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A kinetic model of copper-to-copper direct bonding under thermal compression

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1. Introduction

Copper-to-copper direct bonding has been accepted to be the solution for the next generation of high-density interconnect technology [1], where the pitch of Cu bonds can be scaled down below 1 μm [2,2]. In 2016, Cu-to-Cu hybrid bonding was adopted as interconnects in CMOS image sensors due to its ultra-fine-pitch capability and low resistivity [4]. It was implemented in other high-end devices, such as integration of three-
dimensional integrated circuits (3D IC) and stacking of high bandwidth memory (HBM) [5]. Recently, technology of system-on-integrated-chips (SoIC) was launched [6,7] to combine the advantages of known good dies (KGDs) and 3D IC integration. Therefore, Cu-to-Cu direct bonding has become the key interconnects for devices with ultra-fine-pitch packaging.

Because Cu direct bonding is a state-of-the-art technology in the microelectronic industry, many researchers adopted different ways to accomplish the bonding process. With argon plasma bombardment, surface activation bonding (SAB) can bond two smooth Cu (roughness $R_q = 2 \text{ nm}$) surfaces at room temperature in ultra-high vacuum ($\sim 10^{-8}$ torr) [8,9]. To avoid the high cost of SAB equipment, Cu thermal compression bonding, also known as diffusion bonding, is widely accepted. This bonding process can be done in normal vacuum ($10^{-2} \sim 10^{-3}$ torr) or nitrogen ambient [10,11], while the bonding temperature is over 300°C. In order to lower the bonding temperature, forming gas (96% Ar + 4% H₂) treatment [12], light enhancement [13], and plasma pre-treatment [14] are commonly adopted methods.

Another way to lower the bonding temperature is to fabricate Cu surfaces with high diffusivity. Highly (111)-oriented Cu surfaces, which possess the highest surface diffusivity among the major crystallographic planes, were prepared by sputtering to lower the bonding temperature under 200°C [15]. Electrodeposition of (111)-oriented Cu films was reported, and shows promise due to its compatibility with the fabrication processes of microelectronic devices [16]. The (111)-oriented Cu films can be used to achieve low-temperature (150°C) Cu direct bonding [17]. Surface creep was proposed to account for the mechanism of low-temperature Cu-to-Cu direct bonding. However, there were no models to analyze the surface creep mechanism.

Before Cu diffusion bonding was introduced into microelectronic devices, diffusion bonding was widely used in many materials, such as alloys [18] and ceramics [19]. As a result, several bonding models have been published [20–25]. These models usually started from the morphology of bonding surfaces, and then discussed the plastic deformation and diffusion mechanisms. Those mechanisms were composed of bulk diffusion [26], grain boundary diffusion [27], power low creep [28], and surface diffusion, but did not mention the concept of surface creep. Because diffusion bonding temperature is usually at 0.5 ~ 0.8$T_m$, where $T_m$ is the melting point, and the surface roughness is measured in micrometers, the bonding mechanisms is complicated. With the consideration of all deformation and diffusion paths, bonding mechanism maps could be drawn [20,29]. Like deformation-mechanism maps [30], bonding mechanism maps show different regions based on bonding temperature, pressure and surface roughness. However, no bonding models have addressed the effect of surface orientation on the bonding time.

In this study, the diffusion bonding model is developed through the surface creep mechanism. Especially, low temperature Cu–Cu bonding becomes more and more important, because microelectronic devices, such as images sensors and memory chips, prefer to be joined at a low temperature. The bonding temperature should be lower than 300°C (0.1 ~ 0.25$T_m$), and the surface roughness ($R_q$) must be lower than 10 nm [12]. At that bonding temperature, surface diffusion is the dominant mechanism of atomic flux [31]. We correlate the four bonding parameters, including temperature, time, pressure, and surface roughness. The effect of surface orientation on the bonding model is through diffusivity. The purpose of this research was to focus on surface creep and give a simple bonding mechanism guideline for choosing bonding parameters.

2. A kinetic theory of Cu-to-Cu direct bonding

Copper direct bonding can be divided into several stages, and bonding interface and voids evolution are the key measurements in each stage [25,32,33]. In order to define the range of bonding model in this study, all stages are listed as below:

1. Initial contact of two very flat surfaces [34], and plastic deformation occurs at hills of the wavy surface [24].
2. Grain boundary formation connects two contacted surfaces, and surface creep leads to voids formation.
3. Migration of grain boundaries at bonding interface [12,35,36], and voids ripening [37].
4. Grain growth eliminates the bonding interface [38,39].

Flow chart of the 1st – 3rd stages is shown in Fig. 1.

The main driving force of the irreversible bonding process is the lowering of Gibbs free energy of the system under fixed temperature and external pressure, which can be separated into two parts below.

1. After first contact between the two “wavy” (not ideally even) surfaces, the residual free space between the two surfaces becomes topologically complicated empty (void) space in the system. The volume of the system can be shown as: \( V_{\text{total}} = V_1 + V_2 + V \), where \( V_{\text{total}} \) is the overall volume of the system, \( V_1 \) is the Cu volume at the top, \( V_2 \) is the Cu volume at the bottom, and \( V \) is the empty intermediate space. Thus, any decrease of this empty space during bonding corresponds to a decrease of the product \( pV_{\text{total}} \) and therefore represents the first driving force of bonding. Here, \( p \) is the external pressure.

2. After touching at the contact point, the atoms diffuse to proper sites and form a grain boundary to replace the two free surfaces. For example, a twist-type grain boundary forms between two (111) free surfaces upon contact. Usually, \( \gamma_{\text{GB}} \) is smaller than \( 2\gamma_{\text{surf}} \) [40,41], where \( \gamma_{\text{GB}} \) is grain boundary energy and \( \gamma_{\text{surf}} \) is surface energy. Thus, the change of interfacial energy during bonding...
Bonding conditions published in literatures. The calculated diffusivity on grain boundary (111) surface, effect diffusivity, and the value of $\sqrt{\text{D}_{\text{GB}}t}$ are also listed.

| Bonding condition | Ref. | Surface orientation | Temp. (°C) | Pressure (MPa) | Time (min) | Surface roughness $R_q$ (nm) | Grain boundary $D_{\text{GB}}$ | (111) Surface $D_{(111)}$ | Effective diffusivity $D_{\text{eff}}$ ($\mu$m) |
|-------------------|------|----------------------|------------|---------------|-----------|-----------------------------|----------------|----------------|--------------------------|
| 1                 | [47] | (111): 40%           | 300        | 90            | 0.17      | 5                           | $4.3 \times 10^{-10}$ | $1.5 \times 10^{-4}$ | $7.7 \times 10^{-7}$  | 0.28                     |
| 2                 | [15] | (111)                | 200        | 0.78          | 30        | 3.2                         | $1.0 \times 10^{-11}$ | $9.5 \times 10^{-4}$ | $2.9 \times 10^{-10}$ | 0.38                     |
| 3                 | [17] | (111)                | 200        | 0.69          | 30        | 6.5                         | $1.0 \times 10^{-11}$ | $9.5 \times 10^{-4}$ | $2.3 \times 10^{-10}$ | 0.38                     |
| 4                 | [17] | (111)                | 250        | 0.69          | 10        | 6.5                         | $7.9 \times 10^{-11}$ | $1.2 \times 10^{-4}$ | $7.5 \times 10^{-10}$ | 0.42                     |
| 5                 | [17] | (111)                | 150        | 0.69          | 60        | 6.5                         | $7.9 \times 10^{-11}$ | $6.9 \times 10^{-4}$ | $1.0 \times 10^{-4}$ | 0.47                     |
| 6                 | [36] | (111)                | 230        | 81            | 4         | 5.12                        | $7.9 \times 10^{-11}$ | $1.2 \times 10^{-4}$ | $3.8 \times 10^{-4}$ | 0.49                     |
| 7                 | [48] | (111): 40%           | 146        | 64            | 20        | 5                           | $6.2 \times 10^{-13}$ | $6.7 \times 10^{-4}$ | $6.7 \times 10^{-9}$ | 0.60                     |
| 8                 | [38] | (111)                | 250        | 0.78          | 15        | 4.7                         | $7.9 \times 10^{-11}$ | $1.2 \times 10^{-4}$ | $6.4 \times 10^{-7}$ | 0.95                     |
| 9                 | [13] | Random               | 230        | 10            | 5         | 3.1 ($R_q$)                 | $3.6 \times 10^{-11}$ | $1.1 \times 10^{-4}$ | $1.2 \times 10^{-8}$ | 1.54                     |
| 10                | [39] | (111)                | 150        | 40.6          | 20        | 5.12                        | $7.9 \times 10^{-11}$ | $6.9 \times 10^{-4}$ | $1.2 \times 10^{-4}$ | 2.08                     |
| 11                | [12] | Random               | 175        | 1.7           | 30        | 1.05                        | $3.0 \times 10^{-12}$ | $8.1 \times 10^{-4}$ | $1.6 \times 10^{-11}$ | 3.77                     |
| 12                | [49] | Random               | 300        | 0.4           | 30        | 1.1                         | $4.3 \times 10^{-10}$ | $1.5 \times 10^{-5}$ | $1.1 \times 10^{-10}$ | 8.80                     |
| 13                | [44] | Random               | 300        | 0.7           | 60$^*$    | 5.3                         | $4.3 \times 10^{-10}$ | $1.5 \times 10^{-5}$ | $4.0 \times 10^{-7}$ | 12.4                    |

The abbreviations of “Reference” and “Temperature” are “Ref.” and “Temp.,” respectively.

- a Grain growth has happened.
- b Annealing at 200 °C, 1h.
- c Light enhanced Cu direct bonding.
- d Two-step plasma treatment.
- e Post-annealing at 200 °C, 0.02 MPa, 1h.
- f Taking average temperature.
- g Taking larger roughness.

$(\gamma_{GB} - \gamma_{surf}) \cdot \Delta A_{\text{contact}}$ is negative and favorable, where $\Delta A_{\text{contact}}$ is positive, showing an increase of the contact interface, and $\Delta A_{\text{contact}}$ is the variation of contact area. Thus, $(\gamma_{GB} - \gamma_{surf}) \cdot \Delta A_{\text{contact}}$ represents the second driving force, which is often called capillary force.

On the other hand, the main driving forces for atomic flux are the stress gradient and Gibbs Thomson capillary effect. According to reference [20], the driving forces for atomic diffusion can be divided into three sources:

1. Source from surface of voids: difference of surface curvature, but retarded when the voids have uniform curvature.
2. Source from bonding interface: the bonding pressure gradient and bonding neck curvature.
3. Source from bulk deformation: the bonding pressure leads to plastic deformation at the beginning of bonding, which is the 1st stage in Fig. 1.

The Gibbs Thomson capillary effect of the surface curvature and the bonding pressure gradient coexist all the time during bonding process. However, some high diffusivity surfaces, such as FCC (111) surfaces, which significantly reduces the bonding temperature or time, was not taken into consideration in literature. Therefore, this study aims to focus on the bonding stress gradient to develop a bonding model, and to estimate the bonding time using FCC (111) surfaces. The results indicate that if the bonding surface is wavy with nanometer-scale (<10 nm) surface roughness, the capillary force might not be able to influence the bonding time obviously.

In Fig. 1, during the 2nd stage of the bonding processes, only pressure gradient is taken into consideration for Cu atoms diffusion, which starts from increasing contact areas by surface diffusion and then forming metal bonds by grain boundary diffusion. Certainly, there will be an ambiguous demarcation of the surface and grain boundary diffusion, so there will be an effective driving force between them. In the 3rd stage of the bonding processes, Gibbs Thomson capillary effect will lead to a ripening of voids. In this study, bonding processes at the 2nd stage will be discussed, and theoretical bonding time will be calculated.

In actual samples, the bonding interface has multiple contact points, and the surface morphology is assumed as sinusoidal curves, as shown in Fig. 2(a). For simplicity, the model will start from a single contact, as depicted in Fig. 2(b), where two curved surfaces of a large curvature radius (R) are forming an interface of radius (r), and r is much smaller than R. The complete bonding process stops when r reaches $r_{\text{max}}$. In this case, the maximum value of $r_{\text{max}}$ is the radius of the single contact. Critically, bonding proceeds only due to the squeezing of atoms from the compressed contact interface of radius (r) to the free surfaces outside the contact interface. The distance (h) to the curvature center decreases and the contact radius (r) increases. Thus, dh is a change of distance from the contact spot to the curvature center. It means that the decreasing volume $\Delta V = -r\pi^2 \times 2dh$ is being squeezed out from the contact interface via surface or grain boundary diffusion driven by the gradient of stress. The stress gradient $\Delta p$, see Fig. 2(a), is assumed to be zero outside the contact area at the free surface, but in the center, it is $p^c = p(r/r_{\text{max}})^2$, which $p^c$ is the effective pressure on the contact area. Because the contact area is minuscule, the distribution of effective pressure is assumed to be a constant. Therefore, the conservation of matter gives:
\[ \Delta V = JAt\Omega = (CMF)At\Omega = \left( \frac{D}{kT} \frac{\Delta p\Omega}{\Delta x} \right)At\Omega \]  

(1)

\[ \Delta V = -\pi r^2 \times 2dh \approx \left[ \frac{D}{kT} \left( \frac{\rho_{\text{max}}^2}{r^2} \Omega - 0 \right) \right] \times (\delta \times 2\pi) \times dt \]  

(2)

\[- \frac{r^2}{r_{\text{max}}^2} \cdot dh = \frac{\Delta D}{kT} p\Omega dt. \]  

(3)

where \( J \) is the atomic flux caused by bonding pressure, \( A \) is the total area of atomic diffusion path, \( t \) is the theoretical bonding time, \( \Omega \) is Cu atomic volume, \( C \) is the concentration of Cu and \( C = \frac{1}{\omega} \), \( M = D/kT \) is the mobility, \( D \) is the effective diffusivity of combining surface or grain boundary diffusion, \( k \) is the Boltzmann constant, \( T \) is the bonding temperature, \( \rho_{\text{max}}^2 / r^2 \Omega - 0 \) is an energy difference between the atoms at the already formed contact and the atoms at the still free internal surfaces, \( F = \{ \rho_{\text{max}}^2 / r^2 \Omega - 0 / r \} \) is an average squeezing force per atom, \( J = C(D/kT) \{ \rho_{\text{max}}^2 / r^2 \Omega - 0 / r \} \) is a rough estimate of squeezing outflux. \( \delta \) is the effective thickness of the atomic diffusion path.

In Fig. 2(b), by taking \( r = R \sin \phi = R\phi, h = R \cos \phi = R \cdot [1 - (\phi^2 / 2)], dh = -R\phi d\phi \), Eq. (1) can be derived as:

\[ \frac{R^3}{\rho_{\text{max}}^6} \phi^5 d\phi = \frac{\Delta D}{kT} p\Omega dt. \]  

(4)

Integration of Eq. (3) from the start to the full bonding gives:

\[ \int_{\phi=0}^{\phi_{\text{max}}} \frac{R^3}{\rho_{\text{max}}^6} \phi^5 d\phi = \int_{t=0}^{t_{\text{bonding}}} \frac{\Delta D}{kT} p\Omega dt \]  

(5)

\[ \frac{R^3}{\rho_{\text{max}}^6} \phi_{\text{max}}^6 = \phi_{\text{max}}^3 \frac{\Delta D}{kT} p\Omega t_{\text{bonding}}. \]  

(6)

Thus, the theoretical bonding time (\( t_{\text{bonding}} \)) starting from the single touching point to a complete bonding is:

\[ t_{\text{bonding}} \approx \phi_{\text{max}} \frac{R^3}{\rho_{\text{max}}^6} \frac{kT}{\Delta D} \frac{\rho_{\text{max}}^3}{p\Omega}. \]  

(7)

Since \( r_{\text{max}} \) is difficult measure, it should be transformed into surface roughness (\( R_q \)). In reference [42], the relationship of surface roughness and wave length (\( \lambda \)) of the sinusoidal curves is:

\[ \frac{R_q^2}{\lambda} \leq 2(1 - \rho^2)W_A \]  

(8)

where \( \rho \) is Poisson’s ratio, \( E \) is Young’s modulus, and \( W_A \) is bonding energy of the bonding interface. At room temperature, \( W_A \) of Cu is \(-3\) J/m\(^2\) [43], E of Cu is \(-130\) GPa, and \( \rho \) of Cu is 0.35 [44]. If \( r_{\text{max}} = \lambda / 4 \), the relationship of \( R_q \) and \( r_{\text{max}} \) can be shown as:

\[ R_q \leq 2.7 \times 10^{-6} \text{m} \times \sqrt{r_{\text{max}}}. \]  

(9)

So, Eq. (7) can be changed into:

\[ t_{\text{bonding}} \approx (7.3 \times 10^{15} \text{m}^{-1}) \times \frac{R_q^6}{\rho_{\text{max}}^6} \frac{kT}{\Delta D} \frac{\rho_{\text{max}}^3}{p\Omega}. \]  

(10)

The maximum angle \( \phi_{\text{max}} \) can be assumed about 1 rad. However, it is difficult to obtain an estimated value for the combined effect of surface diffusion and grain boundary diffusion. At higher bonding temperatures, grain boundary formation will be much faster than that at low temperatures. Furthermore, the surface orientation will influence the surface diffusivity [45], and the diffusivity also depends on the type of grain boundary. For instance, the diffusivity of (111) surfaces is at least 3 orders larger than that of other surfaces [17], and (111) surfaces will form a twist type grain boundary where diffusivity is about ten times smaller than a large angle tilt type grain boundary [46]. Hence, effective diffusivity \( D_{eff} \) of different bonding temperatures needs to be obtained from experimental results.

3. Experimental

Based on previous studies [13–15,17,36,38,39,47–49], a summary of Cu direct bonding conditions through thermal
compression bonding is shown in Table 1. Those successful bonding parameters were proved by microstructures or reliability tests. In this table, a bonding temperature of the (111) surface could be lower than 300°C without any process enhancement, such as forming gas, plasma pretreatment, or light enhanced bonding. Nonetheless, the bonding pressure should be larger for non-vacuum ambient or a lower (111) surface ratio (40%). For regular Cu surfaces with a very flat

Fig. 4 – Cu direct bonding results and the void distribution at bonding interface. The bonding condition was 300°C/90 MPa/10 s. (a) Electron and (b) ion images of the cross-section of Cu microbump. (c) The TEM sample of bonding interface, which was cut at the red rectangle of (a). White arrows point out voids in the bonding interface. (d) The enlarged image of red square of (c). (e) Voids in image (d) are emphasized by red marks. (f) Distribution of void diameters in image (d).
surface ($R_q \approx 1 \text{ nm}$), the lowest bonding temperature, pressure, and time was 300°C, <1 MPa, and 30 min, respectively.

Surface morphology of our Cu film was analyzed by atomic force microscope (AFM). Chemical mechanical planarization (CMP) was adopted to polish the as-deposited Cu surface, and the AFM scanning area ($1 \mu m \times 1 \mu m$) was split into a smaller area ($1 \mu m \times 0.4 \mu m$) to show the cross-section profile (blue solid line) in Fig. 3(b).

Another important criterion of the endpoint of bonding is the ratio of the bonding area, which could be estimated by the Greenwood and Williamson (GW) model [34]. The bonding area could affect the contact resistance and mechanical properties, and these properties might cause different failure mechanism during reliability tests [24,35]. However, in Eq. (10), surface morphology was simplified by sinusoidal waves. Consequently, in the present study, the bonding area was observed by transmission electron microscope (TEM), and the TEM sample was cut at the bonding interface, which was indicated by a red square in Fig. 4(a).

The thickness of the sample was about 100 nm, so the voids at the bonding interface could be identified by STEM images. The void distribution and average void sizes were measured using ImageJ software, and the bonding area can be known by deducting the area of voids.

4. Results

4.1. Surface morphology for Cu direct bonding

The $R_q$ of the entire area ($1 \mu m \times 1 \mu m$) in Fig. 3(a) is 3.37 nm, but the smaller area ($1 \mu m \times 0.4 \mu m$) in Fig. 3(b) is 0.81 nm. The cross-section profile is not as smooth as the sinusoidal curves, and the wave can be represented with a red dash curve. There are two periods of waves in Fig. 3(b), so the wave length $\lambda$ is about 365 nm, indicating that the $r_{max}$ is about 91.3 nm. Hence, from Eq. (9), the $R_q$ is about 2.2 nm. The reason of the discrepancy of AFM results and Eq. (9) is that the elastic energy per unit area is smaller than the bonding energy ($W_A$), so the 2.2 nm of $R_q$ is the maximum value. Obviously, the surface profile is not a periodic sinusoidal wave, and Eq. (8) is a one-dimension model. According to reference [42], a two-dimension model has been derived, but it was impossible to combine the actual surface and the model together. In order to simplify this problem, a one-dimensional model was adopted.
4.2 The ratio of bonding area

The bonding interface is pointed out by the white arrows in Fig. 4(a) and (b). There are no voids in the SEM image of Fig. 4(a). Because of the short experimental bonding time of 10 s, no grain growth happened at the bonding interface, which could be clearly verified in the ion image of Fig. 4(b). Figure 4(c) shows the TEM image of low magnification on the bonding interface. There are a few voids (white color) which are pointed by white arrows. Figure 4(d) illustrates the enlarged TEM image of the red square in Fig. 4(c). Some voids can be clearly observed. The voids are marked in red color in Fig. 4(e), and the void size distribution is shown in Fig. 4(f). The average void size is 37.6 nm, while the voids smaller than 20 nm in size could not be verified. In Fig. 4(e), the ratio of the voids area is roughly 2.6%, so the ratio of the bonding area is larger than 95% at the end of the 2nd stage bonding. The voids evolution of diffusion bonding at the bonding interface have been discussed in reference [50]. The interface bonding ratio ranged from 36% to 98%, which is similar to the results from Fig. 4. The total volume of voids shrank during the bonding process, and the reduction of empty space could diffuse through the bonding interface to the free surface.

5. Discussion

5.1 Bonding mechanism of the 2nd stage

The illustration of the 2nd stage bonding mechanisms is shown in Fig. 5. At the beginning, two smooth Cu surfaces with nanometer-scale contact at hills, see Fig. 5(a). The surfaces can be considered as stairs of several layers of atoms. During thermal compression bonding, the atoms move at contact points and on the free surfaces. Layers of atoms are squeezed out and the contact points are extended to the free surfaces through surface diffusion (Fig. 5(b) and c). After a period of time, partial contact surfaces change into grain boundaries, with both continuously expanding until the bonding area is larger than 95%, see Fig. 5(d)–f. When grain boundaries form in the 2nd stage, grain boundary diffusion will participate in the bonding interface. Therefore, the diffusion of Eq. (10) is the combination of surface and grain boundary diffusion, and the 2nd stage ends when bonding pressure of the contact surface is not the major driving force of atomic diffusion at the bonding interface. In the next stage of void ripening is the Gibbs–Thomson effect, thus, the voids will become lenticular [51].

5.2 Effective diffusivity of our bonding model

In order to examine the effects of surface and grain boundary diffusion in the 2nd stage bonding, the theoretical bonding time of Eq. (10) is calculated with grain boundary diffusivity (D_{GB}) and surface diffusivity at (111) surface (D_{111}), respectively. Bonding conditions of experimental data, D_{GB} and D_{111} at bonding temperature are listed in Table 1. The Cu surfaces in reference [15,17,36,38,39] are highly (111)-oriented surfaces (> 90%). Yet the Cu surfaces in reference [47,48] are moderately (111)-oriented surfaces (40%–50%), and Cu surfaces in reference [12–14,49] are randomly oriented Cu surfaces. From bonding conditions in Table 1 and Eq. (10), Fig. 6 shows the bonding time of experimental results (111) surface diffusion (t_{111}), and grain boundary diffusion (t_{GB}). Theoretical bonding time of t_{111} is at least 5 orders smaller than t_{GB}. For (111) surface bonding, the calculated value of t_{111} is close to the experimental data. Therefore, surface diffusion on (111) surface can dramatically decrease the bonding time. For moderately (111)-oriented Cu surfaces, the experimental bonding time is between t_{111} and t_{GB}, and is about 2–3 orders of magnitude larger than t_{111}.

On the contrary, if the bonding surface has random orientation, t_{GB} is close to the experimental value, which indicates that the rate-limiting step of bonding is grain boundary diffusion at the bonding interface. In Table 1, the bonding atmosphere of reference [12] was forming gas (96% Ar+4% H₂) Post-annealing at 200°C for 1 h was conducted after the first bonding process. Light enhanced bonding and two-step plasma pre-treatment were done in references [13,14], respectively. Due to the surface activation pre-treatment, the experimental bonding time can be about 3 orders of magnitude smaller than t_{GB}. In Fig. 6, the number 12 of bonding condition emphasizes the data of reference [49], in which the experimental bonding time is almost the same as t_{GB}. In that study, two Cu films were bonded in normal vacuum without controlling surface orientation and surface pre-treatment. Hence, the bonding time would be determined by the grain boundary diffusion at the bonding interface.

![Fig. 6 – Comparison of experimental results and theoretic calculation. Histogram shows the experimental bonding time of various bonding conditions in previous studies, which is listed in Table 1. The order of the bonding condition follows the value of $\sqrt{D_{p1}}$. The surfaces in conditions 1–8, and 10 are (111)-oriented, and the rest of the conditions adopted random Cu surfaces.](image-url)
The $D_{\text{eff}}$ is calculated by the experimental bonding time, and is listed in Table 1. For Cu direct bonding of (111) surface, the value of $D_{\text{eff}}$ is close to the value of $D_{(111)}$, instead of $D_{\text{GB}}$. It indicates that the (111) surface diffusion can be the dominant bonding mechanism. When the ratio of (111) surface raises to about half of surface area, the $D_{\text{eff}}$ is close to geometric average value of $D_{\text{GB}}$ and $D_{(111)}$. Therefore, the bonding mechanism is the combination of surface and grain boundary diffusion, but the surface diffusion effect is higher than the grain boundary diffusion. If the surface of Cu is randomly-oriented, the $D_{\text{eff}}$ is 1–3 orders larger than $D_{\text{GB}}$ for surface pre-treatment before bonding process, and is at the same order of magnitude without any pre-treatment. It is noteworthy to mention that oxides on the Cu surface may affect the surface diffusion significantly. In this study, we assumed the surfaces to be oxides free. It is reported that the Cu (111) surface have a lowest oxidation rate among all the crystallographic planes in Cu crystals [50]. Thus, the bonding temperatures or time duration using Cu (111) surfaces may be reduced due to the highest effective surface diffusivity.

5.3. Calculation of bonding parameters to the theoretical bonding time

For thermal compression bonding (TCB), bonding temperature, pressure, and time are three basic parameters. Without any surface pretreatment, such as plasma and light scan, surface roughness is the most important factor for TCB. In Table 1 and Fig. 6, several previous studies are introduced to confirm the calculation of Eq. (10), and the concept of $D_{\text{eff}}$ is

Fig. 7 – Calculation results of bonding model using Eq. (10) by using (111)-oriented surface diffusivity of Cu. When the roughness $R_q = 5$ nm, the theoretical bonding time changes with (a) bonding temperature and (b) pressure. If bonding temperature is 250 °C, the theoretical bonding time changes with (c) surface roughness and (d) bonding pressure.
employed to compare the effect of (111) and randomly-oriented Cu surface on bonding times. Then, the influence of bonding temperature, pressure, and surface roughness on theoretical bonding time can be predicted through the calculation of Eq. (10).

In Fig. 7 (111) surface diffusion was taken into consideration to show the relationships among bonding parameters and surface roughness. In Fig. 7(a), if $R_q = 5$ nm, bonding temperature did not decrease the theoretical bonding time more than one order for 100°C to 400°C. This is attributed to the high diffusivity on Cu (111) surfaces. The diffusivity is already as high as $6.9 \times 10^{-6}$ cm$^2$/s at 150°C. In Fig. 7(b) and d, bonding pressure could save about two orders of theoretical bonding time from 1 MPa to 100 MPa. Since the surface roughness in Eq. (10) was a sixth power term, the variation of theoretical bonding time in Fig. 7(c) was more than ten orders. The results indicate that surface roughness plays a crucial role in the theoretical bonding time. However, there was no significant difference for the theoretical bonding time lower than 1 s for TCB process, and it was impossible for the experimental bonding time to reduce below $10^{-13}$ s. For TCB of Cu direct bonding processes, the shortest experimental bonding time was approximately 10 s [47].

On the other hand, theoretical bonding time significantly depends on temperature when the grain boundary diffusion serves as the dominate diffusion mechanism. In Fig. 8(a), theoretical bonding time could be dramatically reduced by more than five orders, which is much more sensitive to bonding temperatures than the (111) surface diffusion. However, the influence of bonding pressure on theoretical bonding...
times was about two orders, as shown in Fig. 8(b) and d, which was the same as (111) surface diffusion bonding. Similarly, surface roughness has a very large effect on theoretical bonding times for the sixth power term, see Fig. 8(c).

In Fig. 9, when $R_q = 5\, \text{nm}$ and $P = 1\, \text{MPa}$, the theoretical bonding time of (111) surface and grain boundary diffusion is compared for different bonding temperatures. Interestingly, the theoretical bonding time of (111) surface diffusion does not change much, but that of grain boundary diffusion can change more than five orders. It means that TCB through grain boundary diffusion is sensitive to the bonding temperature, but due to the limitation of theoretical bonding time, the bonding temperature needs to be over 300°C [49]. Additionally, surface orientation plays an important role in the low temperature bonding process [15], and the experimental bonding time should include the grain boundary formation and local grain boundary diffusion as shown in Fig. 5, which could modify the bonding time through $D_{\text{eff}}$.

5.4. The comparison between the two very flat surface bonding and the nanoscale materials bonding

In addition to the Cu-to-Cu direct bonding with two very flat surfaces, sintering or brazing Ag or Cu nanoparticles is another solution of low temperature diffusion bonding [52–54]. However, the bonding mechanisms are quite different due to the geometric bonding structures. In this study, we assumed that the $r \ll R$ for smooth surface, and bonding stress gradient is the driving force. Thus, a simple bonding mechanism can be used to estimate the bonding time. In contrast, the $R$ of the nanoparticles is much smaller. Due to the high surface-area-to-volume ratio (SAV) of nanoscale materials, surface diffusion is taken into consideration [54]. The Gibbs Thomson capillary effect is the main driving force of the surface diffusion in nanoparticles sintering or brazing. As a result, Eq. (10) is not suitable to estimate sintering or brazing time.

6. Conclusions

A surface creep model has been developed to examine relationships among bonding temperatures, pressure, orientation, surface roughness, and time. Surface creep is driven by the stress gradient, and we proposed that both surface and grain boundary diffusion contribute to the bonding at the interface. During the 2nd stage of bonding, the rate of surface diffusion and the time of grain boundary formation are the two critical issues of the bonding mechanism. The end of bonding is defined as the moment when the bonding ratio is over 95%, which was observed through TEM images. For randomly oriented Cu surface, the theoretical bonding time is close to the value calculated using the grain boundary diffusion mechanism. However, the theoretical bonding time of (111)-oriented Cu is close to the value predicted by the (111) surface diffusion mechanism. From the surface creep model, the theoretical bonding time of grain boundary diffusion bonding is very sensitive to the bonding temperature, while that of (111) surface diffusion bonding is not. In addition (111) surface of Cu facilitates low temperature bonding. The experimental bonding time can be obtained by the modification of diffusivity $D_{\text{eff}}$, which can be obtained from previous research.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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