# Effect of surface microstructure on joints using nanoporous Cu sheet for power devices

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***Abstract*— Wide-bandgap (WBG) semiconductors such as silicon carbide (SiC) and gallium nitride (GaN) are being developed as promising replacements for Si-based semiconductors. The operating temperature of SiC semiconductor is expected to be much higher. The replacement of soldering with new bonding process has been needed for WBG semiconductor devices. We have proposed a solid-state bonding process using nanoporous metal sheet, as a die-attach bonding method for WBG semiconductor devices. In this study, the bonding process using nanoporous Cu sheet as an insert metal was investigated to achieve a Cu disk/Cu disk bonding without solvent and flux. The shear strength of the joint using nanoporous Cu sheet at 350 and 300 °C in formic acid atmosphere exceeded the shear strength of conventional Pb–5Sn solder joints which was approximately 18 MPa.**

***Keywords—Solid-state bonding, nanoporous Cu, dealloying, power module, shear strength***

## I. Introduction

Recently, there has been interest in improving the performance of electronic power modules that are used in electric vehicles and renewable energy sources for effective utilization of energy. And the electronic power modules are needed to endure harsh operating conditions such as more than 200°C. To assemble future power modules, high-thermostability packaging technologies are surely needed. Then, the requirement for a high-thermostability die attach material is also desirable for applications in areas such as aerospace and vehicles. Assembled joints in these power modules are required to exhibit good reliability against harsh environment. Although Pb-based solder has been used to join chips to base materials made of copper, a strong drive exists to find good Pb-free alternatives for power modules. In addition, alternative materials must be able to demonstrate high thermal and electrical conductivity; low coefficient of thermal expansion mismatch between the chip and the substrate; suitable mechanical properties which provide stress relaxation after bonding. Researchers have investigated alternative materials and bonding processes to withstand harsh conditions. A bonding process using nanoparticles have been proposed as a solder alternative [1, 2]. The sintering behavior of nanoparticles has attracted interest, because it is well known that nanoparticles of metals have lower sintering and melting temperatures than the bulk metal, which decouples the bonding temperature from the operating temperature. The other advantages of silver and copper are their high thermal and electrical conductivities in the range 6 to 8 times higher than Sn-Pb solder [3]. The sintering behavior of metal nanoparticles has exploited to join chips to substrates. However, there are some drawbacks of bonding process using metal nanoparticle pastes; for example, it is difficult to produce suitable nanoparticle pastes for the process conditions and the residual organic substances after the bonding process can induce unexpectedly large voids and insufficient densification in the joint [4]. These defects lead to decrease of the long-term reliability of the joint.

To solve these issues, we have proposed a novel solid-state bonding process suitable for application in future power modules. This process achieves nanoporous bonding (NPB) via nanoporous metal sheets in the absence of organic substances. Nanoporous metals are usually prepared by a chemical dealloying method, which involves the selective dissolution of less noble metal atoms into an acid solution from a precursor alloy. More noble metal atoms diffuse along the surface of the alloy to form nanoporous structures [5]. Kim et al. reported that solid-state NPB can be achieved using a nanoporous Ag sheet without the need for any solvent and organic substances [6]. Recently, we try to use nanoporous Cu sheet for solid-state NPB because Cu is less expensive than Ag and Au, while its electrical and thermal conductivities are excellent. Koga et al. reported that solid-state NPB using nanoporous Cu dealloyed from Mg-Cu precursor sheet achieved good shear strength at approximately 40 MPa [7]. Cu-based precursor alloys are generally fabricated by melt spinning method. However, our previous study revealed that the nanoporous Cu sheet by cold-rolled Mn-Cu precursor could achieve a homogeneous and large crack-free nanoporous structure using an adequate annealing process [8]. In this study, the bonding process using nanoporous Cu sheet formed from Mn-Cu precursor was investigated to achieve a Cu disk/Cu disk bonding without solvent and flux.

## II. Experimetal

### *A. Fabrication of nanoporous Cu sheet*

Nanoporous Cu (NPC) sheets were prepared using a chemical dealloying method, which involves the selective dissolution of Mn into 4% HCl from a Mn–30 at.% Cu precursor alloy. Pure Mn (99.99 mass %, Nilaco Co., Japan), and Cu (99.9 mass %, Nilaco Co., Japan) were used to prepare a parent alloy, and Mn–30 at.% Cu ingot was prepared by arc melting in an Ar atmosphere. Then, a cold-rolling process was adopted to fabricate Mn–Cu precursor alloy sheet with a thickness and width of 110–120 µm and 18–20 mm,

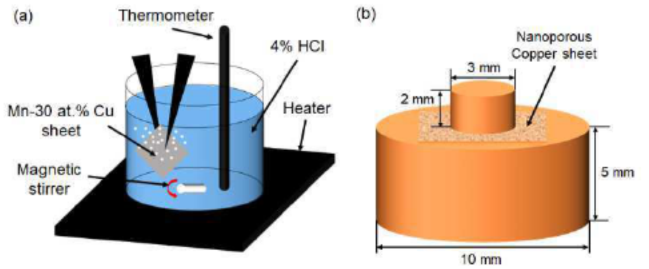


Fig. 1 Schematic diagram of (a) chemical dealloying method and (b) joint sample.

respectively. The cold-rolled sheets were immersed in a 4% HCl solution and dealloyed for 4 h at 50°C, as shown in Fig. 1(a). The dealloyed sheet samples were subsequently washed in distilled water and ethyl alcohol and dried in a vacuum desiccator. The sheet samples were examined using an X- ray diffractometer (Ultima IV, Rigaku, Japan) equipped with a Cu Kα radiation source.

Before a bonding experiment using a Cu disk, the nanoporous Cu sheet itself was heated at 350, 300, 250 °C for 10 min in a N2 atmosphere to clarify the sintering behavior of nanoporous structure on the surface of the sheet.

### *B. Bonding process*

Two oxide-free Cu disks were bonded using the nanoporous Cu sheet as an insert material under various bonding conditions; the diameter and height of the top Cu disk were 3 mm and 2 mm, respectively, and of the bottom Cu disk were 10 mm and 5 mm, respectively, as shown in Fig. 1(b). To remove oxide layer on the Cu disks before bonding, they were first immersed in a 4% HCl solution using an ultrasonic cleaner for 5 min, and then immersed in ethyl alcohol using an ultrasonic cleaner for 5 min. Next, the nanoporous Cu sheet was put on the bottom Cu disk before the top Cu disk was attached. A thermo-compression bonding system (RB-100D, Ayumi Industry Co., Ltd, Japan) was used to achieve a Cu disk/ Cu disk joint in a N2 or formic acid atmosphere. The applied pressure was 10 MPa and the bonding temperature was 350, 300, 250 °C for 10 min.

### *C. Evaluation method*

The shear strength of the joints was evaluated using a shear tester (STR-1001, Rhesca, Japan) at a strain rate of 1 mm/min, and the average shear strength of the five samples was obtained. The shear strength of a joint was calculated as the maximum fracture load divided by the area of upper disk. The surfaces of the NPC sheets after a shear test were observed using optical microscopy (OM, DM2700M, LEICA, Germany). The cross sections of the joints were observed using field emission scanning electron microscopy (FE-SEM, SU-70, Hitachi, Japan). The porosity ration in the joint layer was analyzed.

## III. RESULTS AND DISCUSSION

The oxidation behavior of nanoporous Cu sheer just after dealloying was examined. Fig. 2 shows the XRD patterns of as-dealloyed nanoporous Cu sheet and stored nanoporous Cu sheet in air for 1 h. In the case of the as-dealloyed NPC sheet, diffraction peaks that are characteristic of face-centered cubic (fcc) Cu are observed, corresponding to its (111), (200), and (220) planes. In the case of the stored NPC sheet in air for 1h, low-intensity peaks near 36.6° and 61.3° were observed

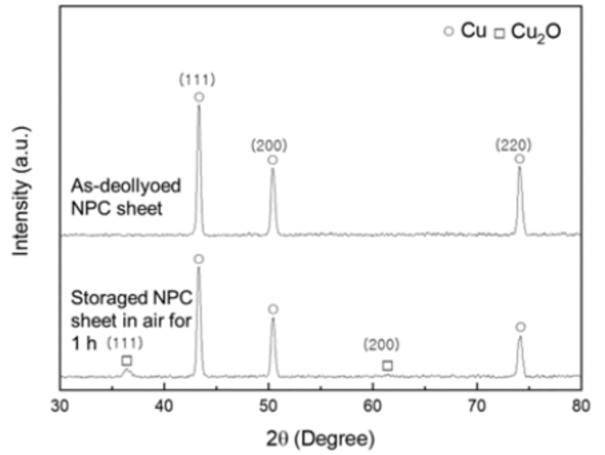


Fig. 2 XRD patterns of as-dealloyed NPC sheet and stored NPC sheet in air for 1 h.

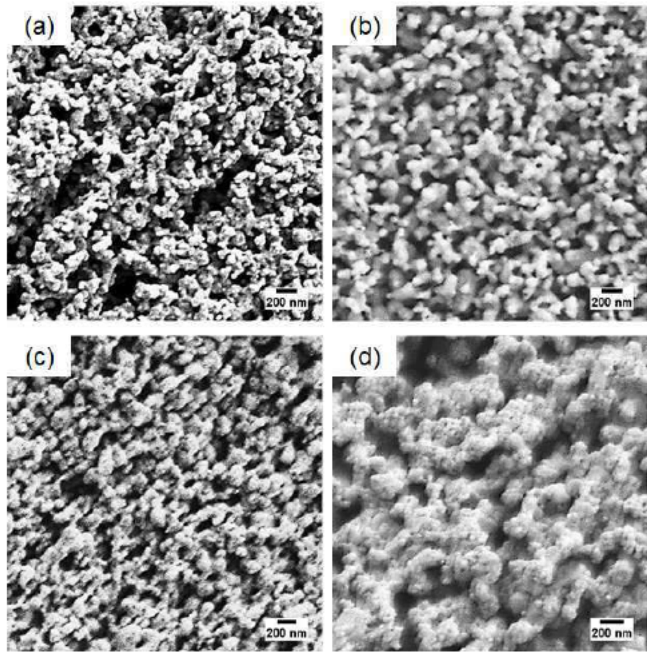


Fig. 3 SEM images of surface structure of (a) as-dealloyed NPC sheet and NPC sheets heated at (b) 250°C, (c) 300°C, (d) 350°C, (e) 350°C for 10 min.

additionally, characteristic of Cu2O, indicating the presence of Cu2O layer on the stored NPC sheet in air for 1 h.

To clary the sintering behavior of nanostructure on the surface of NPC sheet at different temperatures, the microstructure of as-dealloyed NPC sheet and NPC sheets heated for 10 min at 350, 300 and 250 °C were observed by FE-SEM in Fig.3. As shown in Fig. 3, the heated NPC sheets showed three-dimensional porous structures similar to that of the as-dealloyed NPC sheet; however, their structures were coarsened, and the size of their ligaments increased with increasing the heating temperature for 10 min. The average ligament size of the as-dealloyed NPC sheet was 122 nm. The average ligament sizes of the heated NPC sheets for 10 min were 230 nm, 179 nm and 169 nm at 350 °C, 300 °C, and 250 °C respectively. The nanoporous structure was markedly denser. These results indicated that the ligaments were gradually coarsened by an increase of heat-treatment temperature because of accelerating surface diffusion of Cu atoms during heat treatment.

The nanoporous Cu sheet was applied as an insert metal for bonding between Cu disks. A thermo-compression

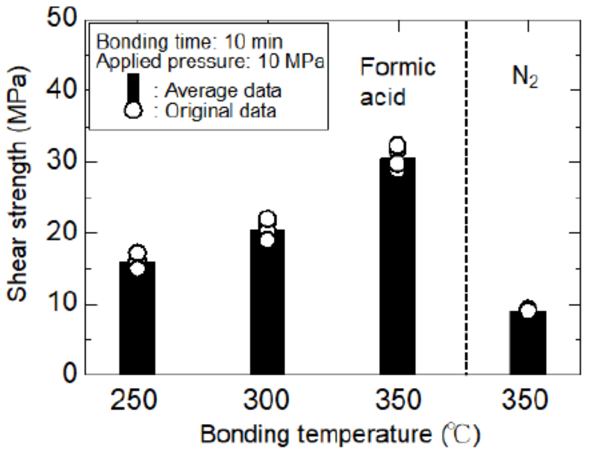


Fig. 4 Shear strength of NPC joints between Cu disks formed in N2 or formic acid atmosphere at various bonding temperatures for 10 min.

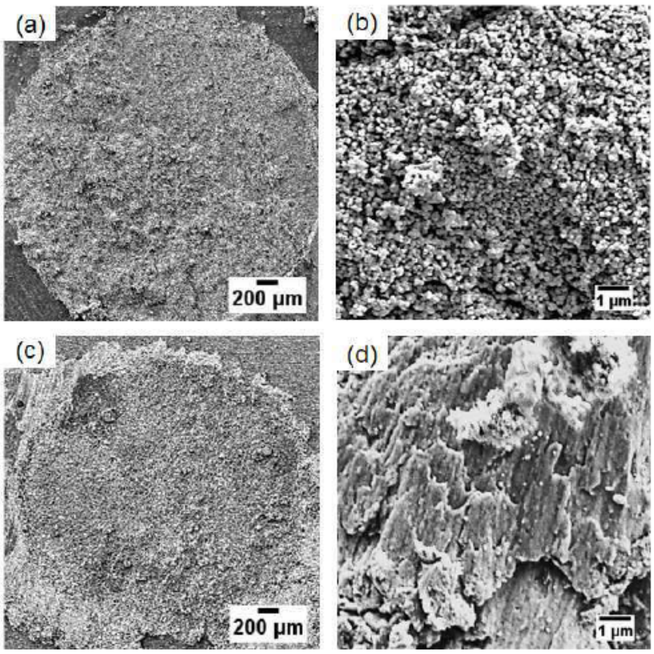


Fig. 5 Fracture morphologies after shear test for NPC joints on Cu disk at 350 °C for 10 min formed under (a and b) N2 and (c and d) formic acid atmospheres.

bonding system was used to achieve a joint at 350, 300 and 250 °C for 10 min in N2 or formic acid atmosphere. The applied pressure was 10 MPa. The shear strength of NPC joints is shown in Fig. 4. In the case of formic acid atmosphere, the shear strength of the NPC joint on Cu disk formed at 250 °C was approximately 16 MPa, and it gradually increased with increasing bonding temperature up to 30 MPa at 350 °C. The shear strength bonded at 350 and 300 °C in formic acid atmosphere exceeded the shear strength of conventional Pb–5Sn solder joints which was approximately 18 MPa. On the other hand, in the case of N2 atmosphere, the shear strength of the NPC joint on Cu disk formed at 350 °C was only around 9 MPa. The results revealed that the shear strength of NPC joints obtained in formic acid atmosphere is much higher than that of NPC joint obtained in N2 atmosphere. Fig. 5 shows fracture morphologies after the shear test of NPC joints under different atmospheres. Differences in the fracture morphologies between NPC joints under different atmospheres were confirmed by SEM analysis. As shown in Fig. 5, the fracture morphology of NPC joint under N2 atmosphere consisted of porous morphology after shear test. In contrast, the fracture morphology of NPC joint under formic acid atmosphere comprised dimple structure from the plastic deformation after shear test. These results indicated that the NPC joint under formic acid atmosphere was well bonded between NPC and Cu disk by reduction of oxidation layer of Cu.

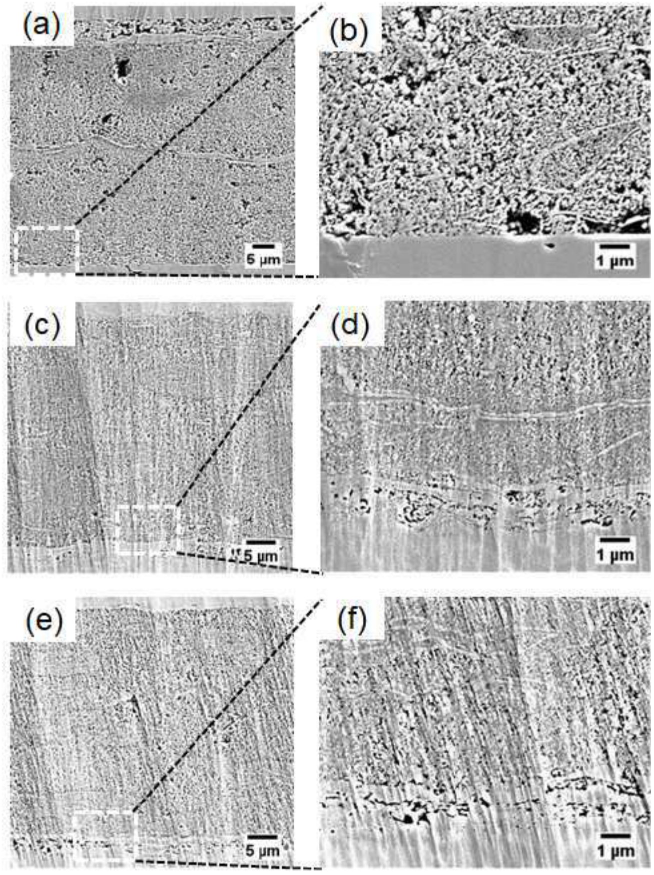


Fig.6 Cross-sectional SEM images of NPC joints formed under formic-acid atmosphere at (a) 250°C, (c) 300°C, (e) 350°C. And (b, d, f) High-magnification images marked by white squares from low-magnification images.

The shear test results revealed that the shear strength of NPC joints under formic acid atmosphere increased clearly with increase of the bonding temperatures from 250 ºC to 350ºC. Therefore, different microstructures of NPC layer with various bonding temperatures were supposed to observe by SEM. Fig. 6 shows cross-sectional images of NPC joints on the Cu disk formed at various temperatures for 10 min under formic acid atmosphere. As can be seen in Fig. 6, the NPC joint on the Cu disk formed at 250 °C were incomplete, and some voids in the NPC layer and gaps between the NPC sheet and Cu disk were observed. The NPC joint on the Cu disk formed at 300°C contained denser structure than low-temperature range at 250 °C that were associated with neck growth that led to the densification of the microstructure. Moreover, in the NPC joint on the Cu disk formed at 350°C, significant denser structure could be observed. The bonding temperature is critical to the formation of the NPC joints on the Cu disk because an appropriate bonding temperature accelerates the densification reaction of NPC layer by applying pressure as well as increase of the diffusion rate of

Cu atoms between the NPC sheet and Cu disk to achieve a robust NPC joint.

## IV. CONCLUSION

The bonding process using nanoporous Cu sheet formed from Mn-Cu precursor was investigated to achieve a Cu disk/Cu disk joint without solvent and flux. The morphology and XRD patterns of a self-oxidized NPC sheet confirmed the presence of a Cu2O film on its surface. The shear strength of the NPC joints on the Cu disk ranged between 9 MPa and 30 MPa, depending on the bonding environment. The shear strength of the NPC joints increased under a formic acid atmosphere as the oxide layer on the surface of the NPC sheet was reduced by formic acid, facilitating the diffusion of Cu atoms. It means the surface nanostructure of nanoporous Cu sheet can enhances rapid surface diffusion of Cu atoms as well as the local plastic deformation.

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