The Effects of Solid-State Aging on the Intermetallic Compounds of Sn-Ag-Bi-In Solders on Cu Substrates

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The growth behavior of the intermetallic compounds that formed at the interfaces between Sn-Ag-Bi-In solders and Cu substrates during solid-state aging is investigated. The compositions of the intermetallic compounds are $Cu_3(Sn,In)$ near the Cu substrates and $Cu_6(Sn,In)_5$ near the solders; very little Bi or Ag was dissolved in the compounds. The aging temperatures were 120°C, 150°C, and 180°C for 5 days, 10 days, 20 days, and 40 days. The change in the morphology of $Cu_6(Sn,In)_5$ from scallop type to layer type was prominent at the aging temperature of 180°C. The thickness of the compound layers did not vary much at the lower aging temperatures but followed the diffusion-controlled mechanism at 180°C. Massive Kirkendall voids were observed in $Cu_3(Sn,In)$ layers at the aging temperature of 180°C.

Key words: Solid-state aging, Kirkendall void, Sn-Ag-Bi-In solder, Pb-free

INTRODUCTION

Solders play an important role as one of the interconnects in electronic devices. To find Pb-free solder systems that possess the same properties as eutectic Sn-Pb solder is crucial due to the urgent demands in electronic device industries. Interfacial reactions between solders and substrates during solid-state aging are critical for the reliability of the joints. There are numerous reports on interfacial reactions in Pb-free solder systems, such as Sn-Ag, Sn-Bi, and Sn-Ag-Cu, on various substrates.[1–4] Sn-Ag solder has been widely used as a substitute Pb-free solder alloy, but with the drawback of a high melting temperature (221°C) compared with that of eutectic Sn-Pb solder (183°C). The addition of bismuth to Sn-Ag alloys is believed to reduce the melting temperature, but wetting behavior and mechanical strength are degraded as well.[5–7] A certain amount of indium alloyed into Sn-Ag-Bi solder systems could decrease the melting point, and also improves the mechanical strength and the wetting

ability. The compositions of the solders used in this study are 84Sn-3Ag-3Bi-10In and 89Sn-3Ag-3Bi-5In (in weight percent, and represented by 84-3-3-10 and 89-3-3-5 hereafter). The melting points of these two solders are 203°C and 212°C, respectively.[8]

Some studies have focused on the mechanical strength of the Sn-Ag-Bi-In solder systems.[9–12] Vianco et al. thermally aged Sn-In/Cu to investigate the interfacial compound reactions. They reported that the growth of the intermetallic compound that formed between 50Sn-50In on Cu substrates displayed an erratic behavior that may be contributed by the microstructure of the solder during solidification.[13] The results for 77.2Sn-20In-2.8Ag on Au/Ni/Cu pads indicated that the thickness of the intermetallic compound layer did not change much during aging at a temperature of 100°C. After aging for a long time, voids were formed along the solder/pad interfaces.[14]

In this study, two compositions, 84-3-3-10 and 89-3-3-5, of Sn-Ag-Bi-In solders were used to investigate the effects of solid-state aging on the inter-metallic compounds that formed at the interfaces between the solders and Cu substrates at various aging temperatures. The growth of compounds that

were formed at an aging temperature of 180°C was found to follow a diffusion-controlled mechanism. However, the thickness of the compounds did not show any significant variation at the aging temperatures of 120°C and 150°C. Furthermore, large amounts of Kirkendall voids could be observed in the $Cu_3(Sn,In)$ layer in the samples aged at 180°C, but few or no voids could be seen in samples aged at the low temperatures. This paper investigates the different growth behaviors of the intermetallic compounds at the interfaces. The formation of Kirkendall voids will be discussed.

EXPERIMENTAL

To prepare Cu substrates for this study, Cu coupons were cut to a size of 10 mm × 10 mm and ground by using SiC paper. Cu substrates were then polished using 1.0-μm and 0.1-μm Al_2O_3 suspensions. Thirty milligrams of samples of the 84-3-3-10 and 89-3-3-5 were dropped onto the Cu substrates and reflowed in a rosin mildly activated (RMA)-type flux for 40 min at a temperature of 252 ± 3°C. The samples were then placed in an oven at 120°C, 150°C, and 180°C for 5 days, 10 days, 20 days, and 40 days. After the samples were removed from the oven, they were cross-sectioned and polished using 1.0-μm and 0.1-μm Al_2O_3 suspensions.

Secondary electron microscopy (FE-SEM, HITACHI S-4700) was employed to examine the cross-section of the samples. The thickness of the IMCs was calculated by measuring the total area of the IMCs and dividing it by the total length of the images. The images were taken over five locations for better accuracy. Emission electron probe microanalysis (FE-EPMA, JEOL JXA-8500F) was employed to investigate the composition of the IMCs that formed in the bulk solders and at the interfaces between the solders and the Cu substrates.

RESULTS AND DISCUSSION

Thickness

Two kinds of IMCs were formed at the interfaces between the solders and Cu substrates. The compositions were determined by EPMA and were $Cu_6(Sn,In)_5$ and $Cu_3(Sn,In)$, located near the solder side and near the Cu side, respectively. Very little or no Bi and Ag was dissolved in the IMCs. During solid-state aging, the thickness of these two kinds of compounds as a function of aging time in 84-3-3-10 and 89-3-3-5 at the aging temperatures of 120°C and 150°C is plotted in Fig. 1. As can be seen in the figure, the thickness of the IMCs in both kinds of solders that were aged at 120°C and 150°C did not change much. The measured thickness was in the range between 5.38 μm and 7.86 μm. No particular trend for the growth of the intermetallic compounds at these two temperatures was observed in either solder. On the other hand, Fig. 2 presents the thickness of the interfacial IMCs of 84-3-3-10
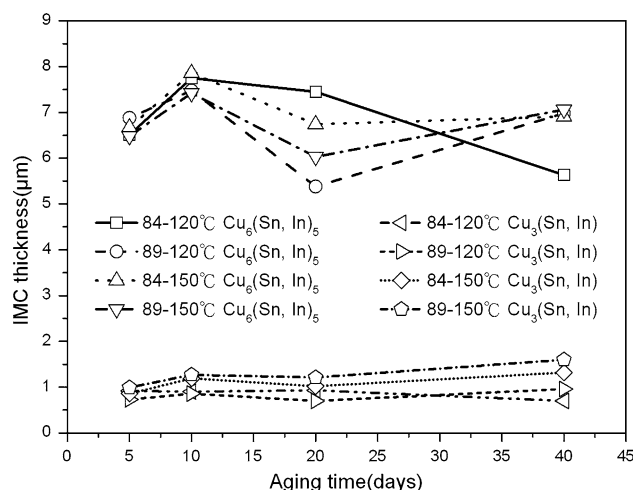

Fig. 1. Thickness of $Cu_6(Sn,In)_5$ and $Cu_3(Sn,In)$ in 84Sn-3Ag-3Bi-10In and 89Sn-3Ag-3Bi-5In solders that were aged at 120°C and 150°C for various times.

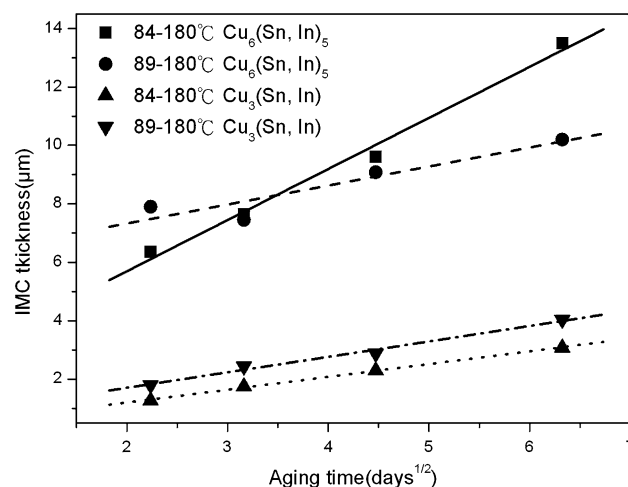Fig. 2. Thickness of $Cu_6(Sn,In)_5$ and $Cu_3(Sn,In)$ against $t^{1/2}$ in 84Sn-3Ag-3Bi-10In and 89Sn-3Ag-3Bi-5In solders.

and 89-3-3-5 solders that were aged at 180°C versus the square root of the aging time. The data could be fitted linearly, indicating that the growth of $Cu_6(Sn,In)_5$ and $Cu_3(Sn,In)$ at 180°C was a diffusion-controlled process. However, the growth of IMCs at the 120°C and 150°C aging temperatures did not show such a dependence.

Morphology

Figure 3 shows images of the IMCs at the interfaces between the solders and Cu substrates for the samples that were aged at 120°C, 150°C, and 180°C for 40 days. After aging for 40 days, the IMCs that formed at 120°C and 150°C in 84-3-3-10 and 89-3-3-5 were of scallop type or of irregular shape. However, the IMCs became layer type after 40 days of aging at 180°C in both kinds of solders. In Sn-Pb and many Pb-free solders, Cu_6Sn_5 is formed during
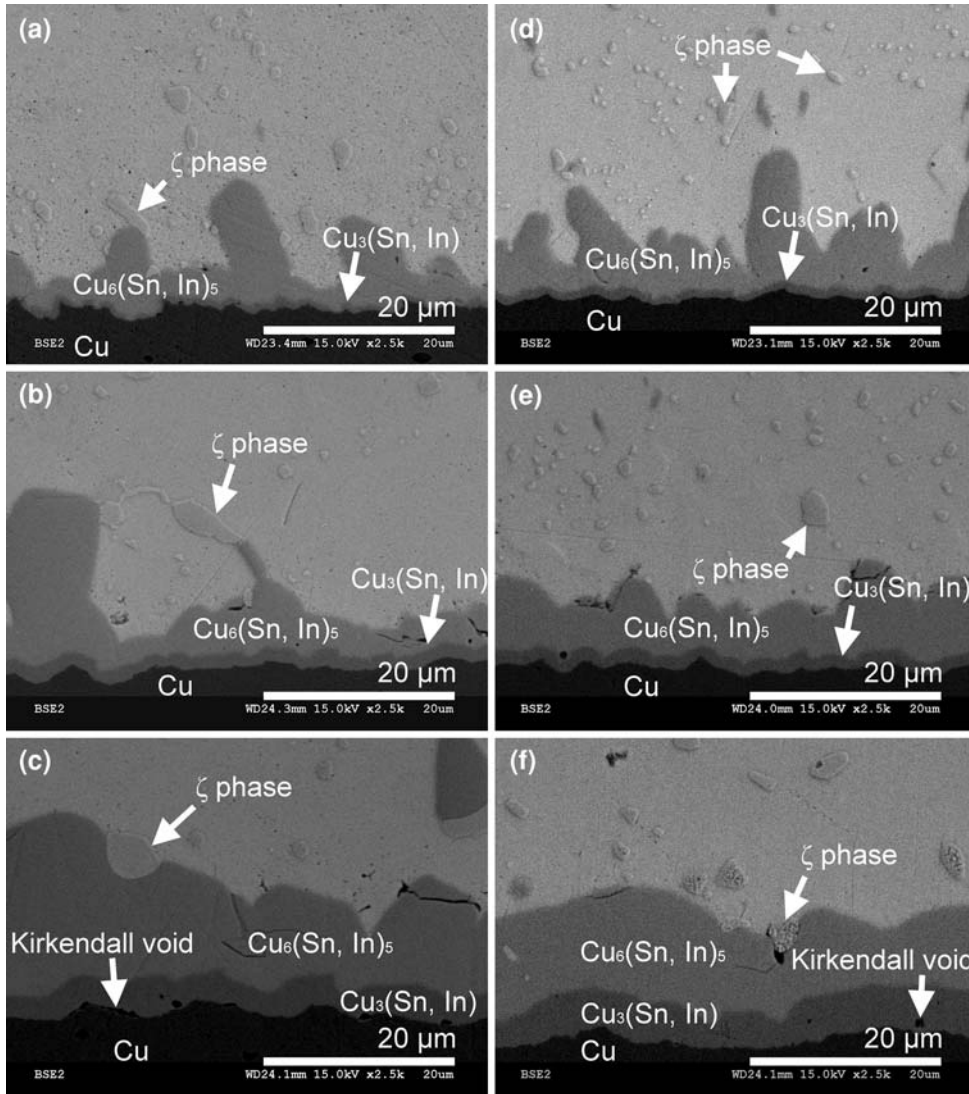
Fig. 3. Intermetallic compounds formed between Cu and 84Sn-3Ag-3Bi-10In at (a) 120°C, (b) 150°C, and (c) 180°C; and 89Sn-3Ag-3Bi-5In at (d) 120°C, (e) 150°C, and (f) 180°C for 40 days.

reflow and exhibits scallop-type morphology. On subsequent thermal aging, Cu atoms would diffuse through Cu_3Sn and Cu_6Sn_5 layers to react with Sn. The diffusion of Cu atoms through the IMCs layers is very slow; hence, it requires a very long time. However, there are valleys between the scallop-type Cu_6Sn_5 that provide relatively wide channels to facilitate the diffusion of copper atoms. The Cu diffusing through the channels would form Cu_6Sn_5 IMCs once it meets the Sn atoms from the solders. Thus, the valleys would be filled more rapidly and the scallop-shape IMCs gradually become flat. Many studies have reported that a change in the morphology of Cu_6Sn_5 in several Pb-free solders could be observed at an aging temperature of 150°C; some results even showed that the phenomenon could occur at 100°C.[1–4] However, our results indicated that the change in the morphology of IMCs was less obvious at the aging temperatures of 120°C and

150°C than at 180°C. The results suggested that either the diffusion of Cu atoms was too slow at low temperature, or that Cu atoms were consumed by other processes rather than forming $Cu_6(Sn,In)_5$.

Kirkendall Voids

Figure 3c and f displays the IMCs layers of the samples that were aged at 180°C for 40 days. Many voids could be observed in the $Cu_3(Sn,In)$ IMC layers in both images. More voids were observed in 84-3-3-10 than in 89-3-3-5. These voids were believed to be Kirkendall voids. As pointed out by Zeng et al.,[15] the formation of Kirkendall voids in Cu_3Sn is dominated by the phase transformation from Cu_6Sn_5 to Cu_3Sn since Cu_3Sn is a thermodynamically stable phase. The voids that formed inside the $Cu_3(Sn,In)$ and at the $Cu_6(Sn,In)_5/Cu_3(Sn,In)$ interfaces were believed to be contributed by Cu

atoms as the dominant diffusing species. Large amounts of Kirkendall voids could be found in the samples that were aged at 180°C. Very few or no voids could be seen in the samples that were aged at lower temperatures for the same time. These results suggested that the massive diffusing flux of Cu from the substrates was prominent at high temperature. Moreover, the amount of voids in 84-3-3-10 was much larger than in 89-3-3-5. Since the melting temperature of 84-3-3-10 is 203°C, almost 10°C less than that of 89-3-3-5, Cu is expected to have greater diffusion capability in 84-3-3-10.

Notably, there should still have been diffusion of Cu at 120°C and 150°C. Nonetheless, the afore-mentioned results suggest that the supply of Cu atoms did not contribute to the formation of Cu_6Sn_5 effectively below 150°C. He and Li[16,17] reported that the segregation of Bi in Cu_6Sn_5 during reflow may inhibit the growth of the IMCs. In this study, the samples of 84-3-3-10 aged at 120°C and 180°C were investigated by EPMA. The results revealed that the amount of Bi in $Cu_6(Sn,In)_5$ was less than 0.1%. No segregation of Bi could be found. Hence, segregation of Bi may not be the cause of the inhibition of the growth of $Cu_6(Sn,In)_5$ IMCs.

In Fig. 3a and d, small particles can be observed at the boundaries between Cu_6Sn_5 and the solder in the samples aged at 120°C. The composition of the particles was identified by EPMA and was believed to be the ζ-phase, a solid solution of Ag_4Sn and Ag_3In. Many ζ-phase particles could also be found in the bulk solders. They formed after the reflow process and grew larger during solid-state aging. To form an intermetallic compound, the reacting species were supersaturated and the solubility was assumed to be at local equilibrium at $Cu_6(Sn,In)_5$/solder interfaces. Previous results[8] have shown very little or no Cu dissolved in the ζ-phase right after reflow. However, up to 5 at.% of Cu was detected in ζ-phase particles at the interfaces in the aging samples. It is plausible that the formation of the ζ-phase would consume a large portion of the Cu atoms that diffused from the substrates. It is uncertain whether the formation of the ζ-phase or $Cu_6(Sn,In)_5$ IMCs would be more favorable. Never-theless, the results for the thickness of the IMCs suggested that the $Cu_6(Sn,In)_5$ layer did not grow during the aging process at 120°C and 150°C.

On the other hand, the diffusion of Cu was expected to be faster at the aging temperature of 180°C. The formation of the Kirkendall voids and the layer-type $Cu_6(Sn,In)_5$ could be evidence of this. The enormous amount of Cu would be more than enough for the ζ-phase to consume. Thus, the $Cu_6(Sn,In)_5$ layer became thick and the growth kinetics obeyed a diffusion-controlled mechanism. It is important to note that some ζ-phase particles were embedded in the $Cu_6(Sn,In)_5$ layers in both 84-3-3-10 and 89-3-3-5 at the aging temperature of 180°C after 40 days, as can be seen in Fig. 4. They could also be observed in the samples that were
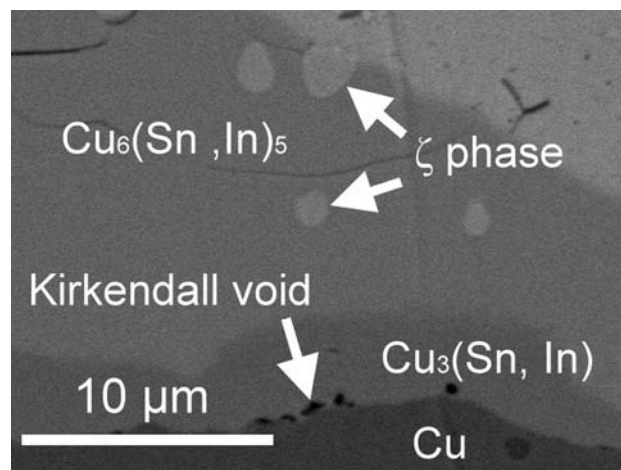

Fig. 4. Enlarged figure of the region at the interface between the 84Sn-3Ag-3Bi-10In solder and the Cu substrate after aging at 180°C for 40 days.
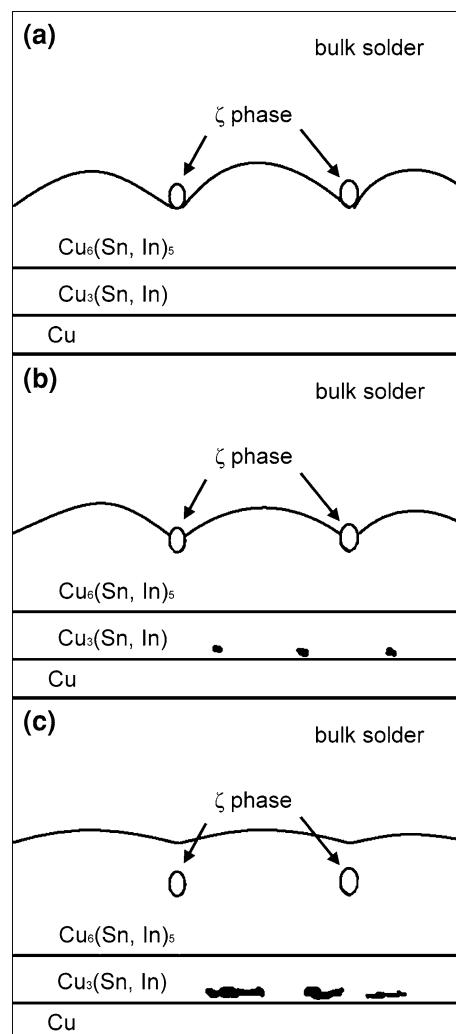

Fig. 5. Illustrative sketches of the growth process of the intermetallic compound at (a) the initial stage of solid-state aging, (b) during aging, $Cu_6(Sn,In)_5$ grew but was pinned by ζ-phase particles, (c) ζ-phase particles were encompassed by $Cu_6(Sn,In)_5$.

aged for a shorter time at 180°C. Nearly no or very little ζ-phase could be found in the samples that were aged at the lower temperatures. It is plausible that these ζ-phase particles pinned the boundaries of $Cu_6(Sn,In)_5$ at the initial stage of aging. The $Cu_6(Sn,In)_5$ layer would eventually encompass these ζ particles when the growth of $Cu_6(Sn,In)_5$ dominated at higher temperature. This process is illustrated in Fig. 5.

CONCLUSION

This paper investigated the solid-state aging of 84-3-3-10 and 89-3-3-5 solders on Cu substrates at various aging temperatures and durations. The thickness of the $Cu_3(Sn,In)$ and $Cu_6(Sn,In)_5$ layers did not vary with aging time for the samples aged at 120°C and 150°C, but it followed a diffusion-controlled mechanism at 180°C. Kirkendall voids were observed in $Cu_3(Sn,In)$ layers in the samples aged at 180°C. The IMCs at the interfaces in the samples aged at 150°C remained intact for 40 days. Therefore, Sn-Ag-Bi-In solder systems may be good candidates for the replacement of Pb-free solders.

ACKNOWLEDGEMENTS

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