Instantaneous fluxless bonding of Au with Pb–Sn solder in ambient atmosphere

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A fluxless bonding technique has been developed as a method of flip-chip bonding for microelectronic packaging. The fluxless bonding technique can be achieved instantaneously in an ambient environment between metallic stud bumps and predefined molten solder. This paper describes the mechanics of the bonding action and verifies the effectiveness of this bonding method through wetting balance tests and scanning electron microscope and energy dispersive x-ray analysis. This technique has been demonstrated by using a gold stud bump to break the tin oxide layer over molten solder. This allows for a fast, solid liquid interdiffusion between gold (Au) and the fresh molten eutectic lead-tin (Pb–Sn) solder for joint formation during solidification. This bonding method has been successfully tested with 130-µm-pitch flip-chip bond pads on a joint-in-via flex substrate architecture. © 2005 American Institute of Physics. [DOI: 10.1063/1.1997291]

INTRODUCTION

In flip-chip packaging, solid-state welding, adhesive bonding, and soldering are often used for joining the interconnect system. These bonding techniques face numerous assembly challenges, as summarized in Table I. Soldering is the preferred bonding technique; thanks to its high-assembly yield, ability to eliminate the probe mark through reflow, allowance for rework after assembly, electrical stability, and high tolerance in placement accuracy because of self-alignment effects. However, some challenges still remain for soldering assembly, such as a long processing time and the need for a flux-based removal of oxides and hydrocarbons for solderability. Processing time is lengthened by flux application, the vision time required for precise alignment, and the need for a reflow process to provide sufficient wetting time for soldering. Flux removal of oxides leaves behind undesirable residues that are deleterious to package reliability. Entrapped residues also cause gross solder voids that can result in premature joint failure. Although chlorofluorocarbons (CFCs) are effective in removing flux residues, they are environmentally hazardous and do not present a long-term solution. Thus, the use of flux and its cleaning processes erects a barrier to flip-chip deployment in the packaging and integration of microelectronic, optoelectronic, and microelectromechanical systems. Fluxless soldering processes, on the other hand, rely on a controlled atmosphere for the reduction of oxides for soldering, but this is cumbersome in high-volume implementation. Obviously, a method of instantaneous fluxless soldering in ambient atmosphere for flip-chip assembly is highly desirable. In this work, a low mechanical force is used to submerge a soldering body into a confined volume of molten solder to realize the joint formation. This paper describes the thermomechanical forces involved in this process and proposes a mechanism for the formation of the bond. The technique is henceforth referred to as thermomechanical (TM) bonding.

THE THERMOMECHANICAL BONDING

The bonding was conceptualized by inserting 60 units of die consisting of 80 Au studs each into a corresponding molten solder bath with the use of the micro-vias in an ambient environment. Once the Au stud submerged into solder, the assembly was released and left to cool. The assembly test yielded 49 good units, which initiated further study of the TM bonding technique. This ambient, fluxless bonding technique is hypothesized to work on the principle of using a mechanical force to break the tin oxide layer over the molten solder, as shown in Fig. 1. A mechanical insertion force is applied on the soldering body to help overcome the surface tension of the molten solder and the strength of the oxide layer (stage I). With sufficient force applied (stage II), the soldering body breaks the oxide layer and contacts with fresh molten solder. Thereafter, a rapid solid-liquid interdiffusion...
The Au studs are chosen for use as the molten solder. A joint-in-via (JIV) architecture, reported by Lee et al., is used to verify the hypothesis that the body experiences “rejection” while the saturated solder solidifies. Figure 2 summarizes the experimental flow.

### EXPERIMENTAL PROCEDURE

In this bonding study, Au is chosen as the soldering body due to its rapid dissolution rate and its inertness to oxidation. Wetting balance tests are performed to characterize its behavior with a solder, as it is a common test for solderability. This test has a similar insertion motion as the proposed TM bonding. A set of different bonding forces—2, 5, 8, and 12 kg—are applied at temperature of 190 °C (above melting point of solder) and bond time 0.5 s. A set of 30 units is assembled in each leg, and assembly yields, based on continuity measurement, are collected as a yardstick for assessment. This evaluation matrix is designed to determine whether a threshold force is necessary to break the oxide layer and overcome the surface tension for bonding. Macroscopic examination is performed on the cross section of the assembled unit for further analysis of the contact angle and the standoff. Microstructure analyses are also carried out using scanning electron microscope (SEM) and energy dispersive x-ray analysis (EDX) to identify the thermodynamic phases. The instantaneous TM bonding is studied with varying bond times from 0.5 to 5 s where the bond timing is well before the wetting time. Both the impact of the soldering temperature and its microstructures are uncovered. The buoyancy effect in stage III is studied with various x-ray analysis to identify the thermodynamic phases. The instantaneous TM bonding is studied with varying bond times from 0.5 to 5 s where the bond timing is well before the wetting time. Both the impact of the soldering temperature and its microstructures are uncovered. The buoyancy effect in stage III is studied with varying bond temperatures from 190 to 250 °C at a fixed submerging depth $x_0$ with the use of a spacer. This experiment verifies the hypothesis that the body experiences “rejection” while the saturated solder solidifies. Figure 2 summarizes the experimental flow.

### RESULT

The wetting balance test results are plotted in Fig. 3. The curves representing samples without flux initially register a large negative counterbalance force; then they increase gradually and eventually end up in the negative-force region. The curves representing samples with flux register a higher
counterbalanced force and then pass through the zero-force line. The presence of the thin oxide layer with flux registers a similar initial counterbalance force, while a large negative buoyancy force is recorded without flux. The initial counterbalance force is a result of the surface tension and oxide layer attempting to “reject” the submerging body. Once this has been overcome, a reaction between the Au and solder takes place and wetting initiates. This wetting force decreases the counterbalance force, but it is not sufficient to overcome the buoyancy force due to the displacement of the solder. Hence, a negative counterbalance force is registered, depicting a poor wetting of Au with molten solder. In the presence of flux, the oxides on the solder are removed where it reduces the initial counterbalance force. As wetting initiates, the wetting force dominates and generates a positive resultant force over the zero line.

Figure 4 plots the assembly yield at temperature of 190 °C at different bond forces. The bonding yield increases with respect to the bond force applied. A 100% yield is observed for a bond force larger than 5 kg. The cross section in Fig. 5 reveals a partial interconnect between the joints. The left joint reveals a physical discontinuity between the Au and solder with some presence of solder remaining on the tip of the Au stud. The right joint has a good contact between the Au and solder, but a relatively high standoff compared to the thickness of the spacer. The macroscopic analysis of a typically good TM joint is seen in Fig. 6(a) in comparison with a conventional soldering joint in Fig. 6(b). The TM joint does not have solder wicking up the Au stud and has a contact angle larger than 90° between the meniscus of the Au and solder, depicting poor solderability per the wetting balance test. The joint architecture differs from conventional soldering where the solidified solder fully engulfs the Au stud with a good contact angle. Figure 7 shows the intermetallics formed under the instantaneous TM bonding. It is observed that a layer of AuSn2 and a layer of AuSn4 have formed along the bond interface, and the bulk solder contains multiple occurrences of rodlike AuSn4. These intermetallics appear to be radiating from the interdiffusion interface between the Au and solder. The microstructure analyses on the TM joint show no sign of tin oxides between the Au and solder interfaces.

As the bond force of 8 kg offers a good assembly yield, it is used to study the joint architecture with time and temperature. Figure 8 shows the SEM pictures for the different bond time of 0.5 and 1 s for bond force of 8 kg. A 99% yield is achieved for 0.5 s in a split second, well below the wetting time of a conventional soldering. The macroscopic examination shows similar standoff, while the SEM shows significant increase in the AuSn phases precipitated.

Figure 9 shows the assembly yields with different joint standoffs as a result of different bonding temperatures. All the samples have a standoff greater than the spacer thickness. An increasing standoff trend is seen with higher bonding...
temperature, and this affects the assembly yield accordingly. With a high bonding temperature of 250 °C and above, a “bottleneck” joint architecture is seen [Fig. 10]. It appears that the joint attempts to withdraw from the molten surface while the surface tension of the solder restrains its motion.

**DISCUSSION**

**Stage I: The insertion mechanism**

The series of wetting balance tests suggests the need for a threshold force to overcome the surface tension and the oxide layer before the soldering body submerges into molten solder to initiate a wetting mechanism. With respect to the assembly, the one-dimensional (1D) force analysis prior to the insertion of the soldered body into the molten solder is shown in Fig. 11, where \( F_R \) is the insertion force, \( P \gamma_{L} \cos \alpha \) is the surface tension of the molten solder, and \( W \) is the weight of the soldering body. The surface tension, strength of the oxide layer, and weight of the soldering body combine to act against the insertion force. Ignoring the strength of the thin oxide layer, an equilibrium force balance is achieved [Eq. (1)] with an increase in the surface tension force as \( \alpha \) changes, and a decrease in the tangential angle of the solder meniscus with the vertical.

\[
F_R - nP \gamma_{L} \cos \alpha - W = 0, \tag{1}
\]

where \( nP \gamma_{L} \cos \alpha \) is the surface tension term, \( n \) is the number of studs, \( P \) is the circumference of the stud tip, and \( \gamma_{L} \) consists of the surface tension of the Pb–Sn eutectic solder with air and the tangential angle \( \alpha \).17,18

The surface tension of the solder is analogous to a frictional force restricting the soldering body from submerging into the molten solder. As a larger force is applied, \( \alpha \) decreases until surface tension is overcome. As per the wetting balance test for oxide without flux, a larger negative counterbalance force is registered. This implies that the presence of the oxide layer may have increased the surface tension with an additional term \( \gamma_o \) against the insertion force. Therefore, a larger insertion force \( F_T \) (threshold force) is required to overcome the surface tension and break the oxide layer.
before the soldering body is submerged. Thus, the balanced force is denoted by Eq. (2), where $\alpha_m$ denotes the tangential angle of the oxidized solder surface before the oxide layer breaks. For simplification, $\gamma$ is termed the sum of the surface tension of solder with air and the oxide layer [i.e., $\gamma = \gamma_s + \gamma_o$ in Eq. (3)].

$$F_T - nP(\gamma_s + \gamma_o) \cos \alpha_m - W = 0,$$

$$F_T - nP \gamma \cos \alpha_m - W = 0.$$

As such, when $F_b > F_T$ is applied, the surface tension and the self-weight of the insertion body are overcome, and the insertion body breaks the oxide layers and submerges into the molten solder. From that moment, the interdiffusion of Au and solder begins and the bonding starts. The assembly yield shown in Fig. 4 provides strong evidence of the necessary condition for TM fluxless bonding. This cross section further supports the hypothesis. Partial joint formation is seen in Fig. 5 when a lower bond force of 2 or 5 kg is applied for a series of joints. As the Au studs and the molten solder are placed together, a moderate force is sufficient to break the solder oxide due to high pressure generated by the small contact area. Since the Au studs have a standoff distribution, the highest Au stud submerges first followed by the next highest Au stud. This will continue until it reaches a limiting condition, such that where $\Sigma[P \gamma \cos \alpha + W + F_T = 0, (n+1)$ studs are not able to overcome the surface tension and break the oxide layer. Hence, partial joints are seen with a low bond force.

**Stage II: Submerging into solder**

Once the soldering body submerges into fresh molten solder, a rapid solid-liquid interdiffusion occurs between the Au and the solder. The microstructure analyses by SEM and EDX show no sign of tin oxides between the Au and solder interfaces. As the oxide layer breaks, rapid solid-liquid interdiffusion between the Au and fresh molten solder takes place to form a joint. The AuSn phases appear to radiate from the interface. The Au diffuses rapidly into the molten solder, and during cooling, the saturated molten solder precipitates to form the rodlike AuSn$_4$ phases. The precipitation of AuSn$_4$ leads to depletion of Sn in the surrounding matrix, resulting in the formation of Pb-rich islands, as shown in Fig. 7.

As the soldering body submerges into the solder, the buoyancy and the wetting forces kick in, as shown in Eq. (4). The buoyancy and wetting forces can be visualized from the gradual increase in the counterforces during the wetting balance test. The soldering body sinks into the molten solder till the spacer thickness.

$$F_b - pgA\gamma_s + nP \gamma_s \cos \theta - W > 0.$$  

The wetting force is represented by $nP \gamma_s \cos \theta$ where $\gamma_s$ is the surface tension of the solder with a Au surface, and $\theta$ is the contact angle between the surfaces. In this equation, a $pgA\gamma_s$ term is introduced as the buoyancy as a result of the solder volume displacement.17,18 According to Archimedes’ principle, the buoyancy is expressed as the product of the density of solder ($\rho$), the mass of acceleration ($g$), the cross section of the submerged body ($A$), and the equilibrium submersion depth into the solder ($x_o$). As a sufficient insertion force $F_b$ is applied, the soldering body will achieve a physical equilibrium position with the use of the spacer.

An instantaneous TM bonding has also been demonstrated in Fig. 8 with a bond time of $t_o$, which is well below the wetting time of solder. The cross section of the joints reveals poor solderability of Au with solder and, hence no self-alignment forces for bonding as demonstrated by the wetting tests. The increase in the bond time does not physically affect the joint architecture but merely increases the amount of Au dissolving into molten solder, forming more AuSn phases as per the solid-liquid interdiffusion. The time of bonding does not affect the joint architecture but promotes the extensive formation of intermetallic compounds.

**Stage III: Solidification of solder**

As the bond force releases in stage III (in the nonwetting state of solder), the soldering body will experience “rejection forces” generated by the buoyancy and the weight of the soldering body. This phenomenon is seen in Fig. 9 where all the joint standoffs are larger than the spacer assembly. The resultant forces on the submerged soldering body are illus-
imated in Fig. 12 as the insertion force released. By equaling the vertical force component, the resultant force \( F_w \) at any depth in the solder can be estimated by Eq. (5), where \( x \) is the ascending displacement from its equilibrium position \( x_o \).

\[
F_w = pgA(x_o - x) + W - P \gamma_1 \cos \theta.
\]

Equation (5) can be explained as a second-order linear differential equation like Eq. (6), where it depicts the motion of the soldering body as bond forces are released from the submerged body. This is analogous to an external, excited, undamped mass-spring system of stiffness \( pgA \) by a force of \( pgAx_o - P \gamma_1 \cos \theta - W \).

\[
\frac{d^2x}{dt^2} + \frac{pgA}{m}x = \frac{pgAx_o - P \gamma_1 \cos \theta + W}{m}.
\]

Assuming \( \theta \) as constant, a general solution for Eq. (6) gives rise to Eq. (7) where \( K_1 = pgA/m \) is the stiffness of the system contributed by the buoyancy force and \( K_2 = (pgAx_o - P \gamma \cos \theta - W)/m \) is the initial acceleration given to the submerged body. The constants \( C_1 \) and \( C_2 \) can be determined by the boundary conditions at the equilibrium position where \( t = 0, x = 0 \), and \( dx/dt = 0 \). The solution for the motion of the submerged body is shown in Eq. (8).

\[
x = C_1 \cos \sqrt{K_1} t + C_2 \sin \sqrt{K_1} t + \frac{K_2}{K_1},
\]

\[
x = \frac{K_2}{K_1}(1 - \cos \sqrt{K_1} t).
\]

To estimate the standoff, assume instantaneous freezing by solder solidification. The time taken for solder solidification, \( t_s \), can be estimated by Eq. (9) using the lumped capacitance model\(^{20} \) where \( T_b \) is the bonding temperature, \( T_s \) the solidified temperature, and \( T_o \) the ambient temperature. The time to solidification is based on the assumption of spatial uniformity at all instances during the transient process.

\[
t_s = \frac{m c}{h A_1} \ln \left( \frac{T_b - T_o}{T_s - T_o} \right).
\]

In the above equation, \( m \) denotes the mass, \( c \) the heat capacity, \( h \) the convection heat transfer coefficient, and \( A_1 \) the surface area for convection cooling of the submerged body. Substituting Eq. (9) into Eq. (8) gives rise to Eq. (10), which is the estimation of the ascending displacement of the forced submerged body. Hence, an increase in standoff is seen in the TM bonding for a particular temperature. The increase in standoff estimated by Eq. (10) matches the increase experimentally obtained in Fig. 9.

\[
x = \frac{K_2}{K_1}[1 - \cos \sqrt{K_1} t_s].
\]

The drop in assembly yield is due to an increase in standoff. For bonding, the body needs to be physically in contact with the solder. Hence, the allowable displacement must be smaller than the equilibrium position \( x_o(x_o > x) \) (i.e., \( x_o \geq K_2/K_1[1 - \cos \sqrt{K_1} t_s] \)). By simplifying the relationship, we obtain Eq. (11) where \( K_3 = (n P \gamma_1 \cos \theta - W)/pgA \).

\[
x_o \geq K_3 \left[ \frac{\cos \sqrt{K_1} t_s - 1}{\cos \sqrt{K_1} t_s} \right].
\]

As such, a minimum submerged distance would be necessary for a specific bonding temperature for the soldering body to be submerged in solder. Therefore, the assembly yield decreases with an increase in bonding temperature for a specific submerged depth. This is a result of longer cooling time \( t_s \) where the buoyancy and its weight component are attempting to reject the soldering body as per Eq. (11). This is more apparent with high bonding temperature of 250 °C where a “bottleneck” joint architecture is seen. Thus, the bonding temperature and the submerged distance are interrelated parameters in TM bonding and, therefore, have to be optimized to achieve a successful TM joint.

**FIELD APPLICATIONS**

The thermomechanical bonding technique has been tested as a flip-chip bonding technique for a flex organic laminate with a JIV architecture. A conventional lead-on-chip bonder with a \( +/−38-\mu m \) placement accuracy is employed for the flip-chip assembly. The JIVs are fabricated on the flexible substrate with a 110- \( \mu \)m diameter size at a pad pitch of 130 \( \mu \)m, as shown in Fig. 13. A 7 \( \times \) 8 \( \times \) 0.25-mm\(^3\) die consisting of 54 Au stud bumps is assembled corresponding to these JIVs. Fig. 14 shows a cross-section view of the die after bonding. In assembly, the JIV architecture assists in fluxless bonding by preventing solder bridging with a small 20- \( \mu \)m inter-via spacing. The assembly has demonstrated that the conventional die bonder can be used for fluxless bonding during flip-chip assembly at a die pad pitch of 130 \( \mu \)m. This instantaneous fluxless bonding technique achieves a high-assembly throughput by eliminating the flux-
ing process and reducing assembly processing time for precise die placement. Further process reduction is achieved through the removal of the reflow process. The instantaneous fluxless bonding in ambient atmosphere has been successfully developed with the JIV architecture to promote wider adoption of flip-chip applications.

CONCLUSION

The TM bonding technique uses a mechanical force to break the oxide layer and overcome the surface tension and weight of the insertion body; once inserted, the submerged body interacts with fresh solder to form bonds via solid-liquid interdiffusion. The bonds are mechanically interlocked upon cooling. This fluxless bonding technique does not rely on its wetting behavior, thus allows instantaneous soldering, and thereby eliminates the need for the fluxing and reflow processes. Due to poor wetting, the buoyancy of the molten solder and the weight of the insertion body tend to “reject” the insertion; therefore, a sufficiently deep submerging is necessary to achieve good joints at a particular temperature. This bonding method has been applied successfully to the JIV substrate architecture and it has achieved a fine pad pitch, robust assembly, and instantaneous fluxless bonding for flip-chip applications.