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

M. O. Alam and Y. C. Chan*

Department of Electronic Engineering,
City University of Hong Kong, Tat Chee Avenue,
Kowloon Tong, Hong Kong

K. N. Tu

Department of Materials Science and Engineering,
UCLA, Los Angeles, California 90095-1595

Received July 28, 2003

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 Ni_3Sn_4 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, Ni_3Sn_4 IMC no longer formed at the interface; instead, Cu_6Sn_5-based ternary intermetallic compounds (TIMC) formed. It is well-established that the binary intermetallic compounds (BIMC) Ni_3Sn_4 forms at the Sn−3.5%Ag solder to the Ni interface during soldering reaction.[20,21] So it is interesting to find the Cu_6Sn_5-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 N_2 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, $(Cu,Ni)_6Sn_5$. On the other hand, Ni_3Sn_4-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.

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* Corresponding author. Fax: (852)-27887579. E-mail: EEYCCHAN@cityu.edu.hk.

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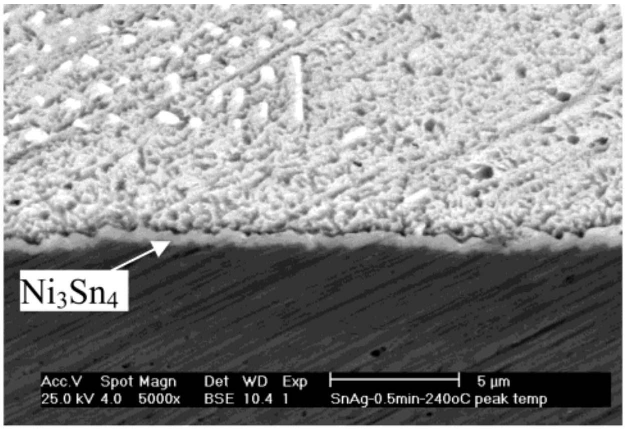
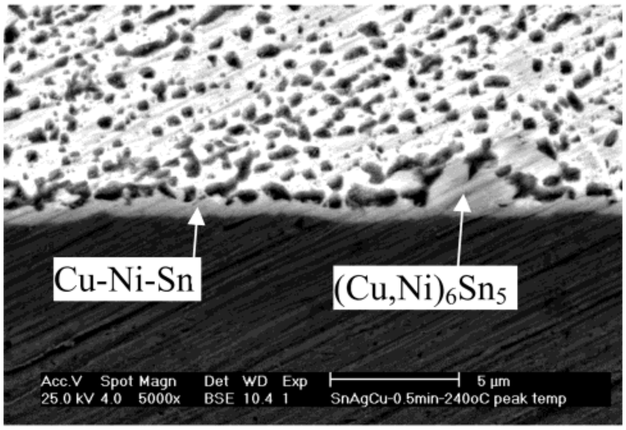
10.1021/cm034692c CCC: $25.00



(a) Sn-3.5%Ag solder



(b) Sn-3.5%Ag-0.5%Cu solder

Figure 1. Microstructure of the as-reflowed interface between Au/Ni/Cu bond pad and the lead-free solder of (a) Sn−3.5%Ag and (b) Sn−3.5%Ag−0.5%Cu.

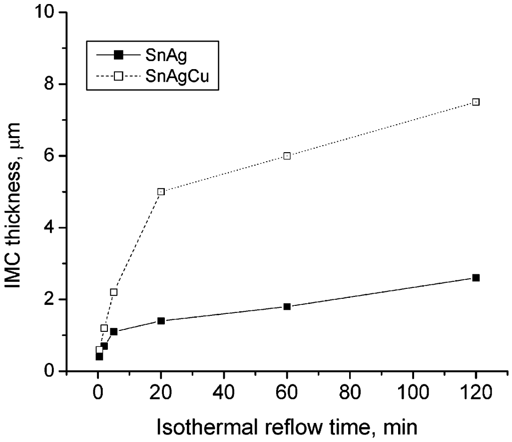
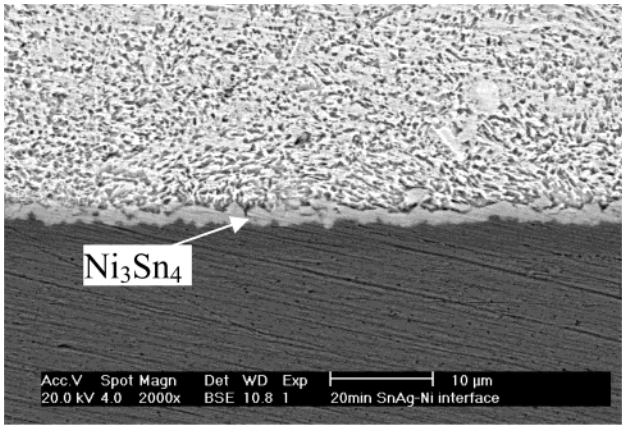
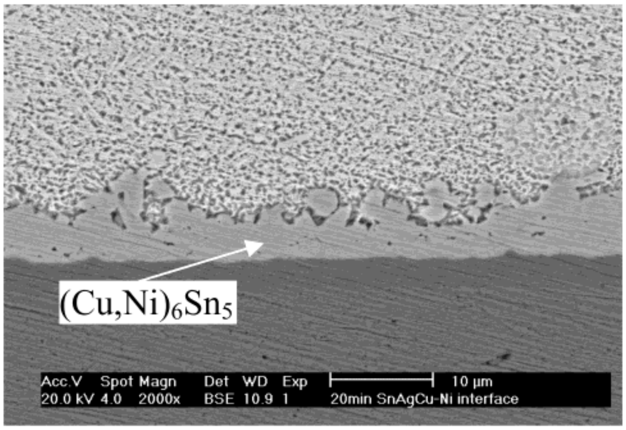


Figure 2. Variation of the total IMC thickness with the reaction time.



(a) Sn-3.5%Ag solder



(b) Sn-3.5%Ag-0.5%Cu solder

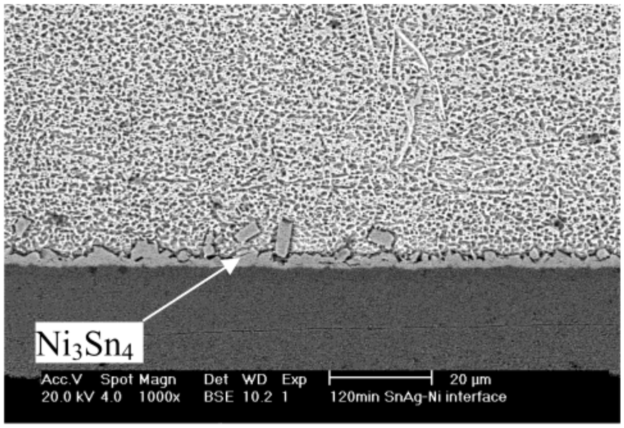
Figure 3. Microstructures of the bond interfaces after 20 min of isothermal reflow at 240 °C.

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 Ni_3Sn_4.

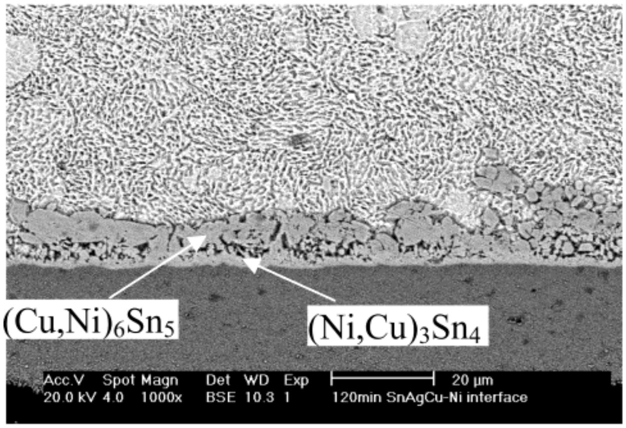
Figure 3 shows the microstructures of the two solder interfaces after 20 min of isothermal reflow at 240 °C. When (a) and (b) in Figure 3 are compared, the interfacial IMC thickness is much higher for the Sn−3.5%Ag−0.5%Cu solder. However, some voids in the thick IMC layer and spalling of the IMC grains 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 Ni_3Sn_4. 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 $(Cu,Ni)_6Sn_5$ and the adhered IMC layer between the Ni layer and the $(Cu,Ni)_6Sn_5$ is $(Ni,Cu)_3Sn_4$.

When a solder ball is reflowed on the Au/Ni/Cu metallization, Au dissolves within a few seconds.[23] Then Ni starts to dissolve into the solder. However, as the



(a) Sn-3.5%Ag solder



(b) Sn-3.5%Ag-0.5%Cu solder

Figure 4. Microstructures of the bond interfaces after 120 min of isothermal reflow at 240 °C.

solubility of Ni in the molten Sn-based solder is very low, Ni_4Sn_3 BIMC nucleates at the Ni/solder interface from the adjacent metastable Ni-rich solder.[13,18-20] In the absence of Cu for the SnAg solder, the formation of BIMC is simple. It is well-known that reaction kinetics of the Cu_6Sn_5-based compound is faster than those of the Ni_3Sn_4-based compound.[13,14,21,24] Korhonen et al. and Kulojarvi et al. found that the growth rate of $(Cu,Ni)_6Sn_5$ TIMC is even faster than that of the Cu_6Sn_5 BIMC.[14,24] Cu_6Sn_5 BIMC grows at a large scallop-type grain projected toward the solder, whereas $(Cu,Ni)_6Sn_5$ TIMC grains are fine needles-type and are piled up on the substrate.[14,22,25] Such IMC structure, due to the high density of the grain boundary, facilitates fast outward diffusion of Ni and inward diffusion of Cu. Thus, $(Cu,Ni)_6Sn_5$ TIMC grows at a faster rate.

In this work, it was confirmed that a continuous layer of $(Cu,Ni)_6Sn_5$ 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

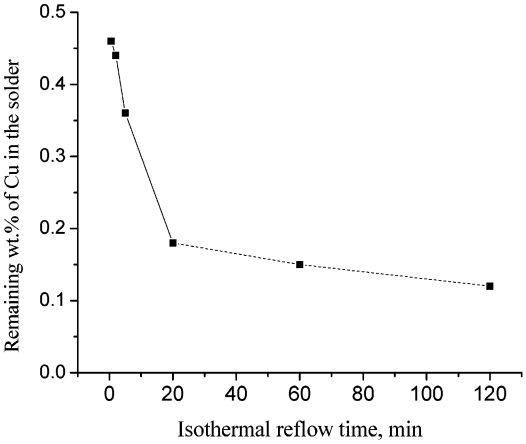


Figure 5. Weight percentage of the remaining Cu content in the molten Sn−3.5%Ag−0.5%Cu solder versus reaction time.

$(Cu,Ni)_6Sn_5$ TIMC,[22] which grows with the expanse of the available Cu in the molten solder. Here, the BGA solder ball of 0.23 mm^3 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 $(Cu,Ni)_6Sn_5$ TIMC. We concluded that $(Ni,Cu)_3Sn_4$ IMC starts to form after 20 min and thus the reaction rate slows down.

From the theoretical calculation based on the ternary phase diagram of Sn−Ag−Cu, it was found that, at 240 °C, molten eutectic SnAg could dissolve 1.54 wt % Cu.[1,15] In this study, Sn−3.5%Ag−0.5%Cu solder was used at 240 °C. This means that this solder is unsaturated with Cu. A simple calculation was made from the total volume of IMC thickness as well as the percentage of Cu in the IMC and the total weight of the BGA solder ball. Weight percentage of the remaining Cu content in the molten Sn−3.5%Ag−0.5%Cu solder versus reaction time is plotted in Figure 5. We can say that when all of the Cu from the solder is extracted to form $(Cu_{0.6,}Ni_{0.4})_6Sn_5$, the thickness would be 8 μm! However, the situation is rather complex due to the formation of $(Ni,Cu)_3Sn_4$ between the Ni and the $(Cu_{0.6,}Ni_{0.4})_6Sn_5$. After 20 min, when the Cu content of the solder ball decreases below 0.2 wt %, $(Ni,Cu)_3Sn_4$ starts to form. Hence, the reaction rate becomes much slower, as shown in Figure 2.

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 $(Cu,Ni)_6Sn_5$. The growth rate of $(Cu,Ni)_6Sn_5$ is much higher than that of the Ni_3Sn_4. However, when the Cu content decreases below 0.2 wt %, $(Ni,Cu)_3Sn_4$ starts to form between Ni and $(Cu,Ni)_6Sn_5$.

Acknowledgment. This research is supported by CityU SRG #7001387. One of the authors (K.N.T.) would like to acknowledge the support by a NSF contract, #DMR-9987484, and a SRC contract, #NJ-774.

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