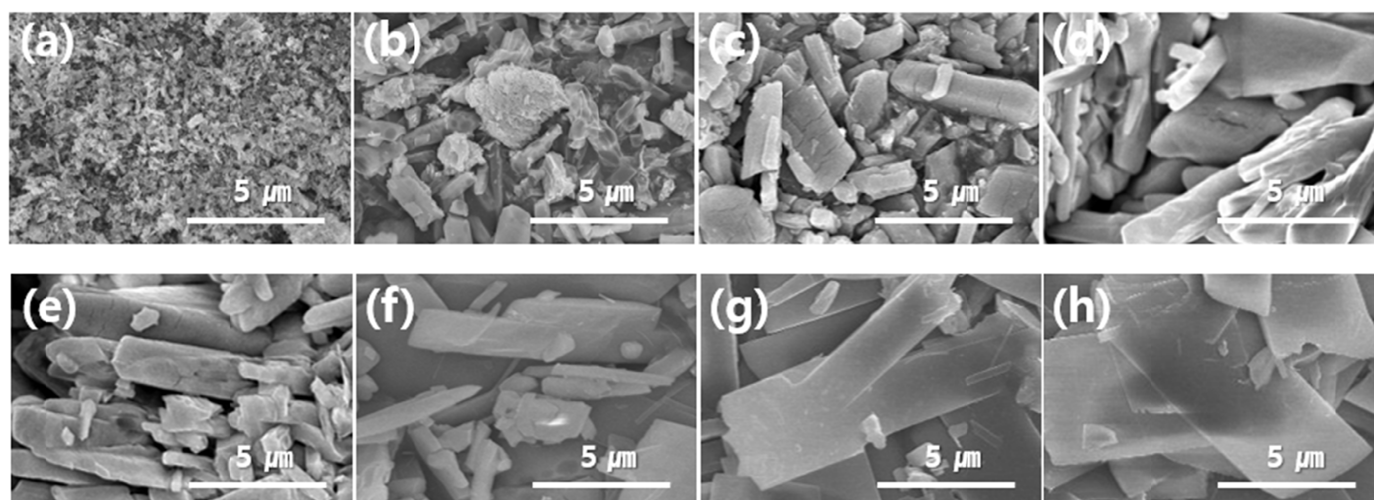

Fig. 1. SEM images of (a) CuO particles and particles synthesized with different reaction times: (b) 5, (c) 15, (d) 30, (e) 60, (f) 90, (g) 120, and (h) 180 min

a similar result is shown in the 120 min sample, the 180 min sample presented a significantly different result; the 32-0331 Cu(e) formate was partially transformed into 32-0332 Cu(II) formate. The results of Figs. 1 and 2 indicate that the following reaction occurred during the immersion reaction:

$$CuO + 2HCOOH \rightarrow Cu(COOH)_2 + H_2O \quad (1)\ [17,18]$$

From the morphological homogeneity, we selected the particles synthesized for 180 min as the filler material.

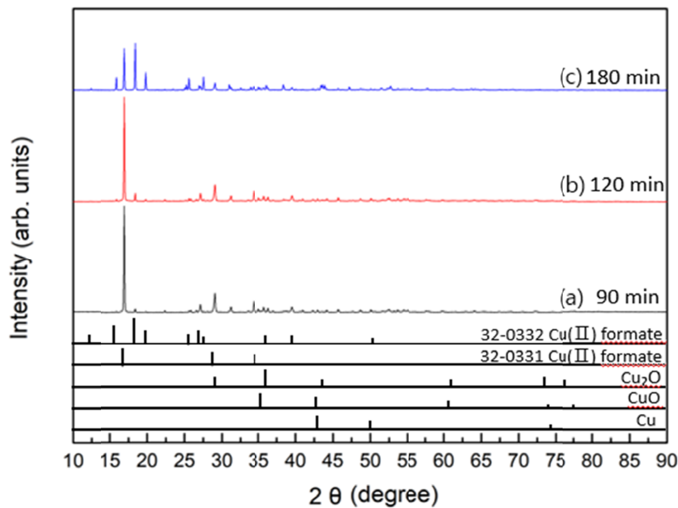

Fig. 2. XRD patterns of particles synthesized with different reaction times: (a) 90, (b) 120, and (c) 180 min

The shapes of resultant particles, after the milling of the 180 min Cu(II) formate particles, are shown in Fig. 3. The plate-like Cu formate particles were chopped into short rods approximately 1 μm wide after five repeated millings. Hence, the high-speed rotation of a blade in the mixer could cut the Cu(II) formate particles down.

Figure 4 shows the backscattered-electron (BSE) images of representative bondlines formed in air at various sinter-bonding times using the prepared Cu formate paste. Because of the significant volume shrinkage by pyrolysis (Equation (2)) from the Cu(II) formate to pure Cu and the elimination of initial voids between the Cu(II) formate rods, the average thicknesses of the bondlines drastically decreased.

$$Cu(COOH)_2 \rightarrow Cu + 2CO_2\uparrow + H_2\uparrow \quad (2)\ [19]$$

For example, the bondline sinter bonded for 1 min exhibited a thickness of 11 μm. Subsequently, the bondline thickness saturated from a bonding time of 3 min, and the average final thickness decreased to 7 μm, that is, approximately 1/14 of the printed thickness. This thin bondline thickness is favorable considering the trend that the profile of the bonded chip structure consistently decreases.

The results indicate that the pyrolysis of Cu(II) formate was not completed during a sinter bonding of only 1 min due to the time required to vaporize the solvent in a paste. The Cu reduced from the Cu(II) formate seemed to present pronounced sintering behavior under pressure during the growth of nanoparticles by coarsening. The drastic sinterability of nanoscale metals has been frequently reported in similar studies [21-25]. In addition, the hydrogen gas emitted by Equation (2) can facilitate robust interfacial sinter bonding at the Cu finish interfaces by reducing the surface oxide on the Cu finish at the sintering temperature with the assistance of pressure. Immediately after the reduction, the active Cu generated from the Cu(II) formate will begin to sinter with the Cu finishes of both substrate and chip. The heat generated from the pyrolysis can also contribute to the sinter bonding. Consequently, sinter bonding between the as-generated Cu and at the upper and lower interfaces was clearly observed, forming a dense microstructure at the bondline. The microstructure was entirely dissimilar from porous structures observed in similar sinter bondings using Cu particles [12,13].

Figure 5 shows the shear strength of the sinter-bonded Cu dummy chips as a function of bonding time. The bondlines bonded at 250°C for 1 min exhibited an insufficient average strength value of 9.0 (±1.0) MPa, and additional bonding for 2 min (bonding time of 3 min) did not significantly enhance the strength. Increasing bonding time to 5 min, however, increased the strength to 16.5 (±2.6) MPa. Eventually, sinter

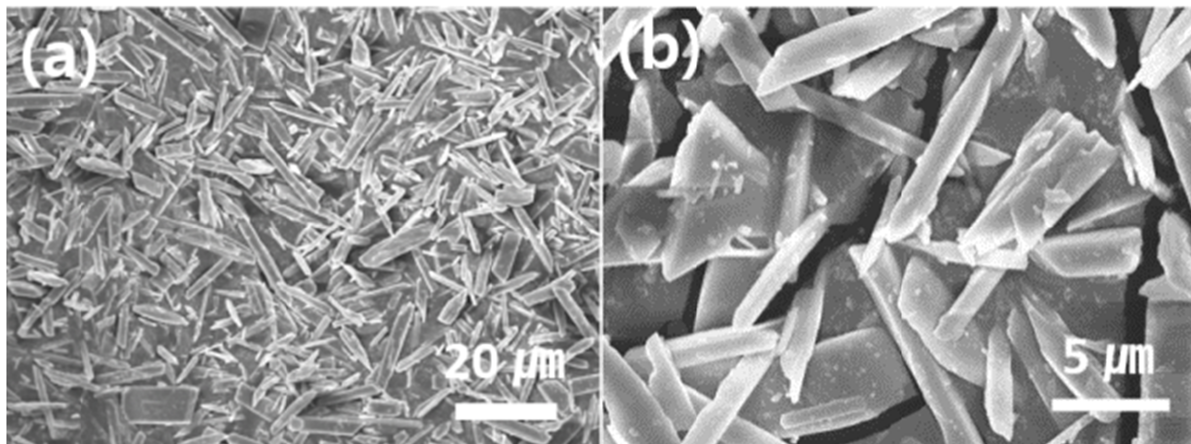

Fig. 3. (a) High- and (b) low-magnified SEM images of Cu(II) formate rods after milling

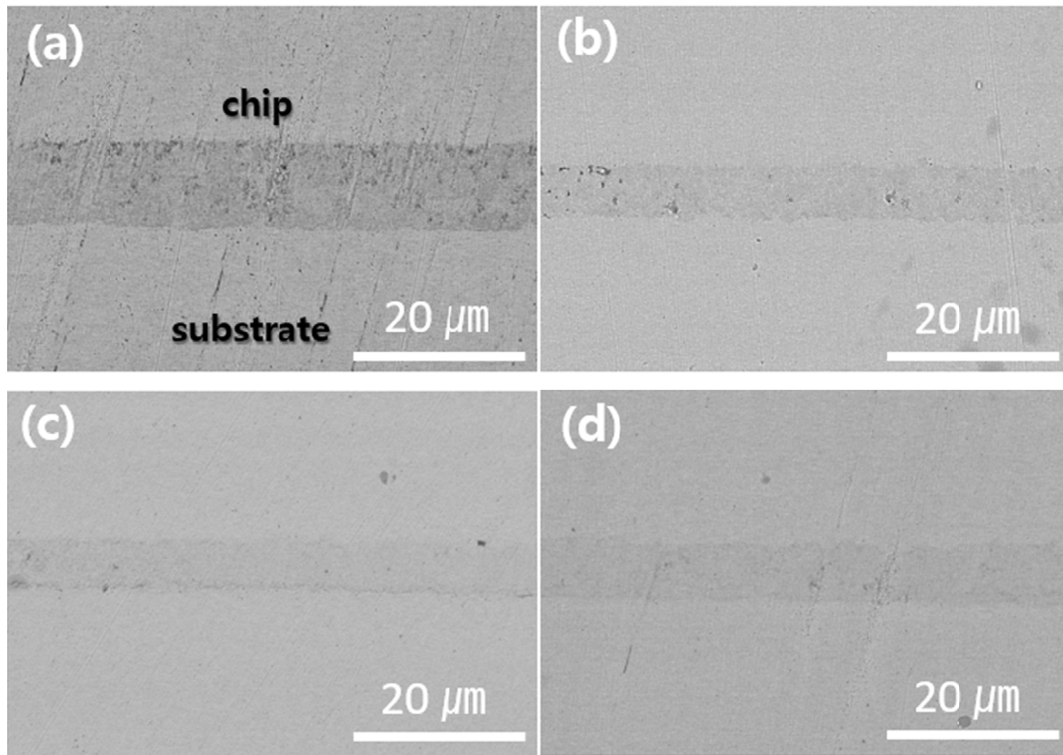

Fig. 4. Cross-sectional BSE images of bondlines sinter bonded at 250°C in air using copper formate particles under 10 MPa external pressure for different bonding times: (a) 1, (b) 3, (c) 5, and (d) 10 min

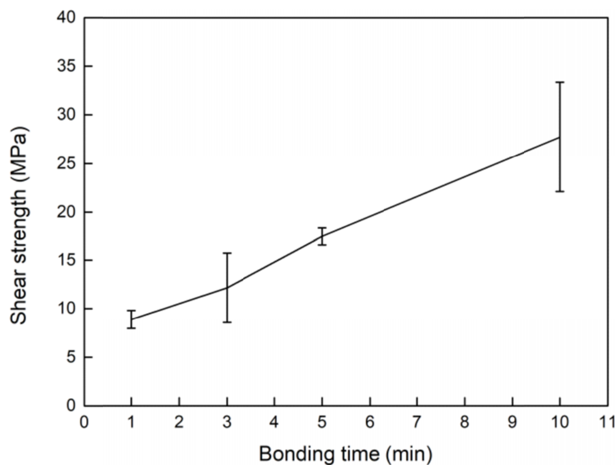

Fig. 5. Shear strength of joints sinter bonded at 250°C in air for different times using copper formate particles

bonding for 10 min presented an excellent value approaching 27.0 (±5.0) MPa.

SEM images indicating the fracture surfaces on dummy Cu chips after the shear testing of joints sinter bonded at 250°C in air are presented in Fig. 6. All samples prepared at different bonding times exhibited a coherent failure (fracture occurring inside the bondline) mode, which implies that the degree of shear strength was dependent on the sintering quality between the reduced Cu particles. Sinter bonding for 1 min (Fig. 6(a)) presented the fracture surface of rough particles that seemed to be composed of Cu and Cu formate particles, indicating that the sintering degree was low owing to non-completion of the pyrolysis reaction. In the sample bonded for 3 min, Cu formate particles were seldom observed and severely sintered regions between the Cu particles were verified. With an increase in bonding time to 5 min, the total area of the compactly sintered regions increased, and minute shear bands by ductile fracture were clearly observed on the regions. Sinter bonding for 10 min presented a significantly dense fracture surface by the overall distribution of compactly sintered regions. This trend corresponded well to the measured shear strength results. The formation of a dense fracture surface by an increased sintering degree was responsible for the increase in shear strength.

4. Conclusions

A novel pressure-assisted die attachment method on Cu finish was accomplished at high-speed in air using a sinter-bonding paste containing Cu(II) formate rods. Sinter bonding was achieved using active Cu in situ reduced by the pyrolysis of the Cu formate, and a robust bonding approaching a shear strength of 27 MPa was accomplished after bonding at 250°C for 10 min under 10 MPa. The carbon dioxide and hydrogen emitted from the pyrolysis suppressed the instant oxidation of the reduced Cu at the sintering temperature and reduced oxide layers of the Cu finishes on the chip and substrate, enabling sintering in the reduced Cu and at the upper and lower Cu finish interfaces. As a result, the final thickness of the formed bondline decreased to 7 μm, which is approximately 0.07 times compared with the initial thickness of the printed paste.

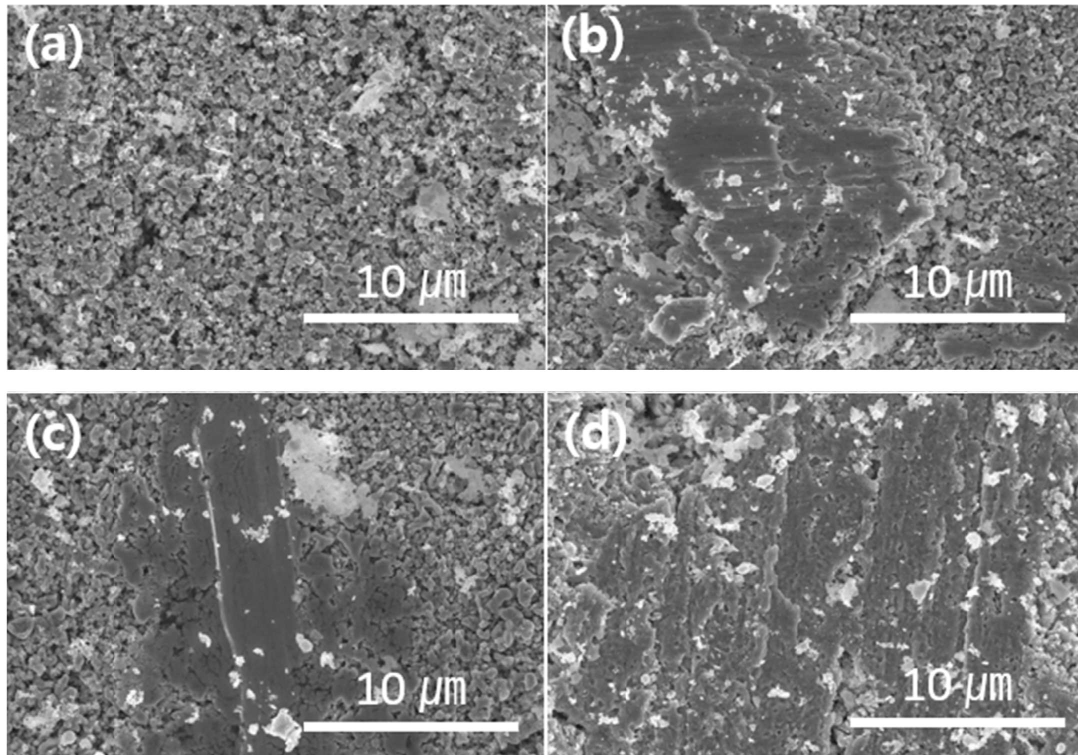

Fig. 6. Fracture structures on dummy Cu chips of the bondlines sinter bonded at 250°C in air at different times: (a) 1, (b) 3, (c) 5, and (d) 10 min

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