Research on Ni$_3$Sn$_4$ intermetallic compound for 5 μm diameter Cu/Ni/Sn-3.0Ag micro bumps

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Abstract for 5 μm diameter micro bumps, the interfacial intermetallic compounds (IMCs) seriously affect the interconnection performance of micro bumps. In this paper, we focused on the discussion of the growth and control mechanism of IMCs of 5μm diameter micro bumps at different temperatures and durations. The growth mechanism and morphology of Ni$_3$Sn$_4$ IMC was studied. Through the EDS analysis of the cross-sectional micro bumps, it could be determined that the composition of the slender columnar crystal IMC was Ni$_3$Sn$_4$. When the heating temperature was higher than the melting point of Sn-3.0 wt% Ag solder, the IMC would exhibit uneven and abnormal growth along the Sn grain boundary. Furthermore, the IMC growth and diffusion mechanisms of solid-solid and solid-liquid interface reaction were discussed respectively. Finally, based on the temperature and duration of the growth and evolution of the Ni$_3$Sn$_4$ IMC, we gave appropriate suggestions for the use of small-sized micro bumps.

Keywords: Cu/Ni/Sn-3.0 wt% Ag micro bump, Ni$_3$Sn$_4$ IMC, grain boundary diffusion, slender columnar IMCs

Classification: Electron devices, circuits and modules

1. Introduction

With the advent of the post-Moore era and the emergence of new fields of electronic products, such as IoT, 5G, mass storage, high performance computing, automatic driving, hologram, etc., electronic components are developing towards miniaturization, and multi-functionalization. Multi-chip 3D integrated packaging becomes one of the best choices [1, 2, 3, 4]. Copper pillar bump is widely used in 3D integrated packaging because of their smaller packaging size, excellent electrical and mechanical properties [5, 6, 7, 8]. Currently, the most advanced three-dimensional integration technologies, such as HBM [9, 10], CoWoS [11, 12], Foveros [13, 14], etc., use the diameter of copper pillar bumps of about 20 μm, while in the field of Micro LED, the size of micro-interconnection has reached 10 μm or even smaller [15, 16, 17, 18]. This size will continue to shrink in the future. However, as the size of copper pillar micro bumps decreases, it will encounter some new challenges in micro-electronic packaging. For example, for micro bumps with a pitch of 10μm, the solder is limited. In order to have some liquid Sn left after the reflow process, the IMC thickness formed at Ni/solder interface should also be limited. Thus the control and limitation of the growth of IMCs becomes nowadays a challenging issue. The IMC's growth and control are the most important factors affecting joint strength of the bonding interface. For large-size micro bumps, the Sn layer is relatively thick, and IMCs of a certain thickness will not affect the bonding characteristics between micro bumps.

When the size of the micro bump becomes smaller and smaller, the thickness of the Sn layer is relatively thin. If the IMCs growth are not well controlled, because Cu has a very fast diffusion rate into the molten Sn, the Sn will be completely consumed quickly and transformed into Cu$_6$Sn$_5$ and Cu$_3$Sn intermetallic compound IMCs [19, 20, 21, 22]. Because of the inherent brittle nature and the tendency to generate structural defects such as voids and gaps, very thick IMCs layer at the Cu/solder interface may degrade the reliability of solder joints. Since Ni diffusion is much slower than Cu, a Ni barrier layer is usually added between Cu and Sn layers to slow the diffusion of Cu to Sn. However, Ni and Sn diffuse each other to form Ni$_3$Sn$_4$ [23, 24, 25] IMC at a certain temperature, which also affect bonding properties. Therefore, it is very important to study the growth and evolution mechanism of Ni$_3$Sn$_4$ IMC for small-sized micro bumps. Studies on the growth and evolution mechanism of Ni$_3$Sn$_4$ IMC have been carried out for a long time. H.H. Hsu et al. [26], adopted the annealed test to observe the microstructure of alloy formation at 100°C and 125°C and 150°C up to 1000 h. The formation of Ni$_3$Sn$_4$ followed a parabolic rate law at each aging temperature. Due to the limited solder volume (the solders pitch was 20 μm), the remaining solder of the micro bumps was completely exhausted after the long time annealing at 150°C. The activation energy for Ni$_3$Sn$_4$ formation in the Ni/Sn-2.5Ag/Ni micro bumps was 171.8 kJ/mol. N. Zhao et al. [27], Interfacial Reactions in Ni/Sn/Ni and Ni/Sn-9Zn/Ni micro solder joints during thermomigration (TM) have been studied by reflowing solder joints on a hot plate. The growth of the Ni$_3$Sn$_4$ IMC in the Ni/Sn/Ni solder joints was always fast at the cold end and relatively slow at the hot end. Chenlin Yang et al. [28], studied the growth of intermetallic compounds in Cu pillar bumps during high temperature aging by microstructural observations and mathematical calculations. For the growth of IMCs, they believed that the surface diffusion was more obvious when the size of the micro bumps decreased. At the same time, they also found the formation

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mechanism of IMCs according to the experimental results and diffusion theory. Yi-Shan Yang et al. [29], investigated the growth of Ni$_3$Sn$_4$ IMC at the liquid-solid interface in micro-scale Ni/SnAg/Ni system under a temperature gradient of 160°C/cm at 260°C on a hot plate. A growth model was established and the growth kinetic analysis suggested that the chemical potential gradient controlled the growth of Ni$_3$Sn$_4$ at stage I (0–120 min) whereas the dynamic equilibrium between chemical potential gradient and temperature gradient forces was attained at the hot end at stage II (120–210 min).

It can be seen that the above-mentioned authors’ research focus mainly on the reliability issues in the use of micro bumps, including but not limited to the following three aspects: the growth dynamics mechanism of IMCs of micro bumps under different durations at a certain temperature, the diffusion activation energy of Ni atoms in fused SnAg solder, and the growth rate of Ni$_3$Sn$_4$ IMC. If the growth of the IMCs is not well controlled for fine pitch or ultra-fine pitch micro bumps of 3D stacking integration, Sn may all react with other metals to form IMCs, eventually resulting in the welding failure, holes, cracks and other issues. Based on the growth mechanism of IMCs at the micro bump interface, the abrupt of temperature and time for abnormal growth of IMCs are studied, and the control mechanism is proposed.

2. Experimental methods

In this section, the composition and size of the micro bumps, as well as the experimental procedure and the fabrication method of the sample cross-section were introduced.

The composition of the bump was Cu/Ni/SnAg. Cu pillar, Ni and SnAg metal layers with different thickness were sequentially electroplated to form micro bump, where the thickness of Cu pillar, Ni layer and SnAg layer were 3.5 µm, 0.7 µm and 3.2 µm, respectively, and a proportion of Ag in SnAg was 3 wt%. The diameter of micro bump was 5 µm. By the way, in order to study the growth mechanism of the interface IMCs, the micro bumps have not been reflowed.

The experimental procedure is as follows: firstly, the heating equipment was set to a certain temperature, and then the micro bump samples were placed in batches in it for different periods of time. Finally, the cross-section samples were obtained and observed by FIB/SEM. Next, Change the temperature of the equipment and repeat the experiments with new samples until enough samples were obtained. A stable temperature environment was required for studying the growth and evolution of Ni-Sn interface IMCs of micro bumps at different temperatures and duration. In this study, the oven was used as a heating equipment. In order to observe the variation of micro bump samples for different time at a specific temperature, the accuracy of temperature and time in the oven must be ensured.

The cross-section samples was obtained by two methods: one was to cut the sample cross-section by Focused Ion Beam Scanning Microscopy (FIB-SEM) and observe synchronically the IMCs of Ni-Sn interface; and the other was to obtain the sample cross-section by molding and polishing and then corrode the sample in the alcohol solution containing 3% HNO$_3$ and 5% HCl for 20 min in ultrasonic environment to make the grain boundaries clearer. Energy Dispersive Spectrometer (EDS) was used to analyze composition characterization of samples.

3. Results and discussion

In this chapter, the microstructure of the copper pillar bump was described firstly, and then the morphology of Cu-Sn interface IMCs at a certain temperatures and durations was analyzed, and the growth mechanism was considered. Finally, the evolution process of Ni-Sn interface IMCs at different temperatures and durations was analyzed and studied, and a method to control the growth of IMC was proposed.

3.1 The microstructure of copper pillar bumps

Fig. 1 showed cross-sectional micrographs of copper pillar bumps before and after conventional reflow condition. As can be seen from Fig. 1(a), the diameter of micro bumps was 5 µm and Cu Pillar, Ni, and SnAg have thicknesses of 3.5 µm, 0.7 µm, and 3.2 µm, respectively. Ni layer was uniform in thickness, and the interface with SnAg solder layer was smooth. The wafer reflow oven with 8-temperature zone was used. During reflow, the speed of conveyor belt was 60 cm/min. The preheating temperature and holding time were 150–200°C and 80 s, respectively. The micro bump samples were held for 60 s at a peak temperature of 255–265°C and then slowly cooled to room temperature. Fig. 1(b) shows the interface morphology of micro bumps after reflow. The thicknesses of Cu pillar, Ni layer, and SnAg layer were 3.5 µm, 0.3 µm, and 3.9 µm, respectively. The metal Pt in the Fig. 1 was the protective layer that was sputtered before sample preparation.

After the conventional reflow conditions, it could be clearly seen from Fig. 1(b) that most of the Ni layer was consumed, and the Ni layer was reduced from 0.684 µm before reflow to 0.293 µm. The interface between the Ni layer and SnAg solder layer appears “staggered”. This shows that the Ni atoms have diffused into SnAg solder layer. The thickness where IMC has the largest thickness is 2 µm, which was almost 50% of the thickness of SnAg. Such micro bumps had very poor reliability and it would seriously affect the bonding quality and the electrical interconnection performance of the device. Therefore, it was particularly important to study the growth mechanism and evolution of Ni-Sn interface IMCs.
3.2 The morphology and growth mechanism of Ni$_3$Sn$_4$ IMC

In order to better describe the morphology and growth mechanism of the Ni-Sn interface IMCs, two samples of microbump were heated in a 240°C oven for 0.5 min and 5 min, respectively, and then the morphology was analyzed. Fig. 2(a) shows the cross-sectional micrograph of the sample heated for 0.5 min. It can be seen from Fig. 2(a) that the IMCs of a certain thickness have grown and that the IMCs thickness at the Sn grain boundary position was much thicker than that at other positions. It could be concluded that the diffusion speed of Ni atoms along the Sn grain boundary was faster and the diffusion of Ni atoms to the molten Sn layer was dominated by the Sn grain boundary. This conclusion was consistent with the study results of Divya Taneja et al. [30].

The interfacial reactions of Ni and Sn mainly have two diffusion mechanisms, namely, grain boundary diffusion and lattice diffusion. Since Ni atoms have a higher diffusion rate than Sn atoms during thermal migration, Ni atoms mainly will migrate in the direction of the Sn layer, and Ni$_3$Sn$_4$ IMC were formed and grown in the Sn layer adjacent to the Ni layer.

The micro bump sample heated for 5 min was immersed in dilute hydrochloric acid for 20 min to corrode residual Sn on the surface of the micro bump and expose IMC. The top microstructure of the upper surface of the micro bump sample is shown in Fig. 2(b). It can be seen from Fig. 2(b) that the IMCs present slender columnar crystals structure. According to EDS energy spectrum shown in Fig. 2(c), Ni and Sn atoms account for 43.67% and 56.33%, respectively. Which is close to 3:4, it can therefore be determined that the composition of the slender columnar crystals metal compound are Ni$_3$Sn$_4$. It can be seen from the above analysis that the IMCs at the Ni-Sn interface grows mainly along the grain boundary between Sn grains and shows a slender columnar crystal morphology. And the main composition of IMCs is Ni$_3$Sn$_4$.

In order to observe the grain distribution of SnAg in the micro bump, the micro bump sample was sealed with resin and then grinded and polished along the micro bump radial direction to obtain the micro morphology as shown in Fig. 3. As we can clearly see, a micro bump of about 5 µm in diameter consists of about 12 Sn grains.

The above analysis shows that Ni$_3$Sn$_4$ IMC grows mainly along the grain boundary direction of Sn grain. For large micro bump, the number of Sn grain boundaries is relatively large, so the growth trend of IMC in one direction does not occur. However, for micro bump of 5 µm diameter, the number of grains and grain boundaries is limited, which results in the growth of IMC being limited to the direction of Sn grain boundaries and uneven. When the heat treatment temperature and time reach a certain degree, IMC will grow rapidly along the Sn grain boundary.

3.3 The evolution of Ni$_3$Sn$_4$ IMC

Fig. 4(a) is a cross-sectional view of a micro bump sample after 3 min of 230°C treatment. The thickness distribution of metals and alloys in micro bump section can be obtained by EDS scanning.

As can be seen from Fig. 4(b), when the scanning distance along Line 1 is 1.1 µm, the proportion of Sn starts to increase, while the proportion of Ni starts to decrease, indicating that Ni-Sn IMC starts to appear here and the composition of the IMC is constantly changing. When the scanning distance reaches 1.6 µm, the proportion of Sn and Ni reaches a rela-
Fig. 5 Cross-sectional FIB images of micro bumps after being heated under 215°C with different duration. (a) After 1 min; (b) after 2 min; (c) after 3 min; (d) after 4 min; (e) after 5 min.

Fig. 6 Cross-sectional FIB images of micro bumps after being heated under 250°C with different duration. (a) After 1 min; (b) after 2 min; (c) after 3 min; (d) after 4 min; (e) after 5 min.

...tively stable state and continues until the scanning distance reaches 2.1 μm. Then the proportion of Sn starts to increase again, while the proportion of Ni starts to decrease. When the scanning distance reaches 2.7 μm, the proportion of Ni decreases to the minimum and the proportion of Sn reaches the maximum and tends to stabilize, indicating the composition in this location is pure Sn. From the above description, that Ni-Sn IMC with different compositions must grow in the two scanning intervals: 1.1 μm–1.6 μm and 2.1 μm–2.7 μm; while in the scanning range of 1.6 μm to 2.1 μm, only a single Ni-Sn IMC grows. Based on the scanning results of Line 1, we can also deduce that the IMC thickness along Line 1 is about 1.6 μm. In the same way, it can be inferred that the IMC thickness along Line 2 is 1 μm.

Generally, there are two kinds of Ni-Sn interface reactions: solid-solid reaction and solid-liquid reaction. When the temperature is lower than the melting point of Sn, the Ni-Sn interface reaction is solid-solid reaction, and when the temperature is higher than the melting point of Sn, the interface reaction is solid-liquid reaction. The solder composition of the micro bump sample used in this study is Sn-3.0 wt% Ag, and its melting point is 221°C. In order to study the growth and evolution of IMC under different interfacial reactions, the micro bump samples were heated at 215°C and 250°C for different durations, respectively, and the morphology of the IMC was analyzed.

The evolution of IMC with increasing heating time can be obtained by observing 5 micro bump samples heated for 1–5 min at 215°C, as shown in Fig. 5. As can be seen from Fig. 5(a), the IMC has started to grow when the micro bumps are heated for 1 min. as the hg time increases, the thickness of the IMC also increases gradually, but the increasing trend is not obvious, as shown in Fig. 5(b) to Fig. 5(e). Even though the micro bumps are heated for 5 min, the IMC does not grow abnormally, but takes on a scallop-like form, and the thickness is only about 500 nm. We can also see from Fig. 5 that the IMC does not show noticeable protrusion along the grain boundary of the Sn grain. According to the theory of Ni-Sn interface reaction, when the heating temperature is 215°C, the Ni-Sn interface reaction is still solid Ni-sold Sn reaction, the growth of IMC in the solid-solid interface reaction is dominated by lattice diffusion.

Fig. 6 shows the evolution of the IMC with increasing heating time at 250°C. It can be seen from Fig. 6(a), that the slender columnar crystal IMC has started to grow when the micro bumps are heated for 1 min. as the heating time increases, the tendency of abnormal growth of the slender columnar crystal IMC becomes more and more obvious, as shown in Fig. 6(b) to Fig. 6(c). When the micro bumps are heated for 4–5 min, the Ni barrier layer is almost depleted, only a very small amount of Sn is distributed among the cracks of the columnar IMC, and the slender columnar crystal IMC even reaches the surface of the Sn layer, indicating that the 250°C has met the conditions for abnormal growth of IMC. When the heating temperature is 250°C, the Ni-Sn interface reaction has reached the solid Ni-liquid Sn reaction. With reference to the experimental results in Fig. 2 and Fig. 6, it can be deduced that the growth of IMC in the solid-liquid interface reaction is dominated by the grain boundary diffusion mechanism of Sn grains.

According to the above analysis, it can be inferred that the transition temperature from solid-solid reaction to solid-liquid reaction is the temperature point at which abnormal growth of IMC at the Ni-Sn interface occurs, which is the melting point of Sn-3.0wt%Ag. In order to verify this inference, we heated the micro bump samples for 5 min at four temperatures of 200°C, 220°C, 230°C and 260°C, respectively, and then analyzed the growth and evolution of the
results in the welding failure, holes, cracks and other issues, ultimately affects the service life of the micro bumps.

4. Conclusions

Since the growth of Ni$_3$Sn$_4$ IMC was attributed to Ni-Sn interdiffusion induced by the concentration gradient, the growth behavior of IMCs for 5 μm diameter Cu/Ni/Sn-3.0 wt%Ag micro bumps has been researched and discussed at different temperatures and durations. The IMCs at the Ni-Sn interface grew mainly along the grain boundary between Sn grains and showed a slender columnar crystal morphology. And the main composition of IMCs was Ni$_3$Sn$_4$. The diffusion speed of Ni atoms along the Sn grain boundary was faster and the diffusion of Ni atoms to the molten Sn layer was dominated by the Sn grain boundary. Due to the finite grain effect, the growth of Ni$_3$Sn$_4$ IMC was restricted to the direction of the Sn grain boundary and presented non-uniformity. When the heat treatment temperature and duration reached a certain degree, the IMC would grow rapidly along the Sn grain boundary. According to the theory of Ni-Sn interface reaction, when the heating temperature is 215°C, the Ni-Sn interface reaction was still solid Ni-solid Sn reaction, the growth of IMC in the solid-solid interface reaction was dominated by lattice diffusion. When the heating temperature is 250°C, the Ni-Sn interface reaction had changed into the solid Ni-liquid Sn reaction. The growth of IMC in the solid-liquid interface reaction was dominated by the grain boundary diffusion mechanism of Sn grains. The transition temperature from solid-solid reaction to solid-liquid reaction was the temperature point at which abnormal growth of IMC at the Ni-Sn interface occurs, which was the melting point of Sn-3.0 wt%Ag. Ni-Sn solid-solid interface diffusion could effectively inhibit the abnormal growth of interface IMC, so it became the best choice for small-size micro bumps three-dimensional integrated interconnection applications.

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