In Situ Reduction-Sintering to Produce Copper Interconnects for High Temperature Electronics

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Abstract
This study presents a special in situ reduction-sintering of CuO and Cu nanoparticles. The microstructure and strength of sintered Cu joints by CuO and Cu nanoparticle were compared. The reduced Cu particles of CuO have a larger size of 1 μm and lower sinterability which results in an insufficient sintering of Cu. In contrast, the sintered Cu nanoparticle structure shows a strong bonding of Cu and plastic deformation after fracture. Owing to the removal of the original oxide and limitation of its re-appearing during sintering by the proposed method, high sintered Cu joint strength over 30 MPa was achieved without the need for pressurized sintering or protective gas atmospheres.

Key words
Joining, Nanoparticle sintering, Oxide, Reduction sintering

I. Introduction
The widespread use of wide bandgap (WBG) semiconductor is limited by the unmatured high temperature packaging technology [1]. Although various bonding techniques have been developed for high temperature electronics, they suffer from different issues. For example, most of the transient liquid phase (TLP) bonding solders have a problem of brittle intermetallic compounds and Kirkendall void formation [2]. Sintering of Ag nanoparticles has a high cost and low electro-chemical migration resistance [3, 4]. Sintering of Cu nanoparticles has an oxidation issue and this could reduce the joint reliability [5].
Cu nanoparticles have been widely studied as a die attach interconnection material due to their comparable conductivity to Ag but high abundance and electro-chemical migration resistance [6-11]. Acid pre-treatment followed by inert gas sintering is a popular way to remove the original oxide and suppress the oxide formation during the sintering process. Mou et al. [12] soaked Cu nanoparticles in a mixture of carboxylic acid and dehydrated ethanol to achieve the surface-modification. The surface-modified Cu nanoparticles were then sintered at 250 °C for 60 min with a pressure of 10 MPa under the protection of Ar-H2 (5% H2) gas mixture. Cu oxidation was not found after sintering and the joints showed a high bonding strength over 30 MPa. Liu et al. [13] treated Cu nanoparticles with formic acid and found that the oxide is removed and copper formate forms on the surface of Cu nanoparticles. The copper formate will decompose into copper, carbon dioxide and hydrogen at the temperature range of 120-160 °C. The following sintering process under the atmosphere of 5% H2/95% N2 prevented the formation of Cu oxide and led to a highly conductive and strong Cu−Cu interconnection. Li et al. [14] and Liu et al. [15] also proved that Cu nanoparticles pretreated by formic acid are free of oxidation after sintering under inert atmosphere.
Reducing atmosphere is an alternative way to reduce Cu oxide into Cu. Formic acid is the most common reducing atmosphere [16-18]. Liu and Nishikawa [16] investigated a complex oxidation–reduction bonding process of Cu microparticles, which involves pre-heating samples at 130 °C for 5 min, heating at 300 °C for 20 min in air for microparticle oxidization, and holding at 300 °C for 40 min while introducing formic acid atmosphere into the oven chamber. Cu nano-oxides formed on the surface of Cu microparticles were reduced by formic acid atmosphere into Cu nanoparticles which could significantly enhance the sinterability of Cu microparticles. Gao et al. [18] further shortened the bonding time of this approach from 65 min to 35 min by pre-oxidizing the Cu microparticle at 300 °C for 8 min. Ethyl alcohol [19], hydrogen [20, 21] and methanol [22] atmosphere have also been used as reducing atmosphere. However, these reducing gases have a relatively low reducing speed and require high reducing temperature of

over 300 °C, while most of them are toxic and flammable. Ogura et al. [23] replaced the complex reducing gas system by using the reducing solvent polyethylene glycol and found that the reduction temperature required for CuO nanoparticles is still high (300 °C).

This study employs an in-situ reduction sintering of both CuO and Cu nanoparticles by glycerol to fabricate the sintered Cu joint without the assist of sintering pressure or protective atmosphere. The microstructure of strength of joints by CuO and Cu nanoparticles were compared and the micro-fracture mechanism of joint was investigated.

II. Materials and methods

CuO and Cu nanoparticles with a mean diameter of 100 nm and 50 nm respectively were purchased from Sigma-Aldrich. The CuO and Cu paste were made by mixing CuO/Cu nanoparticles with the glycerol at a mass ratio of 3.5:6.5 (nanoparticle/solvent). Cu discs of 4 mm diameter and 2 mm thickness (small) and 8 mm diameter and 3 mm thickness (large) acted as component and substrate respectively. Prior to bonding, the discs were polished with emery paper (up to 800-grit), soaked briefly in diluted hydrochloric acid, rinsed in ethanol and dried. The paste was first printed on the smaller Cu disc with a same height of paste drop (2 mm for CuO and 1 mm for Cu) as shown in Fig. 1 (c) and then heated to the reduction temperature of 220 °C for several minutes (3 min for CuO and 1 min for Cu). After that, the smaller Cu disc with reduced Cu particles was bonded with the larger Cu disc under a placement pressure of 3 MPa for 1 min to ensure good contact between the paste and the Cu discs. Next the assemblies were heated to 220 °C in air for 15 min of CuO and 5 min of Cu without pressure on a hot plate (Stuart SD160).

The phase composition of CuO and Cu nanoparticle and reduced Cu particles was measured by X-ray diffraction (XRD, Stoe StadiP, Mo radiation). The shear strength (calculated by the average of five trials) of joints were assessed by shear tester (Nordson Dage 4000) with the shearing speed of 50 μm/s. The morphology of Cu nanoparticles, joint fracture surfaces and cross sections were observed by scanning electron microscope (SEM, Tescan-Delmic SEM-CL).

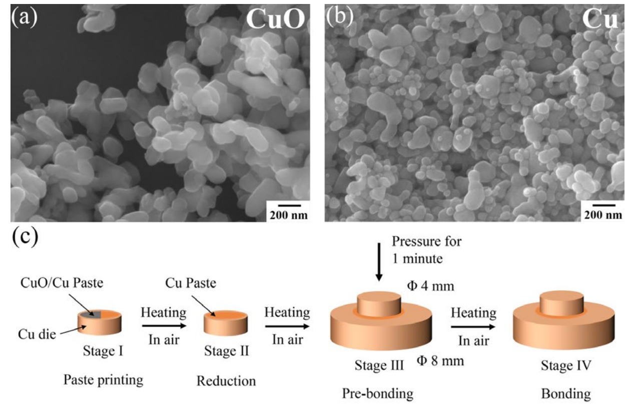

Fig. 1 SEM image of CuO (a) and Cu (b) nanoparticle and schematic illustration (c) of bonding process.

III. Results and discussion

The XRD results of the original CuO and Cu nanoparticle show obvious Cu oxide peaks as shown in **Fig. 2 (a)**. However, after the reduction-sintering process, the oxide peaks in the XRD results of sintered Cu structure (both CuO and Cu) disappear and only Cu peaks remain. It can be concluded that the Cu oxides were completely reduced to Cu by glycerol [24, 25]. The shear strength of joints by CuO for 15 min sintering is about 22 MPa while the joints by Cu nanoparticles for 5 min sintering have a higher strength of 33 MPa. From the SEM fracture surfaces images in **Fig. 3 (a)** and **(b)**, it is found that the reduced Cu particle of CuO has a larger size of 1 μm and the sintered structure shows little deformation after fracture. In contrast, the oxide content in the original Cu nanoparticles is limited according to the XRD result in **Fig. 2 (a)**, so that the growth of reduced Cu particles was significantly suppressed. The high surface activity enables Cu nanoparticles to be sintered sufficiently at the same temperature of 220 °C and the sintered Cu structure shows a plastic deformation after fracture as shown in **Fig. 3 (b)**, which indicates that strong Cu bonding was achieved [26]. The cross section of CuO joint also shows the bad coalescence between the micro-sized reduced Cu particles as shown in **Fig. 3 (c)**.

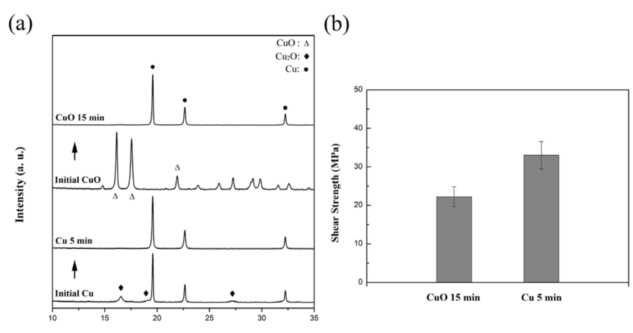

Fig. 2 XRD results (a) of CuO and Cu nanoparticle before and after the reduction-sintering process and the

shear strength (b) of joints by CuO and Cu nanoparticles.

Unlike the traditional sintering process, where the paste undergoes a heating process from room temperature to the desired pre-heating or sintering temperature. The organic solvent evaporates quickly during this process and then the unprotected Cu particles would be oxidized during the subsequent sintering process. For the reduction-sintering process, the remaining organics (glycerol) after reduction are able to prevent the oxidation of Cu during the pre-bonding process. Meanwhile, the reduced Cu particles can be immediately sintered after reduction at the same temperature. The rapid sintering speed significantly depresses the re-formation of oxide during the subsequent sintering process. From the XRD results in **Fig. 2 (a)**, it is clear that Cu oxide did not re-appear in the sintered structure of Cu nanoparticles for 5 min. The reduced Cu particles of CuO have a larger size and higher oxidation resistance, so that the unoxidized sintering time rises to 15 min [25].

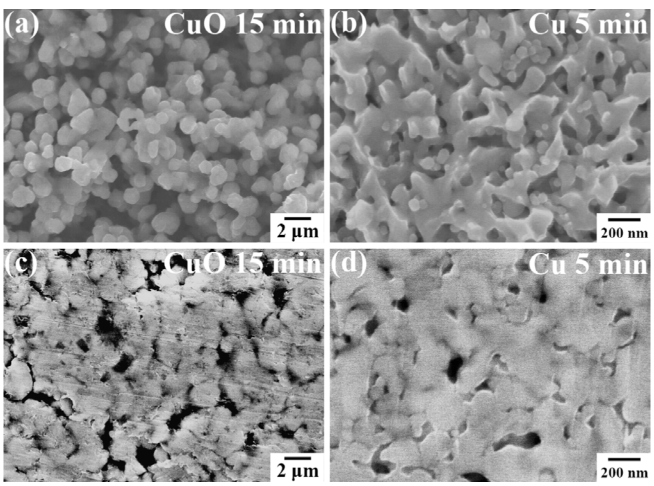

Fig. 3 SEM fracture surface and cross section images of joints by CuO (a, c) and Cu (b, d) nanoparticles.

Cu nanoparticles seem to be more promising than CuO nanoparticles as the interconnection material due to the stronger and deformable sintering structure. Meanwhile, the in situ reduction-sintering process eliminates the use of special storing condition for Cu nanoparticle, which comprises the merit of CuO (free of further oxidation). The micro-fracture mechanism of Cu 5 min joints was investigated and different areas of the dummy Cu die and corresponding areas on dummy Cu substrate were observed as shown in **Fig. 4**. From the macroscopic fracture surface images of joints, it seems that the joint facture occurs at the interface between the sintered structure and Cu substrate as shown in **Fig. 4 (a-b)**. However, the sintered Cu nanoparticles are found to be adhered to the Cu substrate after fracture and shows a similar plastic deformation to the sintered Cu in the corresponding areas of Cu die, which indicates that the joint fracture indeed occurs within the bulk sintered Cu structure. Meanwhile, some sintered Cu nanoparticles adhering to both the Cu die/substrate also show insufficient sintering of Cu and little deformation as shown in **Fig. 4 (a2-b2)**.

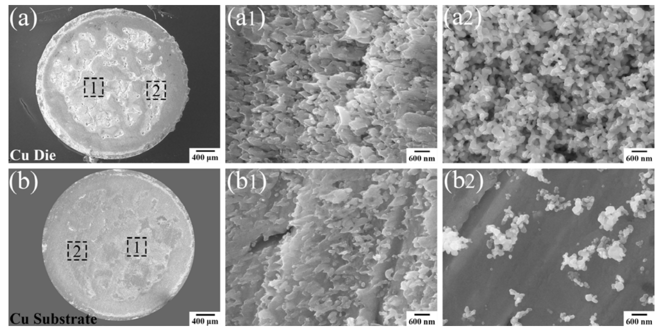

Fig. 4 SEM fracture surface images of joints by Cu nanoparticles.

IV. Conclusion

In summary, an in situ reduction-sintering of CuO and Cu nanoparticles was proposed. The oxide was successfully reduced to Cu by the reducing solvent of glycerol and the rapid sintering depressed the re-appearing of oxide. The reduced Cu particles of CuO has a larger size of 1 μm and the shear strength (22MPa) of joints by CuO nanoparticles for 15 min sintering is lower than the strength (33 MPa) of Cu nanoparticle joint for only 5 min. The sintered Cu nanoparticle structure shows a plastic deformation after facture and the joint fracture is found to be occurred within the bulk sintered Cu structure. This specific in situ reduction-sintering process eliminates the use of pressure and protective atmosphere during sintering and is a promising interconnection bonding technique for power electronics.

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