Interfacial reactions of BGA Sn–3.5%Ag–0.5%Cu and Sn–3.5%Ag solders during high-temperature aging with Ni/Au metallization

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Abstract

The joint strength and the microstructure of Sn–3.5Ag and Sn–3.5Ag–0.5Cu (wt.%) solders on Cu/Ni/Au ball-grid-array (BGA) pad metallization were investigated after high-temperature solid-state aging at 190°C (around 0.86×Tm of solder alloys). Sn–Ag solder gave better results in terms of shear strength on high-temperature aging than Sn–Ag–Cu. Very high consumption of Ni was observed in the case of Sn–Ag–Cu solder alloys. After 16 days of aging at the aforementioned temperature, 5 μm Ni layer was fully consumed from the substrate pad and a thick layer of Cu–Sn intermetallic compounds (IMCs) was found at the base of the interfacial IMCs. Much less consumption of Ni substrate was observed for Sn–3.5Ag solder during high-temperature aging for longer time. The mean thickness of the intermetallics at the interface was higher for Sn–Ag–Cu solder alloy. For both cases Ni diffused through the interfacial IMCs and formed quaternary compounds for Sn–Ag–Cu system and ternary compounds for Sn–Ag system within the bulk solder. It appeared that Sn–Ag–Cu solder alloy was more vulnerable in high-temperature solid-state aging.

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1. Introduction

One of the most influential factors in the solder joint quality of a ball-grid-array (BGA) component is the metal surface finish on the Cu pads. The most common surface on BGA component is electrolytic Ni/Au plated over the copper pad of the flexible substrate. Interaction and interdiffusion behavior between the solder and Cu has been studied extensively elsewhere. It is found that at the Sn-containing solder/Cu interface, tin reacts rapidly with Cu to form Cu–Sn intermetallic compounds (IMCs), which make the solder joint weak due to the brittle nature of the IMCs. The strength of the solder joint decreases with an increasing thickness of IMCs that form at the interface and act as the initiation sites for micro-cracks [1–3]. The electrolytic Ni layer on Cu pad creates good solderable surface and also acts as a good diffusion barrier layer. Many studies have reported that the growth rate of intermetallic compounds is lower in the Ni/solder system than in the Cu/solder system [4–6]. The reaction rate of molten eutectic SnPb on Ni is about a 100 times slower than that of the molten eutectic SnPb on Cu [7].

The common alternatives to the standard eutectic tin–lead solder investigated so far are based on tin alloys in combination with copper, silver, antimony, bismuth, or zinc. A key issue affecting the integrity and reliability of solder joints for high-Sn-containing alloys is the fast interfacial reactions between the molten solder and the under bump metallization (UBM). Among the binary alloys, Sn/0.5–0.8% Cu and Sn/3–4% Ag play a dominant role. The Sn–Ag solders exhibit melting points in the range of 220–221°C, which is more than 30°C beyond the melting point of the standard eutectic tin–lead solder. The melting point of Sn–3.5Ag–0.5Cu eutectic solder was established to be 216.8 ± 1°C [8]. Lee et al. [9] observed that the growth rate of the interfacial IMCs in Sn–Ag–Cu is higher than in Sn–Ag at high-temperature solid-state aging, whereas under low-temperature condition, IMCs layer in the Sn–Ag solder shows higher growth rate than that in the Sn–Ag–Cu solder. The metallurgical behavior of Sn–Ag and Sn–Ag–Cu solder joints with electrolytic

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Ni and the related joint reliabilities have not been sufficiently studied as yet. A detailed study to correlate the microstructures and the mechanical properties of a solder joints with the compositional change as a function of aging time under high-temperature condition is needed. Therefore, the present study was carried out to investigate the interfacial reactions with electrolytic Ni metallization during prolonged high-temperature aging for Sn–Ag and Sn–Ag–Cu solders.

2. Experimental procedures

The solder mask defined copper bond pad on the flexible substrate of the BGA package was used as a base for electrodeposition of Ni and Au. The average thickness of Ni and Au was 5 and 0.5 μm. The compositions of the solder alloys were Sn–3.5Ag and Sn–3.5Ag–0.5Cu (wt.%). The solder mask-opening diameter was 0.6 mm at the ball pad. Lead-free eutectic Sn–Ag and Sn–Ag–Cu solder balls with a diameter of 0.76 mm, were placed on the prefluxed Au/Ni/Cu bond pad of the substrates as shown in Fig. 1 and reflowed at a temperature of 250 °C for 1 min in a convection reflow oven (BTU VIP-70N). The flux used in this work was a commercial no-clean flux. After the reflow, samples were subjected to aging at 190 °C for 2–16 days.

To investigate the microstructure, the samples were mounted in epoxy after each condition. The samples were ground and polished carefully and then gold-coated for examination. The chemical and microstructural analyses of the gold-coated cross-sectioned samples were obtained by using the Philips XL 40 FEG scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectrometer (EDX). Shear tests were performed on both the reflowed and aged samples by using a Dage Series 4000 Bond Tester. The shear tool height and the test speed of the shear test in this work were about 100 μm and 550 μm/s, respectively. Twenty randomly chosen solder balls were sheared to obtain the average and the extent of deviation. The fracture surfaces after the ball shear tests were investigated thoroughly by SEM in secondary electron mode as well as by EDX.

3. Results and discussion

The homologous temperature ($T_H$) used in this experiment is around 0.86 ($T = 190^\circ$ C), which corresponds to around 155 °C for conventional Sn–Pb alloy. The homologous temperature is the ratio of the absolute temperature of a material
Fig. 4. Backscattered electron micrographs illustrating the interface after reflowed at 250°C (a) Sn–Ag–Cu and (b) Sn–Ag solders.

...to its absolute melting temperature ($T_H = T/T_m$). Fig. 2 depicts the solder ball shear test results of electrolytic Ni/Au plating/solder joints. At the time of ball shear test mostly ductile fracture occurs within the solder and the solder-IMC interface for the reflow samples but for the aging mainly ductile fracture is observed for the samples aged up to 4 days for both solder alloys. For long-time aging, ductile–brittle fracture occurs within the solder and/or solder-IMCs interface for Sn–Ag solders and mostly brittle fracture occurs within the IMCs for Sn–Ag–Cu solder alloys (Fig. 3).

Initial average shear load of the solder joints is around 1.75 and 1.85 kgf for Sn–Ag–Cu and Sn–Ag solders, respectively. Sn–Ag solder shows slightly higher shear load in as bonded condition on electrolytic Ni surface finish. Fig. 2 also shows that the solder ball shear load for Sn–Ag solders during aging increases with the increase of aging time up to 4 days and then turn to decrease up to 8 days and after that a stable shear load is observed. For Sn–Ag–Cu solders, a decreasing trend is observed with aging and this tendency is more sharp after 4 days of aging. However, the main differences between the two solder joints are that the maximum average shear load is found after as reflow condition for the Sn–Ag–Cu solder alloys (1.75 kgf) and after 4 days aging for the Sn–Ag solders (2.01 kgf). Solder joint shows minimum value of average shear load (1.49 kgf) after 12 days of aging for Sn–Ag solders, 19% reduction from the initial load, whereas for Sn–Ag–Cu solders, it is found (1.06 kgf) after 16 days aging, 39% reduction from the initial bonded load. The Sn–Ag solders give relatively better ball shear load at about 1.49–2.01 kgf over the whole duration of aging.

These results demonstrate that electrolytic Ni/Sn–Ag solder joints have greater solder joint integrity during solid-state thermal aging as compared to the Sn–Ag–Cu solder joint. To investigate the shear load and the reaction phenomenon of the solder joints, a detail cross-sectional studies are carried out by SEM. During reflow, molten solder absorbs the entire Au layer into solution, allowing Sn and Cu from the solder to react with the Ni layer and to form different types of IMCs at the interface.

After reflow in electrolytic Ni/Sn–Ag–Cu solder joint (Fig. 4a), the thickness of intermetallics is about 2.05–3.06 μm. According to EDX analysis, the IMCs form on the electrolytic Ni layer is composed of Cu–Ni–Sn i.e. (Cu$_{1-x}$Ni$_x$)$_{5}$Sn which is based on Cu$_6$Sn$_5$. Similar results...
are also reported by other investigators [10,11]. The composition of the IMCs layer is determined to be \((Cu_{0.6}Ni_{0.4})_6Sn_5\). As no Ag is detected in the interfacial layer, Ag is not directly involved in the interfacial reactions. Cu–Sn IMCs are found within the bulk solder. For Sn–Ag solder, the thickness of intermetallics is about 1.1–1.48 \(\mu\)m and the IMCs are composed of Ni–Sn. As per EDX analysis, it seems that these IMCs are the mixture of stable \(Ni_3Sn_4\) and \(Ni_3Sn\) and/or \(Ni_3Sn_2\) that have formed on the top of Ni layer (Fig. 4b). The growth rate of the Ni–Sn binary IMCs is much lower than that of the Cu–Ni–Sn ternary IMCs in as-reflowed condition. It is reported earlier that the growth rate of both \(Ni_3Sn\) and \(Ni_3Sn_2\) IMCs are very slow [12]. Relatively higher shear load is observed for Sn–Ag solder with less IMCs thickness in as-reflowed condition. (Dissolve Au from Au–Sn compound within the solder for both cases.)

The IMCs thickness gradually increases with the increase of aging time, as in Fig. 5, for Sn–Ag–Cu solder the growth rate is much higher. By measuring the remaining Ni thickness from the SEM micrograph and by subtracting it from the initial thickness, the consumed Ni thickness is deduced. For both cases the consumed Ni thickness increases with time. Fig. 6 shows the comparison of the Ni consumption thickness from the substrate between the solder alloys at 190 °C. It is seen that Ni consumption is faster in the Sn–Ag–Cu solder than in the Sn–Ag solder during long-time aging. For Sn–Ag–Cu solder, the consumption rate is little bit slower between 4–12 days. The consumption rate is much slower for Sn–Ag solder up to 8 days and beyond that the rate increases a bit.

After 4 days aging Cu–Ni–Sn intermetallics shows more planner morphology in the case of Sn–Ag–Cu solder alloy than the Ni–Sn IMCs in the Sn–Ag solder (Fig. 7). The composition in the middle of the IMCs layer in Sn–Ag–Cu is determined to be \((Cu_{0.62}Ni_{0.38})_6Sn_5\) with small amount of gold in it. The atomic percentage of Au is around 2% in the upper portion of the IMCs near the solder side. Au–Sn and Ag–Sn compounds are found within both the solder alloys. Cu–Sn compounds with Ni and small amount of Au are observed in the bulk Sn–Ag–Cu solder and Au–Sn–Ni compounds are observed in the Sn–Ag system. These compounds are clearly visible after 8 days of aging (Fig. 8). The quaternary phase in the Sn–Ag–Cu system of 4 days aging is found to be 46.0Sn, 19.8Ni, 30.8Cu and 3.4Au (at.%) and the ternary phase is 72Sn, 12.9Ni and 14.1Au (at.%) in the case of Sn–Ag solder. It is seen that Ni atoms has diffused through the interfacial IMCs and forms intermetallic compounds within the solder. For Sn–Ag–Cu solders, diffused Ni react with the existing Cu–Sn compound that is formed during reflow and added.
some Au with it with aging. In the case of Sn–Ag solder Ni reacts with the existing Au–Sn compound. No such Au–Sn–Ni compound is observed on Sn–Ag–Cu solders system. So, it may be stated that the affinity of chemical reactivity of Ni is higher for Cu–Sn compound than for Au–Sn compound. In this stage highest shear load is found for Sn–Ag solder, it may be due to the removal of residual stress and strength hardening effects of the alloys. In Ni/Sn–Ag–Cu solder system, up to 4 days aging the shear load is slightly decreased.

The average shear load of Sn–Ag–Cu solder alloy after 12 days of aging is around 1.14 kgf, which is 35% lower from the initial as bonded condition. In this stage, IMCs thickness of Sn–Ag–Cu solder is about 19 µm and a layer of Ni–Sn IMC with small amount of Cu was observed on the top of electrolytic Ni layer, which is slightly brighter in the backscattered electron micrograph. (Fig. 9a). This (Ni1−xCu)x3Sn4 layer compound is based on Ni3Sn4. The composition of the IMCs layer near Ni layer is determined to be (Ni0.8 Cu0.2)3Sn4. It may be due to the less availability of Cu, most of which is already consumed at the interface. The Au percentage is increased in the upper portion of the IMCs near the solder side and it is about 3–4 at.%. It is already observed that for Sn–Ag–Cu solder, the consumption rate of Ni is little bit slower between 4–12 days. After 4 days of aging, when the Cu content of the solder ball decreases (Ni, Cu)3Sn4 starts to form. The formation of Cu2Sn3-based compound is faster than those of the Ni3Sn4-based compound [6,13–15] and the growth rate of (Cu, Ni)3Sn4 is also faster [13,15]. Hence, the reaction rate becomes much slower from 4 to 12 days as shown in Figs. 5 and 6. For Sn–Ag system, the IMCs thickness is about 6.97 µm. Still some Au–Sn–Ni IMCs are observed within the solder. This ternary phase in the solder contains more Ni and less Au than the short-period aging ternary IMCs and the composition is found to be 57.3Sn, 36.6Ni and 6.1Au (at.%). Although the solubility of Ni in Sn is nearly zero even at 190 °C (from the Ni–Sn binary phase diagram), it is interesting to see the increase of Ni in the ternary IMCs in the bulk solder. Song et al. [16] observes a high Ni solubility in the AuSn4 phase which is approximately 12 at.% at 150 °C. Since the Ni from the interface has the shortest diffusion path to the AuSn4 intermetallics nearest the interface, it will be consumed first and form Au–Sn–Ni IMCs. Ni from Au–Sn–Ni near interface will diffuse toward the intermetallics located further out in the bulk due to the concentration gradient of Ni in the bulk. After 12 days of aging Au–Ni–Sn are also found in the farthest part of bulk. Both Cu–Sn compound and AuSn4 may act as a carrier of Ni from the interface, but ultimately Cu–Sn with small amount Au produce the more stable Cu–Ni–Sn–Au compounds in the bulk Sn–Ag–Cu solder. The minimum shear load is found for Sn–Ag solder alloy after 12 days of aging. It may be due to the increase of IMCs thickness at the interface and also due to the formation of some Au-containing compounds at the interface. (Fig. 9b).

The IMCs thickness of Sn–Ag–Cu is around 31.8 µm after 16 days of aging and a sudden increase of the growth rate is observed during this period. Fig. 10 shows the backscattered electron micrograph of sample after 16 days aging. Electrolytic Ni layer is fully consumed by Sn–Ag–Cu solder. So, the Cu pad is exposed to take part in the reaction with the Sn. A thick layer of Cu–Sn IMCs is found at the base of the interfacial IMCs. Both Cu2Sn3 and Cu3Sn are clearly identifiable in backscattered electron micrograph. Around 1.8 µm of Cu3Sn and 10 µm of Cu2Sn3 is observed at the interface. The growth rate of Cu2Sn3 is quite faster than that of Cu3Sn [17]. When all the Ni is consumed, exposed Cu reacts with Sn quickly and forms Cu2Sn3. Later when the supply of Sn is limited, Cu3Sn compounds are formed at the interface. In this stage, minimum shear load is observed for Sn–Ag–Cu and fracture occurs within these Cu–Sn IMCs (Fig. 3a). For Sn–Ag solder, the shear load does not change to any significant amount. The average IMCs thickness of Sn–Ag solder is around 9.1 µm at the interface. As per EDX analysis the composition of the binary alloy is found to be 60.5Sn and 39.5Ni. Another important thing is to be noticed that even after 16 days of aging at high-temperature, significant amount of Au–Sn reshellment as Au-containing compound at the solder/IMCs interface is not observed for both the solder alloys. The reaction rate even at such high-temperature for the formation of IMCs is slower for the Sn–Ag solders. Relatively...
a smaller amount of Sn participates in the reaction which may be the reason for the reduced attraction of Au–Sn to the formation of Au–Sn–Ni compounds at the interface. On the other hand, higher amount of Au is absorbed in the ternary Cu–Ni–Sn IMCs at the interface of Sn–3.5%Ag–0.5%Cu solder.

In general, we observed a high Ni consumption and a high IMCs growth rate in Sn–Ag–Cu solder alloy. It implies that the reaction rate is much faster for Sn–Ag–Cu solder in the high-temperature solid-state aging. In low-temperature aging, the growth rate of IMCs in Sn–Ag solder is observed to be higher than the Sn–Ag–Cu solder [9]. The anomalous behavior may be due to the higher diffusion rate of reacting species through the Cu–Ni–Sn compounds than the binary Ni–Sn compounds in the high-temperature aging condition.

4. Conclusion

The Sn–Ag solders show relatively better ball shear load than Sn–Ag–Cu solders during a high-temperature aging. The effects of aging on the consumption of electrolytic Ni and the IMCs formation in Sn96Ag3.5Cu0.5 and Sn96Ag3.5 BGA solder balls are also presented in this paper. As the time increases, the consumption of Ni increases. A very high consumption of Ni is observed in the case of Sn–Ag–Cu solder alloys. After 16 days of aging at 190 °C, the entire 5 μm Ni layer is consumed from the substrate pad and the exposed Cu pad reacts with Sn much faster rate. Relatively less amount of Ni is consumed in Sn–Ag solder. The IMCs growth rate in the interface for Sn–Ag–Cu solder is higher than that of the Sn–Ag solder. It is believed that the diffusivity of the reacting atoms through the interfacial IMCs is much higher for Sn–Ag–Cu solders in high-temperature annealing. For both cases Ni diffuses through the interfacial IMCs and forms quaternary compounds for Sn–Ag–Cu system and ternary compounds for Sn–Ag system within the bulk solder. IMCs at the solder interface are well adhered to substrate pads for both type of solder alloy. Overall the Ni/Sn–Ag solder alloy system shows better performance in high-temperature solid-state aging.

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References