Low-Temperature Cu-Cu Bonding Using Spark Plasma Sintering System*

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Diffusion bonding of Cu bars without high vacuum and super-flatening bonding surface was investigated using spark plasma sintering (SPS) system for low-cost Cu-bulk-joint products. Oxygen-free Cu bars were set in graphite jigs, and were moderately compressed due to thermal expansion difference between graphite and Cu. The bonding temperature was measured directly on the Cu bars using a thermocouple. Tensile strength of the Cu-Cu joints increased gradually with increasing bonding time up to 30 min at 350°C and 400°C (respectively, 0.46 and 0.5 T_m , where T_m is Cu melting temperature), and achieved to 25 and 33 MPa, respectively, which were about one order of magnitude lower than the tensile strength of base metals. While, the tensile strength for those bonded at 300°C for 60 min exhibited about 7 MPa. This suggests that the temperature is not enough for removing oxide scale at the Cu-bar surface and/or for enhancing Cu-atom diffusion.

Key Words: Copper, Diffusion Bonding, Spark Plasma Sintering, Tensile Strength, Electrical Resistivity

1. Introduction

Diffusion bonding is one of effective bonding methods for joint materials difficult to weld, such as ceramics, high-temperature metals, and high-conductive metals. Copper (Cu), for example, is one of high-conductive metals, and thus was applied to interconnects, a heat sink, and so on. With increasing temperature and applied stress during the diffusion bonding, a contact-surface area increases in early stage and the enhanced atom diffusion further increases the contact area. Quantitative analysis of solid state bonding was proposed by Nishiguchi et al.¹⁻⁴⁾. Generally, for Cu, diffusion bonding is conducted at 600-700°C to obtain bonding strength similar to that of the base metal. However, the high temperature enhances grain growth leading the strength decrease and high applied stress results in shape change. For specific purpose, the strength decrease and shape change were not desired, and thus low-temperature and low-applied-stress bonding of Cu bulk materials was developed^{5,6)}. The Cu-bulk joints with tensile strength similar to that of a base metal was obtained after bonding in ultra-high vacuum at about 500°C for 60 min and in condition of super-flatening bonding surface. The ultra-high vacuum and the bonding temperature could remove Cu oxide at the bonding surface and super-flatening bonding surface increased contact surface area even though the applied stress was relatively low. However, such the fabrication would take a high cost and this is for expensive products.

Spark plasma sintering (SPS) system is one of facilities for diffusion bonding methods. Direct heating of graphite jigs

produces reducing atmosphere in low vacuum. For example, Cu-Cu bonding using a SPS system was reported for 3-D packaging in a heat-resistant power-saving SiC chip⁷⁾. The finish-polishing of the bonding surface was used 0.05 μm silica. The Cu joints bonded at 200-300°C in the graphite die temperature exhibited plastic deformation and showed 100-270 MPa in a tensile strength, which is similar to that of base metals.

In this study, oxygen-free Cu bars were bonded using the SPS system at temperatures less than Cu recrystallization temperature ($\sim 400^\circ\text{C}$), and the temperature of the Cu-bar-sample surface was directly measured. The Cu-bar bonding surface was left as it was after mechanical milling, and the applied stress was introduced by the thermal expansion difference between Cu bars and graphite jigs. Thus, low-temperature and low-applied-stress Cu-Cu bonding was investigated in the condition of low vacuum and no super-flatening bonding surface. It would be applicable for low-cost Cu-bulk-joint products.

2. Experimental procedure

Oxygen-free Cu bars with the size of $3 \times 4 \times 20 \text{ mm}^3$ were prepared. The bonding surface ($3 \times 4 \text{ mm}^2$) of the Cu bar was left as it was after mechanical milling. Diffusion bonding of the Cu bars was conducted using a SPS system. Figure 1 shows a schematic illustration of the Cu-bars' position arranged in the SPS system. Two Cu bars were directly touched and held between upper and lower graphite punches in a graphite die, which have the inner trench with size and shape similar to the Cu bars. The vacuum pressure in the SPS chamber was about 5 Pa. Note that the compressive stress was not initially applied to the Cu bars, but the stress was increased gradually with increasing temperature due to thermal expansion difference between graphite and Cu.

*Received: 2014.11.28

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Fig. 1 A schematic illustration for position of Cu bars and a K-type thermocouple arranged in the SPS system.

The Cu bars were heated by applying a pulsed DC current to both the Cu bars and graphite jigs, and temperature of the Cu bars was directly measured using a K-type thermocouple installed through the hole in the graphite die. The bonding of Cu bars were conducted at 300°C, 350°C and 400°C for 5-60 min.

In order to evaluate the bonding area of the Cu-Cu joints, their electrical resistivity was measured by a four-point probe method at room temperature (RT). Also, to evaluate the bonding strength of the joints, tensile tests were conducted at RT at a strain rate of $1 \times 10^{-4} \text{ s}^{-1}$ in air. The resistivity measurements and tensile tests were performed using three different samples for each bonding condition. Cross-sectional observation around the bonding interfaces of the Cu-Cu joints was performed using a dual-beam scanning microscope with electron and focused gallium-ion beams (SEM/FIB) equipped with an electron backscatter diffraction (EBSD) analysis system. Cross-sectional planes including a Cu-Cu bonding interface were prepared by FIB (Fig. 2). Macroscopic observation of a fracture surface and elemental analysis of the surface and interface of the Cu-Cu joints were conducted using SEM equipped with energy dispersive X-ray spectroscopy (EDX).

Fig. 2 (a) A schematic illustration and (b) a FE-SEM image of FIB fabrication of Cu-Cu joints bonded using the SPS system for EBSD observation.

3. Result and discussion

The Cu bars were successfully bonded for all the bonding conditions, and no defects such as crack and bulge deformation at the interfaces were observed for all the joints, for example, one of Cu-Cu joints bonded at 400°C for 30 min in the SPS system is shown in Fig. 3. Difference of the Cu-Cu joint length before and after the bonding was negligibly small.

Fig. 3 Cu bars after pulsed electric-current bonding using SPS system at 400°C for 30 min.

Figure 4(a) shows dependence of the average tensile fracture stresses on bonding temperature and time for the Cu-Cu joints bonded using the SPS system. The error bars indicate the region between the highest and the lowest values. Most of the Cu-Cu joints bonded at 300°C were debonded during preparation for the tensile tests. One of the Cu-Cu joints bonded for 60 min could be tested, and exhibited relatively low bonding strength of about 7 MPa. In contrast, the Cu-Cu joints bonded at 350°C and 400°C exhibited relatively high bonding strength even for the shorter bonding time. Their tensile fracture stresses increased with increasing the bonding time up to 30 min, and reached the maximum values of 25 MPa and 33 MPa for them at 350°C and 400°C, respectively. The higher bonding temperature was, the higher the tensile fracture strength was. However, they are about

Fig. 4 Dependence of (a) average tensile fracture stresses and (b) electrical resistivities on bonding temperature and time for the Cu-Cu joints bonded using the SPS system.

one order of magnitude lower than that of base metals, and lower than those of Cu-Cu joints obtained in condition of ultra-high vacuum and super-flattening bonding surface (70-150 MPa in 350°C-400°C⁵⁾).

On the other hand, the electrical resistivity of the Cu-Cu joints exhibited about 1.8 $\mu\Omega\text{cm}$ as the bonding time was less than 30 min, and decreased to about 1.6 $\mu\Omega\text{cm}$ as the bonding time was 30 min or longer, regardless of the bonding temperature (Fig. 4(b)). The resistivity decrease suggests that the bonding area increases, and that it is necessary to take 30 min to obtain a sufficient bonding area. Similarly, tensile fracture stress achieved the maximum value as bonding time was more than 30 min. Note that increase of the bonding time increased the bonding area at the bonding interface. The rough bonding surface left as it was after mechanical milling was deformed by thermal stress due to thermal expansion difference between Cu bars and graphite jigs. While, resistivity change was not dependent on bonding temperature (Fig. 4(b)), although the bonding strength of the Cu-Cu joints was dependent on the bonding temperature. This suggests that creep deformation due to thermal stress did not vary with bonding temperature, but Cu diffusion difference change the further increase of contact area at the bonding interface. The Cu diffusion length at 400°C is one order magnitude longer than that at 350°C. See below for further details.

In order to characterize the bonding area, SEM/EBSD observation was performed. Figure 5(a) shows a cross-sectional SEM image around the bonding interface of as-received Cu bars which were glued with epoxy resin. Figures 5(b), 5(c) and 5(d) show cross-sectional SEM images of the Cu-Cu joints bonded at 400°C for 20 min, at 350°C for 30 min, and at 400°C for 30 min, respectively. Figures 5(a')-5(d') are EBSD images obtained for the same area as the SEM images (Figs. 5(a)-5(d)). The bonding interface glued has micro roughness of irregular rugged pattern after mechanical milling (Fig. 5(a)), and consisted of small Cu grains (Fig. 5(a')). After bonding at 400°C for 20 min, the irregular rugged pattern was compressed, and nonbonded parts decreased at the bonding interface (Figs. 5(b) and 5(b')). However, relatively large voids remained at the bonding interface, which is consistent with large electrical resistivity (Fig. 4(b)). Cu grain growth was also observed in most of Cu grains near the bonding interface, and some of them exhibited black-spot contrast in the EBSD image (Fig. 5(b')), indicating plastic strain introduced by compressive stress due to thermal expansion difference between the Cu bars and graphite jigs. On the other hand, after bonding for 30 min at 350°C and 400°C, the bonded area increased at the bonding interface, although relatively small voids remained (Fig. 5(c) and 5(d)). Thus, electrical resistivity of Cu-Cu joints decreased (Fig. 4(b)). Comparing the EBSD images

after bonding for 30 min at 350°C and 400°C (Figs. 5(c') and 5(d')), the Cu grain sizes increased with increasing the bonding temperature. These suggest that diffusion of Cu atoms increased as the bonding temperature increased from 350°C to 400°C.

Generally, recrystallization temperature is a kind of critical temperature which atoms has adequately long diffusion length. The longer diffusion length is, the larger of vacancy concentration is. The vacancy concentration is defined by n/N , where n and N are number of vacancies and atoms, respectively. The recrystallization temperature is believed to be a half of melting temperature (T_m). Figure 6 shows temperature dependence of vacancy concentration and diffusion length of Cu atoms, together with those of Al atoms for comparison²⁾. The Cu and Al atoms have similar vacancy concentration (about 2.5×10^{-8}) and diffusion length (about 1.0×10^{-1} nm/s) at $0.5 T_m$. While, diffusion length of Cu atoms at 350°C ($0.46 T_m$) was estimated to be 2.5×10^{-2} nm/s, which is a quarter of 1.1×10^{-1} nm/s at 400°C ($0.5 T_m$). This is not large enough for enhancing grain growth near the bonding interface (Fig. 5(c')), nor for increasing bonding strength. However, diffusion length increases drastically with temperature in this temperature region between 350°C and 400°C. In the SPS system, the Cu-Cu joint interface was heated by applying a pulsed DC current, and the interface achieved high temperature quickly and locally. This is why Cu-atom diffusion would be enhanced at

Fig. 5 Cross-sectional SEM and EBSD images around the bonding interface of (a), (a') as-received, (b), (b') bonded at 400°C for 20 min, (c), (c') bonded at 350°C for 30 min, and (d), (d') bonded at 400°C for 30 min.

Fig. 6 Temperature dependence of (a) density of vacancy and (b) diffusion length for Al and Cu. Diffusion length of pure elements is determined by their density of vacancy.

the joint interface locally even at temperatures lower than $0.5 T_m$, leading increase of bonding area at the interface.

Figure 7 shows fracture surfaces of the Cu-Cu joints bonded in the SPS system, with the as-received surface of the Cu bar for comparison. The as-received surface of the Cu bars exhibited liner irregularities with a spacing of about $10\mu\text{m}$ due to milling, which is consistent with cross-sectional SEM/EBSD images of the as-received Cu bars (Fig. 5(a) and 5(a')). In contrast, for the Cu-Cu joints after bonding at 300°C for 30 min which were debonded during preparation for the tensile tests, some parts of liner irregularities got out of shape (Fig. 7(b)). The irregular surface deformed during bonding due to thermal stress, but the stress and/or Cu diffusion were/was not enough for adequate bonding strength. Also contamination was observed in places at the irregular surface (Fig. 7(e)), suggesting formation of Cu oxides during the diffusion bonding at 300°C for 30 min.

After tensile tests at RT for the Cu-Cu joints bonded at 350°C and 400°C , as-received liner irregularities was crushed, and their convex portions changed to wavelike deforming portions, and almost of the bonding surface area was covered with the wavelike deforming portions (Fig. 7(c) and 7(d)). The contact area produced after bonding at 400°C for 30 min (Fig. 7(d)) was larger than that after bonding at 350°C for 30 min (Fig. 7(c)). High-magnification images of the wavelike deforming portions consisted of dimple pattern as shown by arrows (Fig. 7(f) and 7(g)). The dimple patterns became large with increasing bonding temperature (e.g. Fig. 7(g)). This suggests that increasing the surface and bulk diffusion at the interface with increasing bonding temperature led grain growth as well as increase of contact area. Deformation of larger grain produced larger dimple (See Fig. 5(c') and 5(d')). This can explain the higher bonding strength after bonding at 400°C (Fig. 4(a)).

Probably thermal stress during bonding was relatively low, but the stress focused at the convex portions at the bonding surface, leading creep deformation and increase of stress induced vacancies. At the lower temperature and higher stresses, the

Fig. 7 SEM images of as-received and fracture surfaces of the Cu-Cu joints (a) before bonding, (b) bonded at 300°C for 30 min, (c) bonded at 350°C for 30 min, and (d) bonded at 400°C for 30 min. (e), (f), and (g) High-magnification SEM images of the fracture surfaces taken from the specimens as (b), (c), and (d), respectively.

apparent activation volume for creep of Cu decreased with increasing stress and creep strain⁹⁾. Thus, creep deformation became difficult with increasing bonding time. While, the tensile fracture strength was significantly dependent on bonding temperature, suggesting thermal equilibrium vacancy could be dominant compared with the stress-induced vacancy.

Although the vacuum pressure in the SPS chamber was about 5 Pa, graphite jigs as well as the Cu bars were heated by applying a pulsed DC current to both of them, and thus, Cu-Cu joints would be under reduction atmosphere during bonding in the SPS system. In order to investigate oxidation at surface and interface of the Cu-Cu joints bonded in the SPS system, EDX analysis was conducted. Cross-sectional SEM images of the Cu-Cu joints bonded at 350°C for 30 min (Fig. 8(a)) and at 400°C for 30 min (Fig. 8(b)) are shown. The elemental profiles across the bonding interface along L1 and L2 lines in Fig. 8(a) and along the L3 and L4 lines in Fig. 8(b) are shown below Fig. 8(a) and 8(b), respectively. No obvious intensity increase was observed along the L1 and L3 lines (no void at the interface) for all elements,

Fig. 8 Elemental profiles across the bonding interface (a) along L1 and L2 for the specimen bonded at 350°C for 30 min, and (b) along L3 and L4 for the specimen bonded at 400°C for 30 min.

while there are intensity increase at the interface along the L2 and L4 lines for Cu and O, where Cu intensity decreased (indicating void existence). However, the Cu and O peak was higher in the void left side than that in the void right side, although Cu intensity decrease was uniform in all place of the void. This indicates that the Cu and O peak is attributed to edge effects related to the EDX-detector position. Thus, we concluded that no oxidation occurred at the surface and interface of the Cu-Cu joints bonded in the SPS system. The background intensity of the C profiles varied with the measured lines. This is probably deposition-amount difference of contamination at the sample surface. Cu does not react with C, and thus probably C during bonding does not have bad influence upon bonding strength.

4. Conclusions

Cu bars could be bonded using the SPS system at temperatures less than Cu recrystallization temperature ($\sim 400^\circ\text{C}$) in the condition of low vacuum and no super-flattening bonding surface. Their tensile fracture stresses increased with increasing the bonding time up to 30 min, and reached the maximum values of 25 MPa and 33 MPa for the Cu-Cu joints bonded at 350°C and 400°C, respectively. Thus, Cu oxide at the bonding surface could be removed even in low vacuum, when graphite jigs were heated

at more than 350°C. However, the tensile fracture stresses were lower than those of Cu-Cu joints obtained in condition of ultra-high vacuum and super-flattening bonding surface. Thus, bonding-surface roughness significantly affects the tensile fracture stress, i.e. increase of contact area at the bonding surface.

Acknowledgements

This study was financially supported by Special Budget Project of Japan Ministry of Education, Culture, Sport, Science and Technology (Collaborative Research Project of Advanced Materials Development and Integration of Novel Structured Metallic and Inorganic Materials). The authors would like to thank Masayoshi Kamai, Joining and Welding Research Institute, Osaka University, for his help in the SPS work.

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