Effect of 0.5 wt% Cu addition in Sn–3.5%Ag solder on the dissolution rate of Cu metallization

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The dissolution of thin film under-bump-metallization (UBM) by molten solder has been one of the most serious processing problems in electronic packaging technology. Due to a higher melting temperature and a greater Sn content, a molten lead-free solder such as eutectic SnAg has a faster dissolution rate of thin film UBM than the eutectic SnPb. The work presented in this paper focuses on the role of 0.5 wt% Cu in the base Sn–3.5%Ag solder to reduce the dissolution of the Cu bond pad in ball grid array applications. We found that after 0.5 wt% Cu addition, the rate of dissolution of Cu in the molten Sn–3.5%Ag solder slows down dramatically. Systematic experimental work was carried out to understand the dissolution behavior of Cu by the molten Sn–3.5%Ag and Sn–3.5%Ag–0.5%Cu solders at 230–250 °C, for different time periods ranging from 1 to 10 min. From the curves of consumed Cu thickness, it was concluded that 0.5 wt% Cu addition actually reduces the concentration gradient at the Cu metallization/molten solder interface which reduces the driving force of dissolution. During the dissolution, excess Cu was found to precipitate out due to heterogeneous nucleation and growth of Cu₆Sn₅ at the solder melt/oxide interface. In turn, more Cu can be dissolved again. This process continues with time and leads to more dissolution of Cu from the bond pad than the amount expected from the solubility limit, but it occurs at a slower rate for the molten Sn–3.5%Ag–0.5%Cu solder. © 2003 American Institute of Physics.

I. INTRODUCTION

Flip chip and ball-grid-array (BGA) technology are expected to have increasing applications to microelectronic devices in the future because of their higher input–output connection density achieved through area-array solder joints. From the environmental point of view, lead-containing solders are harmful. Recently, much work has attempted to find acceptable lead-free solders for various electronic assembly applications.¹–⁶

The predominant lead-free solder alloys proposed are eutectic Sn-based alloys with Ag and Cu, which have higher melting points (217–227 °C) than that of the eutectic Sn–Pb (183 °C).³–⁶ Hence, the corresponding reflow temperature and dissolution rate of the under bump metallization on the chip side as well as the bond pad on the substrate side are higher. Once the adhesion layer is consumed, the intermetallic compounds (IMCs) formed at the interface are spilled off from the nonwettable layer and the joint become fragile.⁷–¹⁴

Eutectic SnAg (Tₑut=221 °C) and eutectic SnAgCu (Tₑut=217 °C) have been recommended by National Electronic Manufacturing Initiative as a replacement of the SnPb solders in the chip joint process for the manufacturing of low cost, large volume consumer products.⁴,¹⁵ At higher reflow temperature, these solders can dissolve higher amounts of Cu than the eutectic SnPb. Interaction and interdiffusion between molten solder and Cu has been one of the most important metallurgical joining processes.¹–⁹ It is now well known that at the Cu/solder interface, Sn reacts rapidly with Cu to form Cu–Sn IMC. Due to a very limited solubility of Cu in the eutectic SnPb solder, previous studies on the dissolution of Cu during the soldering process were based mainly on the growth kinetics of IMC.⁸,⁹ However, since eutectic SnAg solder can dissolve much more Cu at the higher reflow temperature, it is essential to understand the dissolution characteristics of Cu in the Pb-free solder alloy. In this article, we examine how 0.5% Cu predoping in the Sn–3.5%Ag solder reduces the rate of Cu consumption.

II. EXPERIMENT

The solder mask defined copper bond pad on the flexible substrate of the BGA package was used to study the dissolution of Cu by two lead-free solders. The Cu bond pad is a part of the internal wiring within the flexible BGA substrate which was prepared from the laminated Cu foil adhered to the base polyimide. 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 dissolution of the Cu bond pad. 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. As per industrial BGA soldering process, solder balls were
placed after printing a flux layer on the Cu bond pads and the solders were kept in molten condition at 230, 240, and 250 °C for different time periods ranging from 1 to 10 min. The flux used in this work was a commercial no-clean flux. Figure 1 shows the soldering process between the lead-free solder ball and the Cu bond pad on a tape BGA substrate. 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 carefully to study interfacial microstructure. The scanning electron microscope (SEM) used for this study was a Philips XL 40 field electron gun equipped with energy dispersive x-ray analysis. Backscattered electron (BSE) mode of SEM was used to examine these cross-sectioned samples as well as to measure Cu consumption. The remaining thickness of the Cu bond pad within the solder masked defined area was measured and then the consumed thickness was calculated by subtracting from the original thickness of the Cu bond pad. It enables us to measure the dissolution rate accurately.

III. RESULTS

Figure 2 shows a typical cross-sectional BS–SEM image of a solder ball attached to the Cu bond pad. For quantitative measurement, the interfaces were examined under higher magnification. Such cross-sectional micrographs with the section plane perpendicular to the face of the interfaces were used to compare the consumed thickness of the Cu bond pad between Sn–3.5%Ag solder and Sn–3.5%Ag–0.5%Cu solder.

Figure 3 shows the microstructure of the interface between Cu bond pad and the lead-free solder of: (a) Sn–3.5%Ag solder, i.e., without Cu addition and (b) Sn–3.5%Ag–0.5%Cu solder, i.e., with 0.5 wt % Cu addition. The images shown here are taken from the microstructures formed after 5 min of isothermal reflow at 230 °C. Molten Sn–3.5%Ag dissolved nearly all the Cu from the Cu bond pad [see Fig. 3(a)], whereas, with 0.5% Cu addition, the rate of dissolution slows down dramatically [see Fig. 3(b)].

Figure 4 shows the microstructures of the bond interfaces at higher magnification. Comparing Figs. 4(a) and 4(b), it is clear that the Cu interface is rougher for the Sn–3.5%Ag solder than that of the Sn–3.5%Ag–0.5%Cu solder.

Figure 5 shows the microstructure of the bond interface at the edge of Sn–3.5%Ag solder. To represent the difference between the middle and the edge of the interface, a low magnification image was captured. From the image, it is clear that at the right end of the interface, Cu consumption is higher. Above the edge, there is more molten solder, which is bulged on the solder mask, to dissolve Cu from the edge and hence more Cu is etched out from the edge region. Cross sectioning perpendicular to that interface also revealed the same kind of higher dissolution at the edge that proves that there is an annular ring on the bond pad which suffered higher loss of Cu. For Sn–3.5%Ag–0.5%Cu solder, the same edge effect was noticed, however, to a lesser extent.
Figure 6 shows the variation of the consumed Cu thickness with time ranging from 1 to 10 min during isothermal reflow at 230, 240, and 250 °C. The differences between these two solders in Cu consumption are very clear. For the Sn–3.5%Ag solder, the whole 15 μm Cu pad is nearly dissolved within a very short time. From the trend of the curves at three different temperatures, it is clear that at higher temperature, Sn–3.5%Ag solder might consume even more Cu if it is available for reaction. However, it is clear that dissolution rate is very high at the early stage. Contrary to the Sn–3.5%Ag solder, Sn–3.5%Ag–0.5%Cu solder consumes Cu at a moderate rate even at the early stage of reaction. Temperature dependent consumption rate is also noticeable—at lower temperature the consumption rate is low. From the curves another important point is revealed that after 5 min of reaction time, Cu consumption rate becomes very low. It indicates that this alloy become saturated with Cu. Definitely, such saturation is also temperature dependent which is clear from the curves in Fig. 6(b).

IV. DISCUSSION

Previous works on the dissolution of a wettable metal and the growth kinetics of IMC formation at the solder joint interface were carried out by solder cap experiments, where a large area of substrate was exposed to a relatively small volume of solder.\textsuperscript{7–10} Due to the small amount of solder, it quickly becomes saturated with the substrate metal and any excess solute precipitates out from the molten solder cap to the interface. Further reaction proceeds to grow the IMCs only. Thus, the interfacial IMCs thickness continues to increase with time. However, in this experiment, the ratio of solder volume to substrate contact area was much higher than that of the previous works.\textsuperscript{7–9} Figure 7 illustrates the
When the local concentration of Cu at the interface region exceeds the solubility limits of Cu, i.e., \( c \) becomes higher than \( c_s \), Cu₅Sn₆ starts to form at the interface. On the other hand, Cu atoms in the interfacial region diffuse continuously to the remaining molten solder volume due to the concentration gradient, so the Cu concentration at the interface goes below the solubility limit, then the newly formed Cu₅Sn₆ dissolves to maintain the equilibrium.\(^{17-19}\) Thus, solubility has been found to strongly affect the interfacial reaction between the molten solder and the metallization underneath.

From the theoretical calculation based on the ternary phase diagram of Sn–Ag–Cu, it is found that at 260 °C, molten eutectic SnAg can dissolve 1.54 wt % Cu.\(^{20,21}\) So, eutectic Sn–3.5%Ag solder can dissolve a thin film Cu quickly. To reduce the rate of Cu consumption, it was suggested to dope more than 1.54 wt % Cu in the SnAg.\(^{11}\) However, since a high concentration of Cu may affect the wettability adversely, instead we studied the effect of adding only 0.5 wt % Cu. The concentration of Cu in the molten solder will increase beyond the 0.5 wt % when more Cu is dissolved from the bond pad. To get a better understanding on the effect of the predoped 0.5 wt % Cu content in the Sn–3.5%Ag solder, a simple calculation was made from the consumed Cu thickness of the Cu bond pad and the total weight of the BGA solder ball. Weight percentage of the Cu content in the molten solder versus reaction time is plotted in Fig. 8. For the Sn–3.5%Ag–0.5%Cu solder, the initial 0.5 wt % of Cu is also included with the wt % of the dissolved Cu. Figure 8(b) represents the trend of total Cu content with time for the Sn–3.5%Ag–0.5%Cu solder and Fig. 8(a) represents the Sn–3.5%Ag solder. Even though the initial 0.5 wt % of Cu was included in calculating the total amount of Cu in the Sn–3.5%Ag–0.5%Cu solder, it was very low compared to the consumed Cu content for Sn–3.5%Ag solder. In particular, for the lower temperature, the differences are clear in Fig. 8(b). At the higher temperature, as all the available Cu from the bond pad was consumed by Sn–3.5%Ag solder within 2–3 min of reaction time the dissolution rate was not measured to compare with the Cu containing Sn–3.5%Ag–0.5%Cu solder. By simple calculation, we can say that when the whole Cu from the bond pad is consumed, the Cu concentration would be 2.65 wt % in the solder ball! While the calculated solubility is 1.54 wt %, it appears that 2.65 wt % Cu has been dissolved in the solder when the entire Cu bond pad is gone. However, this is because a huge quantity of Cu₅Sn₆ IMC was found in the upper part of the solder ball. Figure 9 shows the Cu₅Sn₆ precipitates float on the upper region of the solder ball. Although one can say that part of these Cu₅Sn₆ compounds might precipitate at the time of solidification during cooling, we confirm that from our calculation they precipitate during the molten condition. It reduces the Cu content at the surrounding—thus leading to further Cu dissolution from the substrate. Floating Cu₅Sn₆ has been observed in the wetting of eutectic SnPb on Cu and has been suggested to be assisted by the gravity effect.\(^{7,15}\) The density of the Cu–Sn compound is lower than that of SnPb (e.g., 8 g/cm³ for Cu–Sn compound and 8.5 g/cm³ for eutectic SnPb solder). Although, Sn–3.5%Ag solder and Sn–

\[
\frac{dc}{dt} = k \frac{S}{V} (c_s - c),
\]

where \( c_s \) is the solubility of Cu in the molten solder at the reaction temperature, \( c \) is the concentration of Cu in the molten solder, \( k \) is the dissolution rate constant, \( S \) is the surface area of Cu bond pad, and \( V \) is the volume of the molten solder. The same equation can also be used to describe dissolution of the IMCs in a molten solder.\(^{17}\)

Here, the term \((c_s - c)\) plays a crucial role in the dissolution of Cu. The greater the difference between \( c_s \) and \( c \), the higher the dissolution rate (considering \( k \), \( S \), and \( V \) constant). Hence, from the identical setup of experiments, dissolution rate differs only on the initial content of Cu in the solder. Thus, in the Sn–3.5% solder, Cu dissolves out at a very high rate because of higher concentration gradient \( S/V(c_s - c) \).
3.5%Ag–0.5%Cu solder have a density of about 7.3 g/cm³, i.e., lower than that of the Cu–Sn compound. It is surprising to find Cu–Sn compound far from the interface, especially at the top of the solder ball.

It is proposed that the huge Cu₆Sn₅ precipitates at the top of the ball were due to two steps. First is heterogeneous nucleation and growth of Cu₆Sn₅ in the molten solder during isothermal reflow. This is because the molten solder/oxide interface enhances the nucleation of Cu₆Sn₅. Second, during solidification at the time of cooling, the excess Cu precipitates out to grow the Cu₆Sn₅ at the top as well as the pad interface.

For the Sn–3.5%Ag solder, an interesting finding is that even when it has dissolved 0.5 wt % Cu, it still has a higher dissolution rate than that of the Sn–3.5%Ag–0.5%Cu solder, as shown in Fig. 8. This is because in the Sn–3.5%Ag–0.5%Cu solder, the concentration gradient of Cu is smaller due to the initial content of Cu in the alloy. In the Sn–3.5%Ag solder, when 0.5 wt % of Cu is dissolved, it seems to have reached the same average concentration of Cu as the Sn–3.5%Ag–0.5%Cu solder, yet it still has a high Cu concentration gradient in the molten solder, so the rate of Cu flux leaving the Cu pad is higher, and the dissolution rate remains higher.

From a thermodynamic point of view, pure Sn or low Cu content Sn-based solders have higher activity with Cu. This implies that Cu containing solders might have a smaller free energy drop than the solders without predoped Cu. On the other hand, the higher the dissolution rate in the solder, the higher the chance to form the rough Cu substrate with grooves and channels. From Fig. 4, it is clear that the interface between the Cu bond pad and Sn–3.5%Ag solder is rougher than that of the Sn–3.5%Ag–0.5%Cu solder. But, before soldering, an identical Cu bond pad was used. After experiencing a faster dissolution with Sn–3.5%Ag solder, this rough interface is formed which again leads to higher dissolution because of higher contact area with the solder. Morphology of Cu₆Sn₅ grains was not considered for comparison, because we are not sure about the features during the liquid state; however, there must be a higher extent of Cu₆Sn₅ grains adhered to the interface for Sn–3.5%Ag–0.5%Cu solder.

From our study, we tend to confirm that the difference of Cu dissolution between these two solders lies on the concentration gradient and initial reaction rate. The difference in the morphology of the metallic Cu interface is also an important factor at the later stage of dissolution. A rough interface cre-
ates a larger surface area for the Cu bond pad to dissolve in the molten solder. Recalling Eq. (1), we can see that the dissolution rate is higher for increased surface area.

V. CONCLUSION

Dissolution behavior of Cu in the lead-free Sn–3.5%Ag solder was studied with and without predoped Cu. We found that 0.5 wt % Cu addition has reduced the rate of Cu dissolution significantly. Because of the higher dissolution rate in the base Sn–3.5%Ag solder, the Cu interface with the molten solder is very rough with grooves and channels between tiny IMC grains which act as a faster dissolution path of the metallic Cu, whereas, for Sn–3.5%Ag–0.5%Cu solder, as the concentration gradient of Cu in the molten solder is not very high, the Cu flux rate going to the molten solder is low, which makes the interface more smooth with stable IMC.

By calculating the dissolved weight percentage of Cu content in the molten solder, a higher content was observed than the solubility limit. The excess Cu was found to precipitate to the whole solder region, especially near the outer surface. It was concluded that this precipitated IMC nucleated during the molten condition due to heterogeneous nucleation on the oxide/solder interface and facilitated further dissolution of Cu from the interface.

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3 website (http://www.lead-free.org/)
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