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Damage Mechanism of Cu₆Sn₅ Intermetallics Due to Cyclic Polymorphic Transitions

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Abstract: The formation of high-melting-point Cu₆Sn₅ interconnections is crucial to overcome the collapse of Sn-based micro-bumps and produce reliable intermetallic interconnections in three-dimensional (3D) package. However, because of the multiple reflows in 3D package manufacturing, Cu₆Sn₅ interconnections will experience the cyclic polymorphic transitions in the solid state. The repeated and abrupt change in the Cu₆Sn₅ lattice due to the cyclic polymorphic transitions can cause extreme strain oscillations, producing damages at the surface and in the interior of the Cu₆Sn₅ matrix. Moreover, because of the polymorphic-transition-induced grain splitting and superstructure phase formation, the reliability of Cu₆Sn₅ interconnections will thus face great challenges in 3D package. In addition, the Cu₆Sn₅ polymorphic transition is structure-dependent, and the η'↔η polymorphic transition will occur at the surface while the η'↔η ↔ η polymorphic transition will occur in the deep matrix. This study can provide in-depth understandings of structural evolution and damage mechanism of Cu₆Sn₅ interconnections in real 3D package manufacturing.

Keywords: Cu₆Sn₅ intermetallic; solid-state polymorphic transition; superstructure; transmission electron microscopy; damage mechanism; multiple reflows

1. Introduction

Three-dimensional packages (3D packages), which can merge chip technology and packaging technology together, have great application in overcoming the scaling limits in 2D integrated circuits (ICs). The most typical characteristics of this technology are to vertically stack the multi-chips in a tight device space and to continuously minimize the interconnections on a limited chip area. As shown in Figure 1, there are 4 kinds of the solder joints mentioned in 3D packages. The ball-grid-array (BGA) solder joints with 760 μm in diameter are above the printed-circuit-board (PCB). The controlled-collapse-chip-connection (C4) solder joints with 250 μm in diameter are above the BGA package substrate. The Sn-based micro-bumps (Sn-bumps) with 80 μm in diameter are above the interposer substrate. The Sn-bumps with 20 μm in diameter are located between the stacked chips and through-Si-via (TSV) structures. In 3D packages, the Sn-bumps with the diameter of 20 μm must be completely transformed into the intermetallic (IMC) phase in the joints after the 1st reflow to avoid joint collapse during multiple reflow processes [1]. Accordingly, the IMCs, e.g., Cu₆Sn₅, Cu₃Sn and Ni₃Sn₅, are quickly emerging as innovative high-temperature interconnection materials due to their unique abilities to join at low temperatures and operate at high temperatures [2-5]. Among these IMCs, Cu₆Sn₅ has received a substantial amount of attention because of its fast growth rate and high-temperature strength [6,7]. Sakuma et al. even concluded that the realization of the Cu₆Sn₅ interconnections may be a guarantee of manufacturability and reliability in 3D packages [8].

Because of the thermal mismatch between Cu₆Sn₅ and Si during multiple reflow processes, cyclic strains are considered to be the dominant cause of damage to IMC interconnections in 3D packages [9,10]. However, Cu₆Sn₅ has at least two phases in the solid state, and its η phase (P6₃/mmc) can
thermodynamically transform to the \( \eta' \) phase (\( C2/c \)) with a volume expansion of 2.2% below 186 °C [11,12]. Because small joints have elevated heating/cooling rates, the polymorphic transition of \( \eta' \leftrightarrow \eta \)
may be kinetically retarded owing to the insufficient transition time. It is concerning that this retarded polymorphic transition may cause a transition stress that continuously damages the Cu-Sn IMC interconnection [13,14]. Although some researches have begun to explore the effect of the Cu-Sn polymorphic transition on the interconnect reliability [14–16], the intrinsic damage mechanism has seldom been reported during multiple reflow processes. In October 7th, 2019, Samsung Electronics announced that it has developed an industry’s first 12-layer-3D-IC, and the IMC interconnections in such 3D IC may experience over 10 reflow cycles; because the number of stacking layers will never be an end, a 50-layer 3D IC may be fabricated in the near future, and the IMC interconnections in such 3D IC may experience 50 or even more reflow cycles. Therefore, the determination of damage mode of Cu-Sn during multiple reflow processes is urgent in real 3D package manufacturing. The aims of this study are to explore the structural evolution of the Cu-Sn under multiple reflow processes, to study the damage mechanism induced by the cyclic polymorphic transitions, and to confirm the influence of cyclic polymorphic transitions on the reliability of Cu-Sn interconnections in 3D package manufacturing.

![Figure 1. Schematic illustration of a 3D IC using 3D package technology](image)

2. Materials and Methods

The Cu-Sn IMCs were separated via a precipitation method from a supersaturated Sn-Cu melt [17]. To be specific, a solder bath, containing 1 kg of the Sn–0.7wt.%Cu solder and 30 g of the fine Cu powder, was placed in a furnace, heated to 350 °C for 24 h under \( \text{N}_2 \) atmosphere. After the Cu powder was completely dissolved, the solder was quickly cooled down to 250 °C and maintained at this temperature for 10 h. Several rod-type IMCs were then separated from this solder using a quartz screen and quenched down to 0 °C. To expose the pure IMCs, the residual solder on their surfaces was etched by a 10% hydrochloric acid alcohol solution.

Subsequently, the as-prepared IMCs were reflowed under a ramp-soak-spike profile provided by a BGA rework machine (DIC RD-500II). The temperature ranges of the ramp zone, soak zone and spike zone were set at 20-170 °C, 170-200 °C, and 200-220 °C, respectively, with the same ramp rates of 10 °C/min. After heating to 220 °C, the samples were maintained at this temperature for 10 min, and then cooling down to 20 °C with a cooling rate of 20 °C/min. The aforesaid reflow process was repeated 1 time, 10 times, and 50 times.

The structural evaluation of the Cu-Sn IMCs after multiple reflows was observed by a scanning electron microscopy (SEM, Hitachi SU-70). Moreover, the Cu-Sn grains that were reflowed 1 time were milled to obtain a fine powder and studied by an X-ray diffraction (XRD, Bruker D8 Advance, Cu-Kα radiation) and a differential scanning calorimetry (DSC, NETZSCH 214 Polyma). Note that, the XRD measurement was conducted at a cooling rate of 20 °C/min from 220 °C to 20 °C, and the data at each selected temperature were collected in the \( 2\theta \) range of 30°–55° with a scan rate of 1 °/min; the DSC measurement was conducted at a heating/cooling rate of 1 °C/min from 20 °C to 220 °C under an air atmosphere, and the sample of ~28 mg was involved. In addition, to study the \( \eta' \leftrightarrow \eta \) polymorphic transition, two Cu-Sn grains that were reflowed 1 time and 50 times, respectively, were cut by a focused-ion beam (FIB, FEI NanoLab 600i), and the corresponding microstructures were...
studied by a transmission electron microscopy (TEM, Philips Tecnai G2 F20). Note that, the flowchart of preparation, reflow tests and characterization of Cu$_6$Sn$_5$ IMCs was shown in Figure 2.

Figure 2. Flowchart of preparation, reflow tests and characterization of Cu$_6$Sn$_5$ single-crystal rods.

3. Results and Discussion

Figure 3 shows the surface evolution of the Cu$_6$Sn$_5$ IMCs with increasing reflow time. After being reflowed for 1 time, the Cu$_6$Sn$_5$ grains maintain a rod-like shape with flat and smooth surfaces. The diameters of these grains are in the range of 20–25 μm, and each grain is a single crystal based on the previous study [17]. Interestingly, after being reflowed for 10 times, although the overall structures of these IMC grains do not change, the original smooth surfaces have become rough and full of microcracks (Figure 3b). After being reflowed for 50 times, the Cu$_6$Sn$_5$ surfaces become damaged and fragmented, and numerous protrusion-like structures with irregular shapes and sizes have emerged in certain depressed areas (Figure 3c). Apparently, the surface damages of the Cu$_6$Sn$_5$ grains have arisen after multiple reflows, and the damage extent seems to increase with an increasing number of reflow times. Hence, we reasonably hypothesis that the multiple reflows would produce an adverse effect on the reliability of Cu$_6$Sn$_5$ interconnections in 3D package. To verify our speculation, the structural changes inside the Cu$_6$Sn$_5$ grains should be further explored.

Figure 4a shows the XRD patterns of the Cu$_6$Sn$_5$ powder after being reflowed for 1 time at selected temperatures. The patterns in the temperature range of 20–150 °C are roughly identical, and by comparing the peak positions and peak intensities with the reference database, it is concluded that the corresponding main diffraction peaks are attributable to the $\eta'$ phase (ICDD 45-1488, space group of C2/c). The XRD patterns in the temperature range of 170–220 °C are similar, and the corresponding main diffraction peaks are attributable to the $\eta$ phase (ICDD 47-1575, space group of P6$_3$/mmc).

Moreover, there are numerous relatively weak peaks at 2θ values of 32.35°, 39.48°, 48.39° and 49.84° for the patterns in the temperature range of 20–150 °C (marked by the dark-blue squares) and at 2θ values of 38.50°, 46.12° and 47.43° for the patterns in the temperature range of 170–220 °C (marked by the red circles), which cannot be well matched to the standard XRD files of the Cu$_6$Sn$_5$. Because superstructures may be created in the Cu$_6$Sn$_5$ during the polymorphic transition of $\eta'$↔$\eta$ [12], these peaks are very likely structural in origin. In addition, in the 2θ range of 42°–44°, there are two main diffraction peaks (at ~42.82° and ~43.32°) for the patterns in the temperature range of 170–220 °C, but one (at ~42.82°) gradually disappears at decreasing temperatures of 20–150 °C. The main diffraction peaks have fundamentally changed, implying that a reconfiguration of the Cu$_6$Sn$_5$ orientations may occur after the $\eta'$↔$\eta$ polymorphic transition.
Figure 3. Surface microstructures of the Cu₆Sn₅ grains after being reflowed for (a) 1 time; (b) 10 times; (c) 50 times.

Figure 4. (a) In situ XRD patterns of the 1-time-reflow Cu₆Sn₅ powder in the 2θ range of 30–55°; (b) the calculated unit cell volume (V) at selected temperatures. Note that the monoclinic structure of ICDD 45-1488 is used to fit the pattern in (b), and the microstructures of the Cu₆Sn₅ powder used in our XRD tests are also inserted in (b).
Figure 4b shows the unit-cell volumes of the Cu$_6$Sn$_5$ (V) at selected temperatures calculated from our XRD data. Two almost linear increases in V are detected with increasing temperatures ranging from 20–150 °C and 170–220 °C, and a sharp fall of 0.72% occurs from 150–170 °C. The former is in accordance with thermal expansions and contractions, and the latter should originate from the Cu$_6$Sn$_5$ polymorphic transition. Because the theoretical value of V is 781.71 Å$^3$, the difference between the theoretical and actual values in V will inevitably produce the tensile/compressive strains inside the Cu$_6$Sn$_5$ lattice. Especially during multiple reflows, a repeated abrupt change in V due to the cyclic polymorphic transitions may cause strain oscillations at the micro level. Moreover, at the macro or meso level, the transition strain may be partially released from the grain surface and be partially accumulated inside the grain matrix. Finally, the oscillation, release and accumulation of the transition strain will produce the structural damages of the Cu$_6$Sn$_5$, leading the Cu$_6$Sn$_5$ grains to crack (Figure 3b) or even break (Figure 3c).

Figure 5 shows the DSC heat flow curves of the Cu$_6$Sn$_5$ powder after being reflowed for 1 time. Two endothermic peaks (at ~181.1 °C and ~187.1 °C, respectively) are detected during heating, while two exothermic peaks (at ~148.4 °C and ~162.3 °C, respectively) are detected during cooling. The distribution of the two latent heat peaks in the heating/cooling curve reflects that there should be three phases participated in the process. In other words, besides the $\eta'$ and $\eta$ phases, a new phase (defined as the $\eta_s$ phase) may be involved in the Cu$_6$Sn$_5$ polymorphic transition, which is consistent with our XRD forecast. Undoubtedly, if the $\eta_s$ phase indeed exists, the 1$^{\text{st}}$ and 2$^{\text{nd}}$ latent heat peaks will be related to the $\eta'\leftrightarrow\eta$ and $\eta_s\leftrightarrow\eta$ phase transitions, respectively. Therefore, a single-phase state of the Cu$_6$Sn$_5$ powder during cooling can be predicted: e.g., the $\eta$ phase at above 170 °C, the $\eta_s$ phase at close to 150 °C, and the $\eta'$ phase at below 140 °C. However, based on our XRD data, the $\eta_s$ phase seems always to be associated in the $\eta'$ or $\eta$ phase, rather to exist as a separate phase. Hence, it is urgently required to explore the existence of the $\eta_s$ phase.

Figure 6a shows the cross-section microstructure of a Cu$_6$Sn$_5$ grain after being reflowed for 1 time. No grain boundary exists in the Cu$_6$Sn$_5$ matrix, proofing that the original rod-type grain before FIB cutting is indeed single-crystal. As shown in Figure 6b, the selected area diffraction pattern (SADP) analysis confirms that the entire Cu$_6$Sn$_5$ grain is the $\eta'$ phase; the normal direction of the matrix is along the [201]$_\eta'$ direction, and the external surface belongs to the (330)$_\eta'$ plane. Interestingly, after being reflowed for 50 times (Figure 7a), the original Cu$_6$Sn$_5$ single-crystal matrix has split into small grains whose grain boundaries are extended from the external surface to the deep matrix. The grains located close to the external surface (e.g., Grain A and Grain B) seem larger than those located deep inside the matrix (e.g., Grain C and Grain D). Based on the corresponding SADPs in Figure 7b, both Grain A and Grain B are identified as the $\eta'$ phase, and a set of orientation...
relationships are determined as follows: [010]_{\eta'}/[\bar{2} 0 1]_{\eta'\eta} (1 4 0 2)_{\eta'\eta}//(3 3 6)_{\eta'\eta} and (2 0 4)_{\eta'\eta}//(1 5 2)_{\eta'\eta}.

The orientation of Grain B is highly similar to the orientation of the Cu$_6$Sn$_5$ matrix in Figure 6b, but the orientation of Grain A has changed a lot. This, on the one hand, indicates that the newly generated grains should originate from the original Cu$_6$Sn$_5$ single-crystal matrix; on the other hand, it demonstrates that the reconfiguration of the Cu$_6$Sn$_5$ orientations has indeed occurred after multiple reflows, at least for certain grains.

![Figure 6.](image)

Notably, the theoretical interplanar spacings of the (204)$_{\eta'}$, (152)$_{\eta'}$, (010)$_{\eta'}$ and (201)$_{\eta'}$ planes are 2.103 Å, 2.103 Å, 7.294 Å and 5.103 Å, respectively; thus, the lattice mismatch between every one (204)$_{\eta'}$ plane and every one (152)$_{\eta'}$ plane is 0%, while the potential lattice mismatch between every two (010)$_{\eta'}$ planes and every three (201)$_{\eta'}$ planes is -4.71%. Despite such small lattice mismatches, some nanovoids are indeed generated at the boundary between Grain A and Grain B after being reflowed for 50 times (Figure 7c). Therefore, the multiple reflows can indeed result in the damage of inner Cu$_6$Sn$_5$ grains and should be harmful to the reliability of the Cu$_6$Sn$_5$ interconnections in the 3D package. More importantly, as shown in Figure 7b, Grain C has a five-fold superlattice of Grain A running along the [402]$_{\eta'}$ direction, while Grain D has a five-fold superlattice of Grain B running along [060]$_{\eta'}$. This is direct evidence that a superstructure phase of $\eta'$ indeed exists in the Cu$_6$Sn$_5$ matrix, and this finding can perfectly support our speculations in both XRD and DSC studies.

The formation of the superstructure phase is always strain-induced and structure-dependent (e.g., a strain-induced superstructure phase was observed in ZrCu during the martensitic transition [18]). Following this rule, the formation of the superstructure $\eta$ phase and the mechanism of Cu$_6$Sn$_5$ polymorphic transition can be inferred as below (Figure 8a). When the temperature satisfies the requirement of Cu$_6$Sn$_5$ phase transition, the $\eta' \leftrightarrow \eta$ polymorphic transition will begin. Due to the rapid volume change during this transition, the transition strain will inevitably be generated in the Cu$_6$Sn$_5$ lattice; subsequently, such strain will be partially released from the external surface to form a strain-free layer and also be partially accumulated inside the matrix to create a strain-accumulation zone. From the point of view of phase transition energy, the nearer to the surface, the smaller strain energy (i.e., the main resistance to phase transition in solid state) will be, and the more prone to occur phase transition. Hence, the normal $\eta' \leftrightarrow \eta$ polymorphic transition can be detected at or close to the external surfaces of the Cu$_6$Sn$_5$ grains, just as observed in Somidin’s in-situ heating TEM experiments [11,12]. However, when the strain energy between $\eta'$ and $\eta$ phases is larger than the volume free energy change between $\eta'$ and $\eta$ phases (i.e., the driving force of phase transition), the $\eta' \leftrightarrow \eta$ polymorphic transition may stop, and the accumulated strains will promote the metastable phase formation in order to decrease the threshold of $\eta' \leftrightarrow \eta$ phase transition. Hence, the $\eta' \leftrightarrow \eta' \leftrightarrow \eta$ polymorphic transition will occur inside the Cu$_6$Sn$_5$ deep matrix, just as we detected in Figure 7b. Because the $\eta'$ phase is
metastable and only exists inside the matrix, it can thus be detected in accompanied by the $\eta'$ or $\eta$ phase, just as shown in Figure 4a.

**Figure 7.** (a) TEM image of the cross-section microstructure of a rod-type Cu$_6$Sn$_5$ grain reflowed for 50 times; (b) the SADPs for the four grains marked in (a); (c) an enlarged view of the local microstructure at the boundary between Grain A and Grain B.

In addition, because the $\eta\rightarrow\eta'$ phase transition is an expansion transition, we can infer that the $\eta'\rightarrow\eta$ phase transition is also an expansion transition. Based on Figure 4b, the compressive strain will exist in the Cu$_6$Sn$_5$ matrix during cooling below 200 °C; thus, the $\eta$ phase observed in Figure 7b seems to be created only by the compressive strain, and the occurrence of this phase seemed to be in the range of 150-170 °C based on Figure 5. Accordingly, as shown in Figure 8b, the compressive strain generated by the $\eta\rightarrow\eta'$ expansion transition will create the strain energy inside the matrix, producing the delayed occurrence of the $\eta\rightarrow\eta'$ expansion transition (i.e., the exothermic peak of $\eta\rightarrow\eta'$ will shift...
to the left); similarly, the compressive strain generated by the $\eta\rightarrow\eta'$ expansion transition may increase the strain energy inside the deep matrix, and the exothermic peak of $\eta\rightarrow\eta'$ will shift further to the left. Therefore, there should be three exothermic peaks involved in the Cu$_6$Sn$_5$ phase transition during the cooling process. Notably, the compressive strain induced by the thermal expansion of the Cu$_6$Sn$_5$ during the heating process will result in a premature occurrence of the $\eta'\rightarrow\eta\rightarrow\eta$ shrinkage transition; thus, there should also be three endothermic peaks for the Cu$_6$Sn$_5$ phase transition during the heating process. Finally, when the strain is large enough, the splitting of the Cu$_6$Sn$_5$ grains will occur. Accordingly, the strain induced by the cyclic Cu$_6$Sn$_5$ phase transitions is the dominant cause of crack generation that damages the Cu$_6$Sn$_5$ grains under multiple reflow processes. A further study may be verified whether the $\eta$ phase is just one of the $\eta'$ phase, $\eta''$ phase and $\eta^{(i)}$ phase proposed in Nogita’s study [19,20], and evaluate its lattice parameters.

4. Conclusions

The surface and inner structural damage of Cu$_6$Sn$_5$ IMCs after multiple reflow processes were explored in this study. The results show that the superstructure phase formation occurs in Cu$_6$Sn$_5$ due to the accumulation of the strains induced by cyclic phase transitions. Moreover, the nanovoids can be generated at the grain boundaries owing to the lattice mismatch, producing the splitting of the Cu$_6$Sn$_5$ grains after multiple reflows. In addition, the $\eta'\rightarrow\eta$ polymorphic transition will occur at the Cu$_6$Sn$_5$ surface while the $\eta''\rightarrow\eta\rightarrow\eta$ polymorphic transition will occur in the deep matrix. It can be predicted that, if the Cu$_6$Sn$_5$ polymorphic transition cannot be limited effectively during multiple reflows, it may become one of the most dominate causes of failure for the Cu$_6$Sn$_5$ IMC joints in 3D packages.

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