Ishikawa et al.: Bonding Strength of Pressureless Cu Sinter Paste on Metal Surfaces (1/11)

1. Introduction

The trend towards higher energy efficiency and reduced consumption of resources has recently caused silicon carbide (SiC) to gain a foothold in several applications.[1, 2] These novel SiC power devices can operate at temperatures over 473 K. Conventional soldering is still used to bond these dies, but the trend towards higher junction temperatures exacerbates issues with, among others, solder fatigue.[3, 4] Therefore, die-bonding materials with improved thermal conductivity and tolerance towards peak thermal and cyclic stresses are required for newer-generation power modules. Silver sinter pastes (Ag pastes) offer high thermal conductivity as well as increased bonding reliability. These are currently being employed in power modules operating at high temperatures. However, Ag is a relatively expensive metal and most Ag pastes require the application of mechanical pressure-assisted sintering to ensure high-reliability bonding.[5, 6] This constraint may increase the cost of power module assembly, cause chip damage, and consequently reduce yield and throughput when compared with a pressureless die-bonding process. Copper, the cost of which is lower than silver, is promising as a raw material for die-bonding pastes. In addition, a recent study showed that sintered Cu achieved superior thermal cycle reliability compared with sintered Ag because sintered Cu had mechanical properties and fatigue properties superior to those of sintered Ag.[5] Some Cu sinter pastes (Cu paste) for sintering under pressureless bonding conditions have been proposed;[7, 8] however with these, the same issues as in Ag sinter pastes may arise due to the mechanical pressure-assisted bonding process. To overcome such problems, our groups have proposed a Cu paste that can be used to sinter under pressureless sintering condi-
tions.[9, 10] However, the bonding strength and bonding mechanism of Cu paste have been little investigated. To widely apply Cu pastes to power modules operating at high temperature, the effects of bonding performance factors (e.g., bonding strength and bonding microstructure after aging) on Cu sintered to various metallization layers at high temperature should be understood.

Molecular dynamics (MD) simulations have been widely used to study the sintering process of metal nanoparticles and to calculate diffusion coefficients between metallization layers. In particular, Dong et al. investigated the coalescence of Cu nanoparticles on Cu substrates, elucidating how temperature affects the coalescence of nanoparticles.[11] Iwasaki and Li et al. also studied the coefficients of diffusion between Cu and other metallization layers, and successfully reproduced their experimental observations.[12, 13] It is thus expected that studies of MD simulations concerning sintering of Cu nanoparticles on four different metallization layers (Ni, Cu, Ag, and Au) could be helpful for understanding the bonding mechanism of Cu pastes. These four metals were selected because they are commonly of interest as adhesive metal surfaces of power module parts such as chips and substrates. In this study, the MD simulation models with two different sized Cu (Cu nanoparticle, bulk Cu layer) were studied to predict the sintering behavior and bonding strength towards the Cu paste on the metallization layers. One is the nano-sized model with Cu nanoparticles on the bulk metallization layers, and the other is the bulk model with a bulk Cu layer and bulk metallization layers. The validity and effectiveness towards the two MD models were evaluated, comparing the experimental bonding strengths and interdiffusion behavior between the pressureless-sintered Cu layer and the metallization layers.

The purpose of this study was to clarify the bonding strength and interfacial microstructure of pressureless-sintered Cu on the top metallization layers of four metals (Ni, Cu, Ag, and Au) using two approaches: experiments and MD simulation. The bonding strength of Cu layers pressureless-sintered at 533 K on the metallization layers after aging at 573 K was investigated. The aging was conducted under H₂ atmosphere to remove the effects of oxidation of sintered Cu layer and the metallization layers. The shear strength of sintered Cu on the metallization layers was evaluated using a die shear test and fracture-surfaces were observed using confocal laser scanning microscopy. Scanning electron microscopy (SEM) as well as energy dispersive X-ray spectroscopy (EDX) were performed to characterize the bonding interfaces between the sintered Cu layer and the metallization layers. The evolution of the sintering process of the Cu nanoparticles on the metallization layers and the diffusion coefficients of a bulk Cu layer on the metallization layers, were explored using MD simulation.

2. Experimental

2.1 Evaluation of shear strength and analysis of interfacial microstructure

Sub-micron Cu particles within a range of 100 to 500 nm diameter were used to fabricate a Cu paste. The Cu paste was prepared by mixing the Cu particles with Terpineol (98.0%, Fujifilm Wako Pure Chemical Corporation, Japan) at a weight ratio of 88:12, respectively. Silicon (Si) resistor chips (2.25 mm × 2.25 mm, thickness 0.55 mm) with sputter-deposited plating were used in the present work. DBC substrates (39 mm × 32.5 mm, Heraeus Holding GmbH) comprising a 380 μm thick Al₂O₃ core and 300 μm oxygen free copper layers on the top and bottom sides of the Al₂O₃ were also prepared. The electroplating process on the surfaces of the DBC substrates was conducted at Uyemura Corporation. Table 1 lists the metallization layers of the Si chips and DBC substrates. Four different bonding samples were manufactured. The procedures for the die-bonding experiments are described in detail below. The Cu paste

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Table 1 Metal plating of Si chips and DBC substrates.

| Bonding materials       | Target metal surface for Cu sinter bonding |
|-------------------------|--------------------------------------------|
|                         | #1 Cu           | #2 Ni           | #3 Ag           | #4 Au           |
| Sputter-deposited       | Ti: 0.1 μm      | Ti: 0.1 μm      | Ti: 0.1 μm      | Ti: 0.1 μm      |
| plating of Si chip      | Ni*: 0.1 μm     | Ni*: 0.1 μm     | Ni*: 0.1 μm     | Ni*: 0.1 μm     |
| Electroplating of DBC   | None            | Ni*: 4 μm       | Pd: 0.5 μm      | Au*: 0.1 μm     |
| substrate               | (Bare Cu*)      |                 | Pd: 0.5 μm      |                 |
|                         |                 |                 | Ag*: 0.5 μm     |                 |

NOTE: Asterisks (*) indicate the top metallization layer of each plating.
was first stencil-printed on the DBC substrates with a stencil thickness of 80 µm using a stencil printing machine (E5 STS, EKRA). The Si chips were then mounted on the printed Cu paste using a die bonder (Datacon 2200 evo, BESI). The thickness of the Cu paste after die mounting was about 70 µm. Next, the Cu paste was pressureless-sintered at 533 K for 10 min in 100% H₂ gas (1,013 hPa) using an oven (SR0-700, ATV Technologie). The bonding samples were subsequently stored at 573 K for 1 h or 8 h in 100% H₂ gas as an aging test. After the aging test, die shear strengths were determined by die shear tests at room temperature using a shear tester (DAGE 4000, Nordson). The shear velocity was set to 100 µm/s. The shear height from the loading tip of the shear tool to the surface of the DBC substrate was set to 200 µm. Ten specimens were tested for each bonding condition. After the die shear tests, the fracture-surfaces were observed using confocal laser scanning microscopy (VHX-5000, Keyence). Before the die shear tests, the Si chips on the DBC substrates were used to analyze the sintered Cu layer underneath the Si chips and the DBC substrates. A cross-section of the bonded sample was prepared using an ion-milling polishing machine (IB19510CP, JEOL). SEM (LEO1530, Zeiss) inspection and EDX (X-Max N50, Oxford Instruments) measurements were used to characterize the sintered Cu layer and the bonding interfaces. The average porosity (ϕ) of the overall sintered Cu layers was determined by calculation of the fractions of sintered Cu area and voids area in three cross-section SEM images (Magnification: ×5000). In the four specific distances (0–2 µm, 2–4 µm, 4–6 µm, and 18–20 µm) from the bonding interface between the sintered Cu layer and the metallization layer, the porosity of the sintered Cu in the specific region was also calculated to investigate the dependence of porosity on the distance from the bonding interface. Here, the interfacial porosity (ϕ_int) in the regions 0–2 µm from the bonding interface was defined.

2.2 Three-point bending test

The three-point bending tests of pressureless-sintered Cu specimens were conducted to determine their mechanical properties. The procedures for the three-point bending tests are described in detail below. The Cu paste was first stencil-printed on an aluminum (Al) board. Next, the printed Cu paste on the Al board was pressureless-sintered under two different conditions at 533 K for 10 min and at 573 K for 8 h in 100% H₂ gas, respectively. The pressureless-sintered Cu specimens were subsequently detached from the Al board. For the obtained pressureless-sintered Cu specimens (10 mm × 3 mm, thickness 0.2 mm²), the three-point bending tests were conducted in air at 293 K using a bending machine (Model 5948, INSTRON). Five specimens were tested for each condition. The span L between fulcrum points was set to 3 mm. The curvature radius of the bending head and supports was set to 0.4 mm. The testing speed was set to 3.3 µm/s and each test was conducted until the specimen was completely broken. Bending stress σ and bending strain ε were calculated using equations (1) and (2),

\[ \sigma = \frac{3NL}{2wt^2} \quad \text{(1)} \]

\[ \varepsilon = \frac{6dt}{L^2} \quad \text{(2)} \]

where N is load, L is span, w is specimen width (3 mm), t is specimen thickness (0.2 mm), and d is the measured deflection. Young's modulus was then calculated from the slopes of the stress-strain curves.

2.3 Molecular dynamics simulations

The MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.[14] For the numerical study of sintering Cu, we considered Ni, Cu, Ag, and Au metallization layers with face-centered cubic (fcc) structures and lattice constants of \( a_{\text{Cu}} = 0.3615 \) Å, \( a_{\text{Ni}} = 0.3524 \) Å, \( a_{\text{Ag}} = 0.4086 \) Å, and \( a_{\text{Au}} = 0.4079 \) Å. Here the (111) plane was chosen as the surface plane because it had the greatest atomic density and was the most stable in a fcc structure.[15]

Figure 1 shows the simulation model for investigating the process of sintering Cu nanoparticles. A spherical crystalline Cu nanoparticle with 370 Cu atoms (about 1.9 nm in diameter) was constructed by cutting the Cu fcc-lattice, and then nine Cu nanoparticles were inserted...
between two metallization layers on the (111) plane. As the initial configuration of the Cu nanoparticles, the distance between the neighboring Cu nanoparticles, and the distances between the Cu nanoparticles and the metallization layers, were set to about 0.26 nm and about 0.32 nm, respectively. The vacuum domain (thickness 1.5 nm) was subsequently introduced above the upside metallization layer. Table 2 shows the size of the metallization layers on the MD calculations. In this study, the surface area of all the metallization layers was set to about 22 nm². Periodic boundary conditions (PBCs) were applied in all three orthogonal directions. To prevent translational motion in the simulation model, we fixed the position of atoms in the top two layers of the metallization region. Throughout this paper, the embedded-atom method (EAM) of Zhou et al. was applied to describe the interactions between atoms.[16] The cut-off radius ($r_\text{cut}$) of the interatomic interaction for the EAM potential was set to 1 nm, and the time step and the number of steps chosen were 2 fs and $1.0 \times 10^5$, respectively. During the simulations, temperature and pressure were kept at 573 K and 1 atm under the isothermal-isobaric (NPT) ensemble. A Nose-Hoover thermostat and Andersen barostat were applied to control temperature and pressure, respectively.[17, 18]

Next, the diffusion coefficients of the bonding structures with a bulk Cu layer and metallization layers were also evaluated using MD simulation. In the simulation model shown in Fig. 2, the bulk Cu layer on the (111) plane was stacked on the metallization layer with (111) plane. Table 3 shows the size of the bulk Cu layer and metallization layers. During the simulation, PBCs were applied in all directions. To prevent the simulation model from translational shifting, the positions of atoms in the two layers at the top of the bulk Cu region were fixed. The $r_\text{cut}$ and the time step were set to 1 nm and 2 fs. The simulation model was first equilibrated under the NPT ensemble for 400 ps ($2.0 \times 10^5$ steps) at 1 atm and 300 K; then the system was heated to 973 K to accelerate the diffusion of atoms. Next, the diffusion coefficient was calculated at 973 K for 2 ns ($1 \times 10^6$ steps). The intrinsic diffusion coefficients and interdiffusion coefficients were calculated using the following Einstein relation,[19];

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left( r_i(t) - r_i(0) \right)^2 \right\rangle$$

(3)

with,

$$\left\langle \left( r_i(t) - r_i(0) \right)^2 \right\rangle = \frac{1}{N} \sum_{i=1}^{N} \left\langle \left( r_i(t) - r_i(0) \right)^2 \right\rangle$$

(4)

where $N$ is the number of atoms, and $r_i(t) - r_i(0)$ represents displacement of the $i$-th atom from time 0 to $t$.

3. Results and Discussion

3.1 Shear strength and interfacial microstructure

The shear strength of Cu sintered on Ni and Cu layers increased with aging time, whereas that of Cu sintered on Ag and Au layers decreased with longer aging time. Figure 3 shows the average shear strength of the Cu sintered on the four different metallization layers as a function of the aging time at 573 K. The initial shear strengths were found to be 60 MPa on Ni, 54 MPa on Cu, 36 MPa on Ag, and 25 MPa on Au. The fracture mode of sintered Cu was cohesive failure within the layer of Cu sintered on the Ni and Cu layers, whereas that of sintered Cu was interface fail-

Table 2 Size of each metallization layer in the MD simulation.

| Metallization layer | Size               |
|---------------------|--------------------|
| Cu                  | 7.084 nm x 3.067 nm x 3.757 nm³ |
| Ni                  | 7.337 nm x 2.990 nm x 3.662 nm³ |
| Ag                  | 7.507 nm x 2.889 nm x 3.539 nm³ |
| Au                  | 7.493 nm x 2.884 nm x 3.532 nm³ |

Fig. 2 MD simulation model of the bonding structure with a bulk Cu layer and a metallization layer for calculation of diffusion coefficients.

Table 3 Size of a bulk Cu layer and a metallization layer in a MD simulation.

| Metal couple | Size of bulk Cu layer | Size of metallization layer |
|--------------|-----------------------|-----------------------------|
| Cu/Cu        | 3.985 nm x 4.090 nm x 5.009 nm³ | 3.985 nm x 4.090 nm x 5.009 nm³ |
| Cu/Ni        | 15.50 nm x 8.947 nm x 5.009 nm³ | 15.54 nm x 8.971 nm x 4.883 nm³ |
| Cu/Ag        | 7.527 nm x 4.346 nm x 5.009 nm³ | 7.507 nm x 4.334 nm x 5.662 nm³ |
| Cu/Au        | 3.985 nm x 4.601 nm x 5.009 nm³ | 3.996 nm x 4.614 nm x 5.652 nm³ |
ure at the interface between the sintered Cu and the Ag layer or Au layer both for the initial sintering and after aging (1 h, 8 h). Figure 4a and b show optical micrographs of the fracture-surfaces of Cu sintered on the bare Cu layer and on the Au layer for initial sintering. With the sintered Cu, the fracture mode was cohesive failure that remained all over the bare Cu layer. In contrast, a small amount of sintered Cu (the fracture mode of which was interface failure) remained on the Au layer as shown by circles of white broken lines in Fig. 4b. These two different fracture-surfaces on the bare Cu layer and on the Au layer, were similarly observed in corresponding samples aged for 1 h and 8 h.

The initial shear strength, the increase and decrease of shear strength after aging, and the fracture modes differed according to the kind of metallization layer. To elucidate these differences further, the porosity of Cu sintered on samples aged for 8 h were measured. Figure 5 shows the porosities of the layers of Cu sintered on the different metallization layers as a function of the distance from the bonding interface. In the regions about 20 μm from the bonding interface, the porosity was about 22±1% and remained unaffected by the kind of metallization interface. The porosities of sintered Cu/Ag and sintered Cu/Au markedly increased toward the bonding interfaces, and showed the highest values (33% on Ag, 37% on Au) at the regions near the bonding interfaces. The porosities of sintered Cu/Ni and Cu/Cu slightly changed toward the bonding interfaces, and showed values of 24% on Ni and 24% on Cu near the interfaces. Because the porosity near the bonding interfaces of sintered Cu/Ag and Cu/Au was high, their bonding interfaces became weak, which consequently caused interface failure (see Fig. 6a) and decrease of the shear strength. In contrast, because the porosities were almost constant over the entire sintered Cu layer for sintered Cu/Ni and Cu/Cu, there were no vulnerable regions at the interfaces, consequently cohesive failure of the sintered Cu layer occurred (see Fig. 6b). Table 4 shows the porosities and mechanical properties of sintered Cu under the initial bonding condition and after aging. It was found that the Young's modulus and bending stress markedly increased after aging. Hence, enhancing the mechanical properties of sintered Cu by aging seemingly led to increase of the shear strength of Cu sintered on the Ni and Cu layers.

To investigate the cause for the differences in porosities near each bonding interface, the bonding interfaces for the initial bonding and after aging for 8 h were analyzed using SEM/EDX. The porosity approximately 2 μm from
the bonding interface ($p_{\text{int}}$) was also measured. First, in the sintered Cu/Cu system, the sintered Cu included only elemental Cu, and the $p_{\text{int}}$ was 25%, as shown in Fig. 7a (a-1). After aging, the $p_{\text{int}}$ was hardly changed (24%) (see Fig. 7b b-1). Second, in the sintered Cu/Ni system, both the sintered Cu and Ni layers in the initial bonding interface were clearly segregated, and $p_{\text{int}}$ was 25%, as shown in Fig. 7c (c-1). After aging, the sintered Cu and Ni layers also did not change and were still segregated (see Fig. 7d d-1). The $p_{\text{int}}$ was 24% and hardly changed. No interdiffusion was observed between the sintered Cu layer and the Ni layer in the initial sintering or after aging. Third, in the sintered Cu/Ag system, the sintered Cu layer and the Ag layer also remained segregated around the initial bonding interface as shown in Fig. 7e (e-1). The $p_{\text{int}}$ was 30%, but after aging it had increased to 33%. The distribution of Ag atoms was more or less spread (see Fig. 7f f-1). The Ag and Cu atoms somewhat diffused into the reciprocal layers, which means that measurable interdiffusion occurred. Fourth, in the sintered Cu/Au system, the sintered Cu layer and the Au layer were almost segregated into two layers in the initial bonding interface shown in Fig. 7g (g-1). In this case, $p_{\text{int}}$ was 32%, but after aging increased to 37%. The distribution of the Au atoms spread noticeably

Table 4 Porosities and mechanical properties of sintered Cu.

| Sintering conditions | Porosity (%) | Young’s modulus (GPa) | Bending stress (MPa) |
|----------------------|-------------|-----------------------|---------------------|
| 533 K, 10 min        | 24 ± 1      | 13                    | 150                 |
| 573 K, 8 h           | 22 ± 1      | 38                    | 280                 |

Fig. 7 Porosity and EDX mapping of the Cu sinter-bonded on different metallization layers in the initial state and after aging for 8 h: (a, a-1) On initial bare Cu, (b, b-1) On bare Cu after aging, (c, c-1) On initial Ti/Ni, (d, d-1) On Ti/Ni after aging, (e, e-1) On initial Ni/Pd/Ag, (f, f-1) On Ni/Pd/Ag after aging, (g, g-1) On initial Pd/Au, and (h, h-1) On Pd/Au after aging. The porosity for the all initial samples and all aged (8 h) samples in the unaffected bulk region at 20 $\mu$m distance was 24±1% and 22±1%, respectively.
To analyze clearly the sintered Cu/Au interface, high-resolution SEM/EDX inspections were conducted, as shown in Fig. 8. The interfacial voids beneath some of sintered Cu bonded on the Au layer were clearly observed. The EDX results showed that Au and Cu atoms diffused noticeably into the reciprocal layers, which means that marked interdiffusion occurred. Hence, the increase of interfacial porosity in the sintered Cu/Ag and the sintered Cu/Au observed by experiment are seemingly due to atomic interdiffusion between the sintered Cu layer and the Ag or Au layer. Actually, it is widely accepted that such unequal interdiffusion (called the Kirkendall effect) causes the formation of interfacial Kirkendall voids in the Cu/Ag and Cu/Au systems.[20, 21] Thus, the interfacial voids observed in the sintered Cu/Ag and sintered Cu/Au are assumed to be Kirkendall voids.

### 3.2 Sintering of Cu nanoparticles in MD simulations

We closely investigated the sintering behavior of Cu nanoparticles on each metallization layer by employing the MD method. Figure 9 shows the results obtained with increasing simulation time. The atom-migration behavior of the Cu nanoparticles can be seen. First, the deformed Cu nanoparticles begin to connect (see figures at $t = 2$ ps in Fig. 9). This sintering behavior qualitatively agrees with that in previous work.[11] With further increase in the simulation time, the deformed Cu nanoparticles then filled the voids between other nanoparticles, and formed a distinctive sintered Cu structure with a constricted neck part (see figures at $t = 20$ ps in Fig. 9). In the sintered Cu/Cu and Cu/Ni systems (Fig. 9a and b), it can be seen that the shape of the sintered Cu is relatively stable against further increase in the simulation time (see figures after $t = 100$ ps in Fig. 9). No interdiffusion is observed in the Cu/Cu and Cu/Ni systems. In contrast, for the sintered Cu/Ag and Cu/Au systems (Fig. 9c and d), the neck area of the sintered Cu gradually gets narrower with increasing time, and the sintered Cu is eventually disconnected from the sintered Cu/Au system. The interdiffusion in these Cu/Ag and Cu/Au systems is also observed. The extent of interdiffusion in the Cu/Au system is apparently larger than that in the Cu/Ag system. Furthermore, the trend of the differences in the extent of interdiffusion on the MD simulations mostly agrees with that observed on the SEM/EDX analysis. Hence, the MD results suggest that the differences in the extent of inter-
diffusion seem to affect the sintering behavior of Cu nanoparticles and the stability of neck area of sintered Cu on each metallization layer. Let us now consider the relationship between the disconnection behavior of neck area in the sintered Cu/Au system on the MD simulations and the formation of interfacial voids, which are considered to be Kirkendall voids, observed in the Cu/Au system in Fig. 5 and Fig. 8. Note that the disconnection position on the MD simulation is the neck part within sintered Cu. The Au layer absorbs and keeps the partial sintered Cu detached from the neck of sintered Cu. Thus, this disconnection of neck within the sintered Cu seems to be caused by the rapid-unilateral diffusion of Cu atoms into Au layer. The disconnected space within the sintered Cu appears to become a permanent void because the one part of detached-sintered Cu does not attach to the other part of detached-sintered Cu again without some sort of external force. For the experimental result, the Kirkendall voids were observed beneath one part of the sintered Cu bonded on the Au layer (see Fig. 8). This position of Kirkendall voids is consistent with the position of disconnection within the sintered Cu observed on the MD simulations. Thus, the Kirkendall voids are also formed by the rapid-unilateral diffusion of Cu atoms into Au layer. Once the Kirkendall voids are formed, the Kirkendall voids permanently remain under little external force such as a pressureless sintering process with Si chip’s own weight. Hence, we assume that the disconnection process on the MD simulation presents the formation process of Kirkendall voids on the experiments.

### 3.3 Interdiffusion between sintered Cu layer and metallization layers

To quantitatively gain further physical insights into the interdiffusion phenomena at the interface between the sintered Cu layer and the metallization layers, we next calculated the intrinsic diffusion coefficients ($D_{\text{Cu}}$, $D_{\text{Metal}}$) and interdiffusion coefficients ($D_{\text{int}}$) using the MD simulations. The MD models with the bulk Cu layer and the bulk metallization layers were used.

The magnitude of $D_{\text{int}}$ describes the difficulty or ease of atomic interdiffusion at the interface. Here, the ratio of $D_{\text{Cu}}$ and $D_{\text{Metal}}$ is also calculated to clarify the presence of the unequal diffusion process at the interface. A large value for $D_{\text{Cu}}/D_{\text{Metal}}$ (or $D_{\text{Metal}}/D_{\text{Cu}}$) indicates the occurrence of unequal diffusion. Note that a large amount of Kirkendall voids could form at the bonding interface of a system with both large $D_{\text{int}}$ and large $D_{\text{Cu}}/D_{\text{Metal}}$ (or $D_{\text{Metal}}/D_{\text{Cu}}$).

Table 5 displays the intrinsic diffusion coefficients and the interdiffusion coefficients at 973 K obtained by the MD simulations. For comparison, relevant earlier experimental results are also listed.[22–24] The intrinsic diffusion coefficient of the Cu/Cu system is the same as the self-diffusion coefficient ($D_{\text{self}}$) of homogeneous Cu metal. The experimental $D_{\text{self}}$ of Cu was estimated using the Arrhenius equation (5) at 973 K and previous experimental data.[25]

$$D_{\text{self}} = D_0 \exp \left( - \frac{E_a}{RT} \right)$$

where $D_{\text{self}}$ is the self-diffusion coefficient of Cu at temperature $T$ (in K); $D_0$ is the pre-exponential factor; $E_a$ is the activation energy; and $R$ is the gas constant. We emphasize...
that the interdiffusion coefficient $D_{\text{int}}$ obtained using the MD simulations well reproduce the trend of the experimental observations: $D_{\text{int, Au/Cu}} > D_{\text{int, Ag/Cu}} > D_{\text{self, Cu/Cu}} > D_{\text{int, Ni/Cu}}$. Furthermore, the trend of the differences in the extent of interdiffusion on this MD simulations with bulk size also mostly agrees with that obtained on the MD simulations with Cu nanoparticles. Two different sized MD simulations presented in this study are able to account for the diffusion behavior of the experiments, and are thus considered to be valid and of sufficient quality.

Here, we discuss the porosity of sintered Cu on four different metallization layers, focusing in particular on the magnitude of $D_{\text{int}}$ and $D_{\text{Cu/Metal}}$ (or $D_{\text{Metal/Cu}}$). In the sintered Cu/Cu and Cu/Ni systems, interdiffusion seems hardly to occur because the interdiffusion coefficients of these systems are much smaller than those of sintered Cu/Au and sintered Cu/Ag systems (see Table 5). This implies that the small number of Kirkendall voids that arise in the sintered Cu/Ni system, even with the unequal diffusion characterized by the magnitude of $D_{\text{Cu}/D_{\text{Metal}}}$ (or $D_{\text{Metal/Cu}}$), is quite large in the sintered Cu/Ni system ($D_{\text{Cu}/D_{\text{Ni}}} = 39$). This could explain the lower interfacial porosity of the sintered Cu/Cu and sintered Cu/Ni systems in Fig. 7.

Let us next turn to the sintered Cu/Ag and Cu/Au systems. These systems show interdiffusion coefficients $D_{\text{int}}$ of larger magnitude than with the sintered Cu/Cu and Cu/Ni systems. It is therefore, expected that the atomic interdiffusion at the interface of the sintered Cu/Ag and Cu/Au systems would support the formation of Kirkendall voids. This would consequently increase the interfacial porosity of the sintered Cu on the Au or Ag layers, as was observed experimentally (see Fig. 5 and Fig. 7). It should also be mentioned that the magnitude of the unequal diffusion of the Cu/Ag system ($D_{\text{Cu}/D_{\text{Ag}}} = 1.7$) is greater than that of the Cu/Au system ($D_{\text{Cu}/D_{\text{Cu}}} = 1.2$). Hence a larger number of Kirkendall voids might be formed in Cu sintered on an Au layer. These results well explain why the interfacial porosity of Cu sintered on the Au layer was expected to be noticeably increased and why it was the highest value among all the metallization layers considered in this study (see Fig. 5 also). We thus conclude that the atomic interdiffusion characterized by $D_{\text{int}}$ and $D_{\text{Cu/Cu}}$ (or $D_{\text{Metal/Cu}}$) can affect the formation of Kirkendall voids, and thereby influence the interfacial porosity in sintered Cu.

In Fig. 10, we finally show the relation between the initial shear strength obtained experimentally and the interdiffusion coefficients calculated by the MD simulation. The interdiffusion coefficients are apparently correlated with the shear strength. Thus, the $D_{\text{int}}$ obtained in the MD simulations could be used as an index to find metallization layers that have strong adhesion to the sintered Cu layers.

4. Conclusions

In this work, the thermal stability of pressureless-sintered Cu bonded on four different metallization layers (Ni, Cu, Ag, and Au) was investigated experimentally and using MD simulation. The investigation results can be summarized as follows. With aging at $573 \text{ K}$, the shear strength of Cu sintered on Ni and Cu layers increased with time, whereas those of Cu sintered on Ag and Au layers decreased with time. Thus, Ni and Cu make suitable adhesive metallization layers for sintered Cu layers. The differences in shear strengths of Cu sintered on the different metallization layers in the initial bonding, and after aging, are explained by the porosity of the sintered Cu near the bonding interface. In the sintered Cu/Ni and Cu/Cu, the interfacial porosity hardly changed after aging. However, in the sintered Cu/Ag and Cu/Au, the interfacial porosity increased after aging, which decreased their shear strength. The porosity of sintered Cu at the bonding interface arises by the Kirkendall effect. The interdiffusion coefficients calculated in the MD simulations seem to be correlated with the shear strength of sintered Cu, and could be used as an index to find metallization layers suitable for bonding with sintered Cu layers. In this study, we focused on the thermal stability of the sintered Cu bonded on the metallization layers under $\text{H}_2$ atmosphere. Further studies are required for the thermal stability and the oxidation resistance of sintered Cu bonded on metallization layers under air atmosphere that would demonstrate feasibil-
ties of Cu sinter die-bonding pastes under an actual use environment of power device applications.

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