Indium Addition on Intermetallic Compound Evolution in Tin-Silver Solder Bump

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The formation of large Ag₃Sn plate in Sn-Ag solder joint has restricted its application in lead-free electronic industry. There is a great interest for finding new approach to suppress the growth of Ag₃Sn. In this paper, Sn-2.1Ag and Sn-1.8Ag-9.4In solder bumps are prepared by electroplating of Sn-Ag and indium in sequence. After reflow at 260 °C for 30 min with cooling rate 0.33 °C/s, the phase composition, microstructure and undercooling of solder alloys are characterized by X-ray diffraction, Scanning electron microscopy and Differential scanning calorimeter, respectively. It is found that after indium addition, large Ag₃Sn plate is substituted by Ag₃In₄ with irregular polygon morphology. It is also found that indium addition can significantly reduce the undercooling of β-Sn, which promotes the solidification of β-Sn and inhibits the growth of Ag₃In₄ during slow cooling. [doi:10.2320/matertrans.M2011058]

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1. Introduction

Tin-silver solder is potential candidate for lead-free electronic application because of its better mechanical properties compared with the widely used eutectic Sn-37Pb solder.¹,² However, there are still some problems to be resolved. As one case, the formation of large Ag₃Sn plate in Sn-Ag solder joints, especially when solidified at a relatively slow cooling rate, may cause strain localization and degradation in ductility, and thus raises reliability concerns.³-⁵

The growth mechanism of large Ag₃Sn plate in slowly-cooled eutectic Sn-Ag solder is attributed to the formation of fine Ag₃Sn crystal nuclei at the onset of the eutectic reaction and the high drive force for the growth of Ag₃Sn in eutectic Sn-Ag solder with a minimal degree of undercooling during solidification.⁶,⁷ In order to avoid large Ag₃Sn plate, much work has been carried out from different perspectives, such as the cooling rate and the introduction of third alloying elements in eutectic Sn-Ag solder. It was revealed that an increase in cooling rate would provide greater undercooling to induce nucleation of primary β-Sn crystal and suppress the formation of large Ag₃Sn plate in eutectic Sn-Ag solder. However, a high cooling rate is not always practical in the electronic industry, where the range of cooling rate is typically from 0.2 to 4 °C/s.⁸,⁹ The effects of third alloying elements such as Cu, In and Zn on the formation of large Ag₃Sn plate in eutectic Sn-Ag solder were also investigated.¹⁰-¹² It was found that minor Zn addition was effective in reducing the amount of undercooling required for Sn solidification and therefore suppressing the formation of large Ag₃Sn plate. However, the effects of In on the formation of large Ag₃Sn plate in Sn-Ag solder still needs further investigation.

In this contribution, we report our experimental results of intermetallic compound (IMC) evolution in Sn-2.1Ag and Sn-1.8Ag-9.4In solder bumps with a reflow at 260 °C for 30 min. The cooling rate is 0.33 °C/s, which is slow enough for Ag₃Sn plate growing at undercooling condition during the reflow process. By comparing these two solder bumps, the role of indium in the reflow process will be better understood.

2. Experiment Method

The Sn-Ag-In flip chip solder bumps used in this study were prepared as follows: The substrate utilized was a virgin silicon dummy wafer with aluminum bond pads. Prior to the sputter deposition, the wafer surface was cleaned by sputter etching at 1.5 kilowatts of RF power. Afterwards, a 50 nm thick layer of TiW was sputtered as the adhesion and barrier layer, followed by a 200 nm layer of Cu, forming the electroplating seed layer. With the purpose of making a pattern for the electroplating of solder bumps, a positive photoresist (PR) AZ9260 was spin-coated by 600 r/min on the above substrate. Thickness of the PR was 45 μm, and it was heated at 100 °C for 90 s. Then the PR was exposed to light and developed. The area of the PR opening for electroplating was 70 μm in diameter with 300 μm pitch. Prior to electroplating, the wafer surface was treated with oxygen plasma to remove the resist residues inside the bump openings. The bump plating process was conducted in three consecutive steps. In the first step, a 5 μm thick copper under bump metallization (UBM) was electroplated in an acid copper bath, then the Sn-Ag solder with 40 μm thickness was electroplated using a SLOTOLOY SNA 30 plating bath, followed immediately by a 5 μm thick indium electroplating in an indium sulfate plating bath. For Sn-Ag flip chip solder bump specimen, the indium electroplating was omitted and the Sn-Ag thickness was controlled to 45 μm. After stripping the photoresist, an aqueous ammonia based etchant was utilized to etch back the sputtered Cu and TiW. Afterwards, samples were reflowed in a N₂ atmosphere oven at peak temperatures of 260 °C for 30 min. Then samples were cooled down to room temperature with cooling rates 0.33 °C/s.
After heat treatment, the specimens were mounted in an epoxy. The cross-sections of the solder/Cu interfaces were prepared using standard metallographic procedures. The microstructures were characterized by scanning electron microscopy (SEM). Energy dispersive X-ray spectroscopy (EDX) was used to determine the phase composition. In order to observe the crystalline morphology of Ag₃Sn, some samples were also etched with 12% nitric acid to dissolve selectively the remaining solder.

X-ray diffraction (XRD) and differential scanning calorimeter (DSC) measurements were performed and the samples were prepared as follows: Several 1 × 1 cm² TiW/Cu/electroplated Cu/Sn-Ag/In samples on Si substrate with the same thickness as the solder bumps were prepared and then reflowed together with the solder bumps. Then the metal layers on Si were scraped and immersed into an aqueous ammonia based etchant at room temperature to etch the redundant TiW/Cu/electroplated Cu. At last, only the solder alloy with a very thin IMC layer was used as the XRD and DSC samples. For DSC, about 10 mg sample was placed in alumina sample holder and high-purity N₂ was used as a protective gas. The testing temperature range of DSC measurement was from 25 to 300°C with a ramp slope of 10°C min⁻¹.

3. Results and Discussion

Figure 1 shows the XRD patterns of Sn-Ag and Sn-Ag-In solder after reflow. It is clear that no reflection peaks from Ag₃Sn are detected in Sn-Ag-In solder system, instead, reflection peaks from In₅Sn₄ and Ag₉In₄ are observed. This indicates that after indium addition, Ag₃Sn phase is substituted by Ag₉In₄ phase.

Figure 2(a) and (b) show the cross-sectional SEM image of Sn-Ag and Sn-Ag-In flip chip samples, respectively. EDX area analysis (the rectangle area in Fig. 2(a) and (b) shows that atomic ratio (except Cu) in Sn-Ag is Sn : Ag = 97.9 : 2.1, and that in Sn-Ag-In is Sn : Ag : In = 88.8 : 1.8 : 9.4. After long time interfacial reaction, little Cu is left. Two types of IMC layers are formed at the interface between solder and Cu UBM. According to EDX analysis, for Sn-Ag flip chip sample, the composition (at%) of the IMC near the solder side is Cu : Sn = 52.7 : 47.3, which corresponds to Cu₆Sn₅, and the composition of the IMC near the Cu side is Cu : Sn = 73.9 : 26.1, which corresponds to Cu₃Sn. For Sn-Ag-In flip chip sample, the composition of the IMC near the solder side is Cu : Sn : In = 53.3 : 43.7 : 3.0, which corresponds to Cu₆(Sn₀.94In₀.06)₅ and is based on Cu₆Sn₅, and the composition of the IMC near the Cu side is Cu : Sn : In = 74.7 : 23.3 : 2.0, which corresponds to Cu₃(Sn₀.92In₀.08) and is based on Cu₃Sn.

In addition to the interfacial intermetallics, two other intermetallics are formed in the solder matrix. The EDX

![Fig. 1 XRD patterns of Sn-Ag and Sn-Ag-In solder after reflow on Cu.](image)

![Fig. 2 Cross-sectional SEM image of (a) Sn-2.1Ag, (b) Sn-1.8Ag-9.4In solder bump, and SEM photograph of IMC layer after etching (c) Sn-2.1Ag and (d) Sn-1.8Ag-9.4In solder bump.](image)
analysis shows that the composition (at%) of the large IMC plate in Sn-Ag solder bump is Ag : Sn = 73.03 : 26.97, which corresponds to Ag$_3$Sn. And the composition (at%) of IMC in Sn-Ag-In solder matrix is Ag : In = 68.43 : 31.57, which corresponds to Ag$_3$In$_4$ and is based on the XRD analysis result. According to the microstructure observation, large Ag$_3$Sn plate is connected to the Cu$_6$Sn$_5$/solder interface and appears to have grown out from the interfacial intermetallics (as shown in Fig. 2(a)). According to the Sn-Ag binary phase diagram, the equilibrium phase of the composition of Sn-2.1Ag at 260°C is the molten Sn(Ag) phase. During reflow, the local composition of the solder near the interface becomes enriched in Ag due to the reaction to form Cu$_6$Sn$_5$ and Cu$_3$Sn. Therefore, the composition of molten solder will go towards the liquidus line or into the two-phase region consisting of molten Sn-Ag solder and the Ag$_3$Sn. Hence, some Ag$_3$Sn will nucleate near the interface and then grow into large grains during slow cooling. After indium addition, Ag$_3$In$_4$ is formed dispersively in Sn-Ag-In solder matrix instead of Ag$_3$Sn. This indicates the higher reactivity between Ag and In than Ag and Sn. After etching solder matrix, we can see the specific morphology of IMCs in the solder matrix, as the arrows shown in Fig. 2(c) and (d). Compared with large Ag$_3$Sn plate, the Ag$_3$In$_4$ IMC shows irregular polygon morphology.

Figure 3 shows the DSC curves of Sn-2.1Ag and Sn-1.8Ag-9.4In solder. It can be found that the endothermic peak of Sn-1.8Ag-9.4In upon heating appears at a temperature lower than that of Sn-2.1Ag solder, while the temperature corresponding to the exothermic peak of Sn-1.8Ag-9.4In is higher than that of Sn-2.1Ag solder upon solidification. This means that the introduction of indium can significantly reduce the undercooling, which can be represented by the difference between the peak temperatures of the endothermic and exothermic reactions. The specific temperatures for DSC curves are listed in Table 1.

As we know, the required undercooling of Ag$_3$Sn is smaller than that of β-Sn in Sn-Ag solder. Therefore, Ag$_3$Sn crystal nucleus should form at the onset of eutectic reaction. During slow cooling, there is a much longer undercooling process for Ag$_3$Sn growing to a large size in the liquid phase before the final solder solidification. After indium addition, small Ag$_3$In$_4$ nucleus will be formed at the initial period of solidification instead of Ag$_3$Sn. But, because the undercooling of β-Sn is significantly reduced, which may promote the solidification of β-Sn, the growth of Ag$_3$In$_4$ will be inhibited due to the crystalline orientation mismatch between β-Sn and Ag$_3$In$_4$. So Ag$_3$In$_4$ exhibits slow growth rate and irregular polygon morphology.

4. Conclusion

Intermetallic compound evolution in Sn-2.1Ag solder with approximately 10 mass% indium addition at slow cooling rate is investigated. It is found that after indium addition, large Ag$_3$Sn plate is substituted by Ag$_3$In$_4$. Because indium addition significantly reduces the undercooling of β-Sn, which promotes the solidification of β-Sn during cooling, the growth of Ag$_3$In$_4$ is inhibited. So Ag$_3$In$_4$ exhibit slow growth rate and irregular polygon morphology.

<table>
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<tr>
<th>Solder</th>
<th>$T_p$-endo/$^o$C</th>
<th>$T_p$-exo/$^o$C</th>
<th>$\Delta T$/$^o$C</th>
</tr>
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<tbody>
<tr>
<td>Sn-2.1Ag</td>
<td>492.4</td>
<td>453.5</td>
<td>38.9</td>
</tr>
<tr>
<td>Sn-1.8Ag-9.4In</td>
<td>488.6</td>
<td>465.3</td>
<td>23.3</td>
</tr>
</tbody>
</table>

$^1$Temperature corresponding to endothermic peak.
$^2$Temperature corresponding to exothermic peak.
$^3$Undercooling.

REFERENCES