Inhibiting Effects of the Ni Barrier Layer on the Growth of Porous Cu3Sn in 10 μm Microbumps

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Abstract

With the shrinkage of size, porous Cu$_3$Sn have become a new potential threat of the reliability in micron Cu pillar bump. The formation of porous Cu$_3$Sn is contributed the decomposition of Cu$_6$Sn$_5$, which is caused by the overgrowth of intermetallic compounds (IMC) and the stress introduced by the phase transition of Cu$_6$Sn$_5$. In this paper, uniform Φ10 µm Cu/Sn and Cu/Ni (~0.6 µm)/Sn microbumps have been fabricated by multilayer electrodeposition and the effect of the Ni layer on the growth behavior of porous Cu$_3$Sn was investigated by comparing the evolution of IMC in Cu/Sn and Cu/Ni/Sn bumps aged at 170 ºC and 200 ºC. The ~0.6 µm Ni layer can effectively retard the Cu atoms diffusion, which can hinder IMC from overgrowth. Moreover, with the help of X-ray diffraction (XRD), the ability of the Ni layer in stabilizing Cu$_6$Sn$_5$ phase is strengthened, which weakens the tendency of the porous Cu$_3$Sn formation. Under the conjoint action of retarding the growth of IMC and stabilizing Cu$_6$Sn$_5$ phase, the Ni layer can inhibit the formation of porous Cu$_3$Sn efficaciously.

1. Introduction

Three-dimension integrated circuit (3D IC) is a promising solution for smaller size and high performance mobile devices.[1–3] In 3D IC packaging, the size of Cu microbump has scaled down dramatically and in recent years more attention has been paid to several microns.[4–6] When the size of Cu pillar bumps reduces to several microns, the physical characteristics of the solder joint will change significantly, which raises new potential threats.[7, 8] During the reflow and solid-state aging process, the excessive growth of intermetallic compound (IMC) would deplete the Sn solder[9]. Subsequently, abundant porous Cu$_3$Sn is produced in the interface of Cu/Sn, [10, 11, 6] which decreases the mechanical strength of the solder joint. Previous literatures have pointed out that a porous-type of Cu$_3$Sn is formed due to the decomposition of Cu$_6$Sn$_5$. [12, 13, 7]

Andriy M. Gusak et al.[10] concluded that one of the necessary condition for the porous structure formation is the overgrowth of IMC to deplete the free Sn. Therefore, retarding the overgrowth of IMC has become an increasingly important issue to inhibit the formation of porous Cu$_3$Sn and ensure the stability of micro-interconnects. Ni barrier layer is extensively inserted into the interface between Cu/Sn to retard the IMC growth, which has been proved to be a prominent approach.[14, 15] Aside from the atomic diffusion rate, stress is also contributed to the IMC evolution.[16, 17] Cu$_6$Sn$_5$ includes hexagonal η-Cu$_6$Sn$_5$ phase and monoclinic η'Cu$_6$Sn$_5$ phase,[18] and the η-Cu$_6$Sn$_5$ will transform into η'Cu$_6$Sn$_5$ at 186 ºC, which generates a 2% volume expansion introducing considerable stress in the IMC layer [19, 20] to promote the evolution from Cu$_6$Sn$_5$ to porous Cu$_3$Sn. Hence, research on the phase transition stability of η-Cu$_6$Sn$_5$ is another essential aspect about the formation of porous Cu$_3$Sn. Nogita et.al[21] found that 8.3 at.%-9 at.% Ni additions in solder can stabilize the hexagonal phase and minimize solid-state transformations. However, it is more difficult and costly to form Ni-Sn alloy than multilayer electroplate Sn-Ni layer. Meanwhile, few literatures have investigated the effect of Ni barrier layer on Cu$_6$Sn$_5$ phase
transition, so a purposive research needs to be carried out, which play an important role in retarding the formation of porous Cu$_3$Sn.

Here, Cu/Sn and Cu/Ni/Sn microbumps of 10 µm were fabricated by multilayer electroplating and the thickness of Ni layer was ~ 0.6 µm. The growth behavior of IMC in two types of bumps during the aging process at 170 °C and 200 °C was investigated, respectively. The influences of the Ni barrier layer on the growth and evolution of IMC were discussed: The Ni barrier layer can restrain the diffusion of Cu atoms, slacken the depletion of Sn and don't introduce voids in Ni$_3$Sn$_4$ layer; more importantly, Ni barrier layer can retard the transition of $\eta$-Cu$_6$Sn$_5$ to $\eta'$-Cu$_6$Sn$_5$, which reduces the stress in IMC layer, so that the Ni layer inhibits the formation of porous Cu$_3$Sn effectively. The inhibiting effects of the Ni barrier layer on the growth of porous Cu$_3$Sn in 10 µm microbumps is deeply clarified.

2. Experiment

Cu/Sn and Cu/Ni/Sn microbumps were fabricated by multilayer electrodeposition. The thickness of Cu, Ni and Sn were particularly controlled to be 4–5 µm, 0.5–0.6 µm and 4–5 µm, respectively. The electroplating baths mainly consisted of the followings: copper electroplating (copper sulfate, sulfate, different additives), tin electroplating bath (Sn sulfate, additives), which were purchased from Shanghai Sinyang, and nickel electroplating bath (nickel sulfate, boric acid, butynediol and sulfate).

The as-fabricated Cu/Sn and Cu/Ni/Sn microbumps were all aged at different temperature (170 °C and 200 °C) for 1 h to most 169 h, respectively. Then the structures were quenched in air, mounted in epoxy, and polished after grinding with water sandpaper from #800 to #7000. Correspondingly, the back-scatter electron (BSE) images of overall morphology and composition were observed by field-emission scanning electron microscope (Mira3 FE-SEM; JEOL7001F). In addition, Ni/Sn was electroplated on Cu plates (P194) and the planar samples after aging were analyzed by Rigaku D/max 2500 X-ray diffractometer (XRD) to get the phase characteristics of interface IMCs evolution. It should also be noticed that 10 to 15 random sites of each cross-section were applied with the perpendicular line scanning of energy disperse spectroscopy (EDS) to precisely obtain the thickness of Ni layer.

3. Results And Discussion

The morphology of the as-fabricated Cu/Sn and Cu/Ni/Sn microbumps is presented in Fig. 1, which is uniform in shape, neatly arranged, smooth in surface and highly flush, meeting the experimental requirements. The cross-section of Cu/Sn bump as shown in Fig. 1 (b) indicates the thickness of Cu layer is ~ 5 µm, and that of Sn layer is ~ 4 µm. Figure 1 (d) exhibits a Ni layer in interface between Cu and Sn. However, it is difficult to distinguish the Ni layer and Cu pillar, since the atomic number of Ni is close to Cu. So EDS line scanning was applied to obtain the thickness of Ni layer as shown in the inset in Fig. 1 (d). In order to obtain results more precisely, 10 to 15 random sites of each cross-section were scanned and the average thickness of Ni is ~ 0.6 µm.
3.1 IMC growth during isothermal aging of Cu/ Sn microbumps

As shown in Fig. 2, BSE micrographs of Φ10 μm Cu/Sn microbumps aged at 170 °C and 200 °C for different time duration were investigated. At 170 °C, scallop-type \( \text{Cu}_6\text{Sn}_5 \) was generated at the interface during the early aging stage. (Fig. 2a) Proceeded with aging, the Cu/Cu\(_6\text{Sn}_5 \) interface became a rich Cu region, which introduced layer-type Cu\(_3\text{Sn} \) and the reaction rate was controlled by the diffusion of Cu atoms. With the diffusion of Cu atoms, Cu\(_6\text{Sn}_5 \) continued to grow and transformed into Cu\(_3\text{Sn} \) at the same time, which caused the thickening of the IMC layer and the depletion of Sn after aging for 81 h, as shown in Fig. 2 (b). More significantly, after aging for 169 h, Cu\(_6\text{Sn}_5 \) decomposed and transformed into porous Cu\(_3\text{Sn} \) as shown in Fig. 2 (c). When the aging temperature reached 200 °C, the Cu/Sn microbumps interface had completely changed into IMC after aging only 16 h (Fig. 2d), indicating that high temperature greatly promotes the formation of IMC. Figure 2 (e) shows that all the Cu\(_6\text{Sn}_5 \) has transformed into porous Cu\(_3\text{Sn} \) after aging 36 h and the sidewall of Cu pillar has become a sink for Sn atoms decomposed by Cu\(_6\text{Sn}_5 \), which formed the sidewall Cu\(_3\text{Sn} \). Compared with the microstructure at 170 °C, the time node of porous Cu\(_3\text{Sn} \) formation also advances. In general, as the aging temperature increases to over 170 °C and the aging time goes on, the Cu\(_6\text{Sn}_5 \) will decompose into porous Cu\(_3\text{Sn} \) after the depletion of Sn, and high temperature will accelerate the progress.

3.2 IMC growth during isothermal aging of Cu/Ni/Sn microbumps

To observe the growth and evolution progress of IMC in Cu/Ni/Sn microbumps, the isothermal aging processes at 170 °C and 200 °C were recorded by BSE as shown in Fig. 3. At 170 °C, during the early stage of aging, the BSE results of Fig. 3 (a-b) indicates that Cu\(_6\text{Sn}_5 \) didn't form on the interlayer but only Ni\(_3\text{Sn}_4 \) grew on the Ni layer, which is attributed to the resistance of Ni layer to Cu atoms. [22] As the reaction between Ni and Sn went on, Ni had been largely consumed and Cu atoms began to diffuse. Figure 3 (c) shows that Ni\(_3\text{Sn}_4 \) gradually transformed into the upper thicker (Cu, Ni)\(_6\text{Sn}_5 \) layer and lower (Ni, Cu)\(_3\text{Sn}_4 \) layer with a large volume of Sn solder remained after aging for 64 h. It can't be ignored that the growth of Ni\(_3\text{Sn}_4 \) didn't introduce voids caused by the volume shrinkage, which demonstrates the superiority of ~ 0.6 um Ni layer to traditional Ni barrier layer. Further aging to 121 h, Fig. 3 (d) exhibits that IMC evolved into a typical (Cu, Ni)\(_6\text{Sn}_5 \) / (Cu, Ni)\(_3\text{Sn} \) layered structure with a small quantity of Sn remaining. When aging temperature is raised to 200 °C, the evolution of IMC was similar to that at 170 °C as shown in Fig. 3 (e-h). However, IMC formed more rapidly to make Sn completely deplete. Nevertheless, it's worth noting that the (Cu, Ni)\(_6\text{Sn}_5 \) still maintained stable and didn't decompose to form porous Cu\(_3\text{Sn} \) even at high aging temperature as shown in Fig. 3 (e), which demonstrates that the thin Ni barrier layer possesses an excellent inhibition effect on the decomposition of Cu\(_6\text{Sn}_5 \). Compared with the Cu/Sn bumps, the time node in Cu/Ni/Sn bumps of the Sn depletion is postponed and porous Cu\(_3\text{Sn} \) disappear,
which demonstrates that the Ni layer tremendously reduces the growth rate of IMC, and the Ni layer effectively retards the porous Cu$_3$Sn formation.

### 3.3 The impact mechanism of thin Ni layer to the porous IMC growth

According to the BSE analysis, the most intuitive impact of the Ni layer on the porous Cu$_3$Sn formation is retarding the IMC growth. In order to confirm the inhibition effect of the thin Ni layer on atoms diffusion, EDS mapping was applied to Cu/Sn and Cu/ Ni/ Sn microbumps aged at 200 °C as exhibited in Fig. 4. For Cu/Sn bump (Fig. 4a-b), abundant red Cu atoms diffused into Sn solder (green) during aging process. On the contrary, by inserting the thin Ni layer, few Cu atoms were observed in Sn solder area as shown in Fig. 4 (c-d), which indicates that the Ni layer can effectively inhibit the Cu atoms diffusion. Moreover, the reaction rate of Ni and Sn is slower than that of Cu and Sn$^{23, 24}$, demonstrating that the Ni barrier layer can significantly retard the growth of IMC, which controls one of the necessary condition for the porous Cu$_3$Sn formation.

In addition to obstruct the diffusion of metal atoms, the Ni barrier layer plays an important role in stabilizing $\eta$-Cu$_6$Sn$_5$ and limiting its decomposition to inhibit the growth of porous IMC. XRD analysis was applied to observe the phase transitions of the interface IMC aging at 200 °C for Cu/Sn and Cu/ Ni/ Sn plane samples as shown in Fig. 5. For Cu/Sn system, the diffraction peaks of IMC show the characteristics of monoclinic $\eta^2$-Cu$_6$Sn$_5$, whose feature 2θ angle is 30–80°, indicating the phase transition of Cu/Sn structure during the solid aging stage. Nonetheless, for Cu/ Ni/ Sn, the characteristic peaks only contain hexagonal $\eta$-Cu$_6$Sn$_5$, demonstrating that the thin Ni layer hinders the phase transition. The effect contributes to the growth of ternary IMC such as (Cu, Ni)$_6$Sn$_5$, (Ni, Cu)$_3$Sn$_4$ and so on. After the Cu atoms in the Cu$_6$Sn$_5$ cell being replaced by Ni, the volume of the cell contracts and the distance between the atoms is also reduced, which enhances the bonding force between atoms.$^{[21, 25]}$ Besides, (Cu, Ni)$_6$Sn$_5$ possesses greater formation energy than Cu$_6$Sn$_5$ and thus the possibility of phase transition is relatively remote.$^{[21, 25]}$ Consequently, the stable (Cu, Ni)$_6$Sn$_5$ without phase transition effectively reduces the interface stress, weakening the tendency of the porous Cu$_3$Sn formation. In addition, a ~ 0.6 µm Ni layer with short diffusion distance ensures the earlier formation of stable ternary IMCs, which helps to maintain the stability of the structure in the long run.

### 4. Conclusion

In this research, Cu/Sn and Cu/ Ni (~ 0.6 µm)/Sn microbumps were prepared and the effect of Ni layer on the growth of porous Cu$_3$Sn was investigated. It showed that few Cu atoms diffused into Sn solder and the time node of Sn depletion in Cu/ Ni/ Sn was later than that in Cu/Sn, which demonstrates the ~ 0.6 µm Ni layer possesses an excellent ability to suppress the overgrowth of IMC. Moreover, compared to traditional Ni barrier layer, one of the advantages of ~ 0.6 µm Ni layer is that the growth of Ni$_3$Sn$_4$ won’t
introduce voids caused by the volume shrinkage. Except the inhibition effect on IMC growth, the impact of Ni barrier layer on stabilizing Cu₆Sn₅ phase transformation was observed by XRD. By inserting the Ni layer, (Cu, Ni)₆Sn₅ didn't transform from hexagonal phase to monoclinic phase by forming ternary IMC, which reduces the possibility of the decomposition of Cu₆Sn₅. In addition, a ~ 0.6 µm Ni layer ensures the earlier formation of stable ternary IMCs.

**Declarations**

**Data availability**

The raw data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

**Declaration of competing interest**

The authors declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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