Effect of 0.5 wt % Cu in Sn–3.5%Ag Solder on the Interfacial Reaction with Au/Ni Metallization

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The demand for lead(Pb)-free solders and high-density input–output interconnection technology is rapidly growing for advanced electronics production. Today, most of the Pb-free solders are tin(Sn)-based with a small amount of silver (Ag) and copper (Cu). Among them, Sn–3.5%Ag and Sn–3.5%Ag–0.5%Cu solders are the most common.1–6 Copper has been the most widely used solderable metal layer in the “under bump metallization” (UBM) for flip-chip and in the bond pad for “ball grid array” (BGA) applications. Hence, interaction and interdiffusion between molten solder and Cu has been intensively studied.1,7–9 It was found that Cu dissolves into the molten Sn-rich solder very quickly during the soldering process and Cu–Sn intermetallic compounds (IMCs) form at a very high rate at the solder interface during thermal aging.10–18 As an alternative to Cu, nickel (Ni) has been found to be a good solderable metal. The rate of dissolution of Ni in the Sn-based solder is very low at the soldering or reflow temperature.13,14,19 Only a very thin layer of the Ni3Sn4 compound is generally observed between the Ni and a Sn-based solder.13,14,20,21 Recently, Ho et al. found that Cu concentration in the Sn–Ag–Cu solder has a vital role in the interfacial reaction with the Ni metallization.22 They reported that above 0.5 wt % Cu, Ni3Sn4 IMC no longer formed at the interface; instead, Cu5Sn3-based ternary intermetallic compounds (TIMC) formed. It is well-established that the binary intermetallic compounds (BIMC) Ni3Sn4 forms at the Sn–3.5%Ag solder to the Ni interface during soldering reaction.20,21 So it is interesting to find the Cu5Sn3-based TIMC at the solder interface because of only 0.5 wt % Cu in the solder. However, there is not any comparative study on the growth kinetics of these IMCs during prolonged reaction time that has been done elsewhere. Besides, for a finite volume of BGA solder ball reflowed on Au/Ni/Cu bond pad, IMC’s growth behavior should have high industrial value too. In this communication, we examine how 0.5 wt % Cu predoping in the Sn–3.5%Ag solder changes the interfacial reaction products and the reaction rate.

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 were 3 and 0.5 μm, respectively. Commercially available BGA solder balls of Sn–3.5%Ag and Sn–3.5%Ag–0.5%Cu were used to compare the effect of predoped Cu on the interfacial reaction with the Ni metallization. The compositions are given in weight percent. The solder mask-opening diameter was 0.6 mm and the diameter of the BGA solder ball before melting was 0.76 mm. After dipping into the flux, solder balls were placed on the Au/Ni/Cu bond pads and reflowed in a N2 atmosphere oven. The flux used was a commercial no-clean flux. The peak reflow temperature was 240 °C and the time over the melting point of the solders is about 0.5 min. For prolonged reaction study, samples were kept at 240 °C for a different time period ranging from 2 to 120 min. Solder balls of Sn–3.5%Ag and Sn–3.5%Ag–0.5%Cu were placed side by side to experience identical conditions of reaction. The cross-sectioned samples were prepared to study interfacial microstructure by a Philips XL 40 FEG scanning electron microscope (SEM) equipped with energy-dispersive X-ray analysis (EDX). Back-scattered electron (BSE) mode of SEM was used to examine the morphology of cross-sectioned samples and to measure IMC thickness.

Figure 1 shows the microstructure of the as-reflowed interface between the Au/Ni/Cu bond pad and the Pb-free solder of (a) Sn–3.5%Ag and (b) Sn–3.5%Ag–0.5%Cu. The IMC thickness in them is more or less similar except in some region where exceptionally large scallop-type grains are noticed for the case of the Sn–3.5%Ag–0.5%Cu solder interface. By EDX analysis, it was found that this scallop was based on TIMC, (Cu3Ni)Sn4. On the other hand, Ni3Sn4-based BIMC formed in the Sn–Ag solder interface.20 With the prolonged isothermal reflow at 240 °C, thickness of IMCs for both these solders increased at a distinctly different rate.
Figure 2 shows the variation of the total IMC thickness with time ranging from 0.5 to 120 min during isothermal reflow at 240 °C. At the beginning, the reaction rate is very high for both these solders, which is typical for most molten solders on noble and near-noble metals. However, the difference between them in the growth rate of IMCs is very clear—up to 20 min the growth rate is very high for Sn–3.5%Ag–0.5%Cu solder. After 20 min, although the rate is slow, the Sn–3.5%Ag–0.5%Cu solder shows a higher growth rate of IMCs than that of the Sn–3.5%Ag solder. In the case of Sn–3.5%Ag solder, the IMC is always Ni₃Sn₄.

Figure 3 shows the microstructures of the two solder interfaces after 20 min of isothermal reflow at 240 °C. When (a) and (b) in Figure 3 are compared, the interfacial IMC thickness is much higher for the Sn–3.5%Ag solder. However, some voids in the thick IMC layer and spalling of the IMC grains are noticeable for the Sn–3.5%Ag–0.5%Cu solder.

Figure 4 shows the microstructures of the two solder interfaces after 120 min of isothermal reflow at 240 °C. For Sn–3.5%Ag solder, small grains of the IMC were spalled off from the upper portion of the IMC layer; see Figure 4a. The composition of the IMC was Ni₃Sn₄. On the other hand, layer-type spalling is visible from Figure 4b of the Sn–3.5%Ag–0.5%Cu solder interface. EDX analysis confirmed the existence of different types of IMCs at the interface. The outer spalled off IMC is (Cu,Ni)₆Sn₅, and the adhered IMC layer between the Ni layer and the (Cu,Ni)₆Sn₅ is (Ni,Cu)₃Sn₄.

When a solder ball is reflowed on the Au/Ni/Cu metallization, Au dissolves within a few seconds. Then Ni starts to dissolve into the solder. However, as the...
solubility of Ni in the molten Sn-based solder is very low, Ni₃Sn₃ BIMC nucleates at the Ni/solder interface from the adjacent metastable Ni-rich solder. In the absence of Cu for the SnAg solder, the formation of BIMC is simple. It is well-known that reaction kinetics of the Cu₆Sn₅-based compound is faster than those of the Ni₃Sn₄-based compound. Korhonen et al. and Kulojarvi et al. found that the growth rate of (Cu,Ni)₆Sn₅ TIMC is even faster than that of the Cu₆Sn₅ BIMC. Cu₆Sn₅ BIMC grows at a large scallop-type grain projected toward the solder, whereas (Cu,Ni)₆Sn₅ TIMC grains are fine needles-type and are piled up on the substrate. Such IMC structure, due to the high density of the grain boundary, facilitates fast outward diffusion of Ni and inward diffusion of Cu. Thus, (Cu,Ni)₆Sn₅ TIMC grows at a faster rate.

In this work, it was confirmed that a continuous layer of (Cu,Ni)₆Sn₅ TIMC continued to form at the Sn–3.5%Ag–0.5%Cu solder interface from 2 to 20 min of isothermal reflow. In fact, it has been reported that above 0.6% Cu concentration, Cu is available to nucleate (Cu,Ni)₆Sn₅ TIMC, which grows with the expanse of the available Cu in the molten solder. Here, the BGA solder ball of 0.23 mm³ contains a limited amount of Cu; it can be exhausted soon. From the curve of the growth rate of IMCs for Sn–3.5%Ag–0.5%Cu solder, the growth kinetics of IMCs slows down after 20 min; see Figure 2. EDX analysis for the sample of 60 min of isothermal reflow revealed a higher content of Sn between the Ni layer and the (Cu,Ni)₆Sn₅ TIMC. We concluded that (Ni,Cu)₃Sn₄ IMC starts to form after 20 min and thus the reaction rate slows down.

In summary, the presence of the Cu in the solder dramatically altered the phase selectivity at the solder/Ni interface and affected the growth rate of intermetallics. As long as sufficient Cu was available, it would combine with Ni and Sn to form (Cu,Ni)₆Sn₅. The growth rate of (Cu,Ni)₆Sn₅ is much higher than that of the Ni₃Sn₄. However, when the Cu content decreases below 0.2 wt %, (Ni,Cu)₃Sn₄ starts to form between Ni and (Cu,Ni)₆Sn₅.

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