Microstructures and Shear Strength of Interfaces between Sn-Zn Lead-free Solders and Au/Ni/Cu UBM

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Microstructure and shear strength of Sn-Zn lead-free solders and Au/Ni/Cu UBM joint under thermal aging conditions were investigated. The samples were aged isothermally at 373 K and 423 K for 300, 600, and 900 hours. The IMCs at the interface between solder and UBM were examined by FESEM and TEM. The results showed the shear strength was decreased with aging time and temperature. The solder ball with highly activated flux had about 8.2% increased shear strength than that of BGA/CSP flux. Poor wetting and many voids were observed in the fractured solder joint with of the latter flux. The decreased shear strength was caused by IMC growth and Zn grain coarsening. In the solder layer, Zn reacted with Au and then was transformed to the \( \beta \)-AuZn compound. At the joint interface, although AuZn grew first, \( \gamma \)-Ni\( Zn_2 \) compounds were formed with aging time.

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1. Introduction

Microelectronic components have been evolved to become smaller, lighter, and more functional. As environmental pollution continues to be a worldwide concern, the apprehension about the hazard of lead has also increased. As a measure to solve this problem, there have been tremendous efforts to develop lead free solders.¹ ²

Recently, compared with the Sn-Ag solder, the Sn-Zn solder has been highly recommended as the substitution for Sn-Pb eutectic solder due to its low melting point. Sn-Zn solder can be also used without replacing the existing manufacturing lines or electronic components. Moreover, because Zn is a low cost metal, Sn-Zn is advantageous from an economic point of view. However, Sn-Pb eutectic solder is difficult to handle in the practical uses due to its high activation characteristic. In addition, problems such as decreased wettability, controlling voids and oxidation, and coping with flow soldering still remain.³ ⁶ To test validate reliability of a Sn-Zn solder joint, various experiments have been conducted, but they are still lacking in meaningful results in this area of research. Furthermore, unlike the general reaction layer having a Sn base solder, stable binary Au-Zn, Cu-Zn, and Ni-Zn intermetallic compounds (IMCs) are formed between Sn-Zn solder and under bump metallurgy (UBM) by different experiment conditions. Many studies have reported that the thickness and shape of IMCs changes according to the aging time and temperature.⁷ ¹³

This paper presents the differences in shear strengths of solder interface by isothermal aging after low temperature Sn-Zn lead free solders is soldered to the chip size package (CSP). Also, the growth reaction layer and microstructure of the IMCs in the Au/Ni/Cu UBM structure are investigated, and the effect of two kinds of fluxes on the shear strengths and Sn-Zn solder joints is analyzed.

2. Experimental Details

In this study, 288 I/O CSP packages were used. The external dimensions of the package were 13 mm \( \times \) 13 mm, and the thickness was 1.0 mm. The ball size was 0.3 ± 0.01 mm in diameter and 0.5 mm in pitch. Solder ball pads surface was formed by nickel and gold continuous plating on the copper pattern surface wired on bismaleimide triazine (BT). The UBM structures were made up of Au(0.5 \( \mu \)m)/Ni(10~15 \( \mu \)m)/Cu(22~32 \( \mu \)m) layers. The fluxes were used to eliminate oxides and shape of the solder balls uniformly. To compare the effect of the fluxes on shear strengths and low temperature Sn-Zn solder joints with both Zn rosin activated (RA) flux (ZA650: Nihon genma) and BGA/CSP rosin mildly activated (RMA) flux (390DH3LV: Alpha metal) were used in the package application. Also, the solidus and liquidus of Sn-8Zn-3Bi (mass%) were 460 K and 470 K, respectively. Zn-7Zn, had solidus and liquidus of 472 K and 474 K, respectively, Figure 1 shows the reflow temperature profile of the Sn-8Zn-3Bi solder. The reflow was performed by infrared and hot air convection heating system. The overall reflow time was 5 minutes, and the velocity of the conveyor was 0.55 m/min. The peak reflow temperatures for Sn-8Zn-3Bi and Sn-7Zn were 503 ± 5 K and 513 ± 5 K, respectively, and both dwell times were 10 seconds. The time above liquidus was 60 seconds.

![Fig. 1 Temperature profile for the reflow soldering.](image-url)
To analyze the effect of aging time and temperature, the samples were aged at isothermal temperatures of 373 K and 423 K for 300, 600, and 900 hours. After the samples were aged, their shear strengths were measured by using a bond tester. The tip of the machine moved at 0.3 mm/s. The distance between the surface of the solder mask and the tip was 3.0 μm. The shear strengths of the samples at each condition were measured on 30 bumps from 2 samples. The average value of the strengths was calculated, discarding the maximum and minimum values. The samples were cut and finely polished with 0.05 μm Al₂O₃ powder. An optical microscope (OM) and field emission scanning electron microscopy (FESEM) were used to observe the fractured surface of the solder joints. Using transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS), the microscopic structure of the IMC layers were analyzed. Tungsten was evaporated onto TEM samples. The TEM samples were prepared with a focused ion beam (FIB) that has a Ga⁺ ion source at acceleration voltage of 30 keV. Final thinning was performed by micro milling with a 100 pA ion beam. The TEM samples were observed by using JEM-2010UHR (JEOL) at an acceleration voltage of 200 keV.

3. Results and Discussion

Figure 2 shows the shear strengths of the two kinds lead free solders according to aging times and temperatures. The average initial shear strength of Sn-8Zn-3Bi was 4185 mN. However, after 900 hours of aging at 423 K, the average shear strength of Sn-8Zn-3Bi was 3744 mN, a decrease of about 11% from the initial value. In the case of Sn-7Zn, after 900 hours of aging at 423 K, the average shear strength was varied from 2646 to 2185 mN, a decrease of about 18%. However, after 900 hours of aging at 373 K, the average shear strength of Sn-8Zn-3Bi and Sn-7Zn decreased about 0.5% and 12% from the corresponding initial values, respectively. As the result of thermal aging, the shear strength tended to decrease with aging time and temperature, and it was not affected by the compositions of lead free solders. Also, it was confirmed that as the aging temperature increased, the shear strength decreased more. The Sn-8Zn-3Bi solder had higher initial shear strengths than Sn-7Zn solder. A small amount Bi is inclined to enhance the shear strength of the Sn-8Zn-3Bi solder. After 900 hours of aging, the shear strength of Sn-7Zn solder had apparently decreased, and the decrease was due to the 390DH3LV flux, which caused poor wettability of Sn-7Zn solder.

Figure 3 shows the shear force vs. displacement curve of a Sn-8Zn-3Bi solder according to aging time. Only a reflowed specimen for forming solder balls showed bigger displacement because the solder was ductile. The solder ball with 900 hours of aging showed 29% decreased displacement than that of a reflowed solder ball. This is because that the solder became brittle as the aging time is increased.

Figure 4 shows the fracture surface of the Sn-7Zn solder after the shear test. The fracture surface before aging indicates the dimple considered as ductile fracture mode. The partial alteration of fracture mode from ductile to brittle was observed at the fracture surface of the solder after 900 hours of aging.

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**Fig. 2** Relation between aging times and shear strengths.

**Fig. 3** Shear force-displacement curves of Sn-8Zn-3Bi solder balls.

**Fig. 4** Fracture surfaces of Sn-7Zn solder ball; (a) before aging (b) after aging at 423 K for 900 h.
Figure 5(a) presents the fractured surface of the Sn-8Zn-3Bi at which the ductile fracture was observed. Figure 5(b) shows the fracture surface of the solder ball after 900 hours of aging at 423 K, and the appearances of both the IMC and brittle fracture were apparently observed. Moreover, the fractured surfaces revealed that Sn-8Zn-3Bi was better than Sn-7Zn in soldering results. Sn-Zn solders did not wet to Cu or Ni UBM, and cause the critical defects such as bridges or voids.7)

Figure 6 shows the effect of two kinds of fluxes. As shown in the Fig. 6, the majority of voids and poorly wetted solder parts were scattered in the fractured surface of solder applied with the 390DH3LV flux. However, with ZA650 flux, the poorly wetted solder parts hardly appeared because of the effect of a high activated element in the ZA650 flux, which is considered to enhance the wettabilities between the solder and UBM.

The same conclusion was derived from Fig. 7, which shows the different shear strengths before aging. The figure shows that the solder ball with the ZA650 flux had about 8.2% more shear strength than that with 390DH3LV flux. The poor wetting between the solder and UBM caused the stepped shear strengths in Fig. 7.

Figures 8 to 10 show the microstructures cross section in the solder balls aged at 423 K. The solder consists of Sn, the base phase with bright gray, and Zn, the scattered phase with dark gray. The Zn phase in both solders grew in proportion to the aging time, but the shapes of the Zn grains differed according to the composition of the solder. Whereas the Sn-8Zn-3Bi solder had mixed small cellular-shaped and coarse needle-shaped phases, Sn-7Zn did cellular Zn phase, which grew relatively little even after 900 hours of aging. The Zn phase grew more easily in Sn-8Zn-Bi had a coexistence area of the solid and liquid than in Sn-7Zn solder which reaction is similar to the eutectic one during its solidification.

The 0.5 μm thick Au layer used to prevent oxidation dissolved quickly into the liquid solder during reflow soldering. The band-shaped compounds formed in the solder were confirmed as Au-Zn IMC of 47.4 at%Au and 52.6 at%Zn by TEM-EDS analysis. The Zn phases, which appeared in the initial structure of the solder, were drained by the growth of IMCs according to the increased aging time. Only the Sn zone filled up the interface and gradually expanded as the aging time increased. However, small amount of Zn was detected by TEM-EDS. Au-Zn compound formed in Sn-8Zn-3Bi solder grew to a thickness from 4.2 μm to 5.0 μm after 900 hours of aging at 423 K. As the aging time
increased, three-divided Ni-Zn compounds grew into the side of Ni layer because of the reaction between Ni and Zn. The initial thickness of the Ni-Zn compounds ranged from 0.5 to 0.8 μm, but it grew to a thickness of 11.0 to 12.5 μm after 900 hours of aging at 423 K. Also, Ni-Zn compounds formed in Sn-Zn solder grew to a thickness about from 6.5 to 7.2 μm, which was the smaller growth than that formed in Sn-8Zn-3Bi. These results shows that Ni-Zn compounds was formed in
earlier in Sn-Zn solders different from the common Sn base solder. This formation occurred early because the high active Zn, which was not dissolved into Sn matrix, reacted with Ni faster than Sn.

Figure 11 and Figure 12 show the bright-field cross-section TEM image and electron diffraction patterns of the interface between the Sn-8Zn-3Bi solder and UBM after 600 hours of aging at 423 K. Microstructures of the solder and the IMCs layer were clearly observed. Figure 11 shows the interfacial reaction of Au investigated by SEM and TEM study. The results showed that the porous Au-Zn compound was formed between Sn and Sn, and its structure is \( \text{C12}_{\text{1}} \)-AuZn of cubic phase (S.G.: Pm3m, JCPDS 30-0608).

Figure 12 shows the interfacial reaction between Ni and Zn, investigated in the TEM study. In the TEM image, three-divided layers between Sn and Ni were observed with column-shaped grains. The layers indicated by Ni-Zn(1), (2), and (3) were formed with the thickness of \( \sim 0.7 \mu m \), \( \sim 4 \mu m \), and \( \sim 2 \mu m \), respectively. By indexing the electron diffraction patterns, we found that all reaction layers were the structure of \( \text{C13}_{\text{1}} \)-Ni\(_5\)Zn\(_{21}\) (cubic phase, JCPDS 06-0653). The results showed that the porous Au-Zn compound was formed between Sn and Sn, and its structure is \( \text{C12}_{\text{1}} \)-AuZn of cubic phase (S.G.: Pm3m, JCPDS 30-0608).

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4. Conclusion

The shear strength between the Sn-Zn solders and Au/Ni/Cu UBM was measured according to isothermal aging, after low temperature Sn-Zn solders was soldered to the an CSP package. Also, IMC growth and microstructure of the solders were observed.

(1) The shear strength decreased as the aging temperature and time increased, regardless of properties of the lead free solders.

(2) In the solder joint interface, AuZn initially formed on the side of the solder, but as the aging time increased, Ni\(_5\)Zn\(_{21}\) grew into the side of Ni layer because of the reaction between Ni and Zn.

(3) AuZn grew to a thickness of from 4.2 to 5.0 \( \mu m \) after 900 hours of aging at 423 K. As the aging time increased, the IMCs consumed the Zn-rich phases had
formed around the AuZn. Therefore, the Sn zone seemed to be gradually expanded.

(4) After 600 hours of aging at 423 K, Ni$_5$Zn$_{21}$ has three-divided layers, which thicknesses are ~0.7 µm, ~4 µm, and ~2 µm, respectively.

(5) Zn phases grew in both Sn-8Zn-3Bi and Sn-7Zn solder, but the coarse needle-shaped Zn phases were more observed in the Sn-8Zn-3Bi than in the Sn-7Zn solder.

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