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Mechanism of the Delayed Growth of Intermetallic Compound at the Interface between Sn-4.0Ag-0.5Cu and Cu-Zn Substrate

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A Cu-Zn wetting layer was very effective to depress the excessive growth of intermetallic compound (IMC). The effect of Zn addition to the Cu layer on the IMC growth and microvoid formation in the solder interface was similar to the effect of Zn addition into the Sn-Ag-Cu (SAC) solders. In this study, the mechanism of slow IMC growth at the SAC/Cu-Zn interfaces was investigated. As the aging time increased, Zn atoms accumulated at the Cu_6Sn_5/Cu interface and formed a Zn-rich layer. By adding Zn into the Cu wetting layer, the IMC growth was delayed due to the retardation of the formation of the Cu_3Sn layer. Since the low driving force for the formation of Cu_3Sn became smaller by adding Zn, the diffusion of Cu in Cu-Zn into SAC solder was delayed. Also, the CuZn phase formed at the Cu_6Sn_5/Cu-Zn interface plays a role as a diffusion barrier of interdiffusion of Cu and Sn.

Keywords: Intermetallic compound, Pb-free solder, Cu-Zn wetting layer, diffusion barrier

1. INTRODUCTION

Nowadays, Pb-free solders have been developed to replace the conventional Pb-Sn eutectic solder used in the electronics packaging industry.[1-3] The Cu metallization is widely used due to good wettability with solder materials. Among the various Pb-free solder alloy choices, Sn-Ag-Cu (SAC) alloys are currently most popular because of their relatively good soldering performance, excellent mechanical properties, relatively low melting temperature comparing to Sn-Ag or Sn-Cu solder alloys and thermal fatigue reliability, as well as their compatibility with the current components.[4-6] However, with SAC solder on a Cu pad, solder joints still cause reliability issues such as rapid consumption of Cu layer, excessive growth of intermetallic compounds (IMCs), large Ag_3Sn plates and microvoids formation during the reaction of Sn-Ag-Cu alloys with the Cu layer.[7-9]

To enhance the solder joint reliability, various alloying elements such as Ni, In, Bi, Zn, Fe, Mn, and Ti, as well as rare earth elements have been added to Sn-based solders.[9-15] One of the attractive elements among these is Zn because its mechanical properties and creep resistance were enhanced and IMC growth as well as the formation of large Ag_3Sn plate was remarkably suppressed during reflow and thermal aging caused by adding Zn to the solder.[11,12,14] Also, the drop impact reliability after a small amount of Zn is added to Sn-3.5 Ag solders/Cu solder joints was improved because of the suppressed IMC growth and formation of Zn containing IMCs such as Ag_5Zn_8 and Cu_5Zn_8 at the solder joints.[16] However, Sn-based solders containing Zn are susceptible to oxidation and corrosion and have poor wetting properties.[17,18]

Recently, Cu-Zn metallization as a Pb-free solder wetting layer has been developed to solve the problems of Zn containing solder.[19-21] We have already demonstrated that the Cu-Zn alloy substrate as a solder wetting layer for Pb-free solders is very effective to reduce the IMC growth and microvoid formation as well as large Ag_3Sn plates in the interfacial reaction with SAC solders.[19-21] Other research groups[22,23] have also investigated the interfacial reaction between the Cu-Zn layer and Pb-free solders and their results were very similar to ours. Furthermore the drop impact reliability of solder joints formed on Cu-Zn wetting layers was excellent.[21,24] This approach showed a similar effect for Zn addition to the solder.[11,12,14] Therefore Cu-Zn alloy layer has potential as a promising wetting layer for Pb-free solder. The purpose of this study is to investigate the mechanism of slow IMC growth on the Cu-Zn layer with SAC solder during aging.

2. EXPERIMENTAL PROCEDURE

A Solder mask defined (SMD) type of flame resist-4 (FR-4) printed circuit board (PCB) was prepared for Cu-Zn alloy plating with Cu metallization, which has a pad opening of 680 μm in diameter, as shown in Fig. 1. The 10 μm thick Cu-Zn layer was electroplated. The composition of the Cu-Zn layer was 80 wt. % Cu-20 wt. % Zn. A Cu layer of iden-

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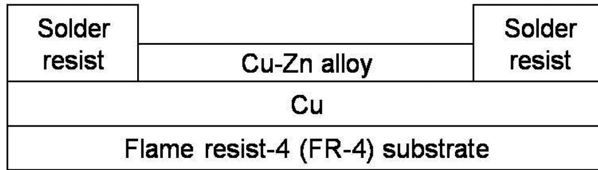

Fig. 1. Schematic illustration of Cu–Zn wetting layer electroplated on Cu.

tical thickness was also electroplated on the same substrates to compare with the Cu-Zn wetting layer. The Pb-free solder composition used in this study is Sn-4.0Ag-0.5Cu solder alloys with 760 μm diameter. Sn-4.0Ag-0.5Cu alloy balls were placed on both Cu-Zn and Cu pads with a halide free water soluble flux, and were then reflowed at 260°C for 20 s. Subsequently, Cu-Zn solder joints were aged in a convection oven at 150°C for 1000 h. After isothermal aging, these specimens were mounted and polished mechanically for observation of the microstructure area of the solder/Cu-Zn interface with aging time. Before scanning electron microscopy (SEM) observation, specimens were slightly etched by the use of 5% HCl for several seconds to delineate the morphologies of IMCs in solder joints. To investigate the formation and growth of IMCs at the solder joints, SEM equipped with energy dispersive X-ray spectroscopy (EDS), and a field emission-electron probe microanalyzer (FE-EPMA, JEOL JXA-8500F) were used.

3. RESULTS AND DISCUSSION

Backscattered electron (BSE) micrographs of the solder/Cu or solder/Cu-Zn interfaces after reflow and isothermal aging are shown in Fig. 2. During the reflow, the solder was in a molten state and the formation of Cu_6Sn_5 had a scallop-type morphology that is favored by a high rate of free energy change.[25] The morphology of the Cu_6Sn_5 formed on the Cu-Zn layer was a little flatter than that on the Cu layer and the thickness of the Cu_6Sn_5 was thinner on the Cu-Zn layer than that on the Cu layers after reflow. Large Ag_3Sn plates were frequently observed in the solder interface formed on Cu metallization. The formation of large Ag_3Sn plates was remarkably suppressed on the SAC/Cu-Zn interface compared to the SAC/Cu interface since the Zn from the Cu-Zn layer dissolved into the solder joints during reflow and reduce the undercooling temperature of the SAC solder.[14]

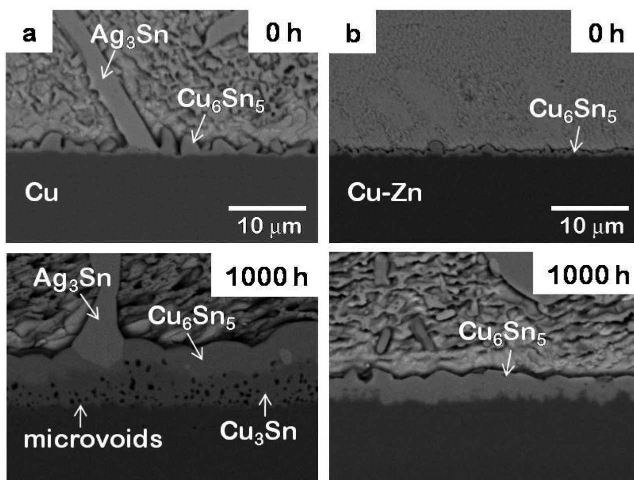

Fig. 2. Backscattered electron (BSE) images of (a) Sn-4.0Ag-0.5Cu/Cu interfaces and (b) Sn-4.0Ag-0.5Cu/Cu-Zn interfaces before and after isothermal aging at 150°C for 1000 h.

During aging, the total IMC thickness increased and the morphology of the Cu_6Sn_5 formed both on Cu and Cu-Zn substrate flattened with aging time. The flattening process is driven by thermodynamics because of the high interfacial energy between the solid solder and Cu_6Sn_5.[25] Meanwhile, a Cu_3Sn phase formed between Cu_6Sn_5 and the Cu substrate during aging through a solid-state reaction to satisfy the requirements of local equilibrium.[25] After aging for 1000 h, the thickness of the Cu_3Sn layer increased and a number of microvoids formed within the Cu_3Sn layer because of the unequal flux of the atomic species since Cu is the dominant diffusing species of the two reacting elements, Cu and Sn.[25] The growth of Cu_3Sn tends to induce the formation of microvoids.[8,25] In contrast to the interfacial reaction of SAC/Cu, only Cu_6Sn_5 grew and Cu_3Sn was not found at the SAC/Cu-Zn interfaces after aging. And Cu_5Zn_8 or Ag_5Zn_8 IMCs, which were observed in Zn containing solder/Cu systems,[15] were not observed in the solder/Cu-Zn system since the Cu-Zn layer contained 20 wt. % Zn. The maximum Zn concentration from the Cu-Zn wetting layer into the SAC solder alloy with diameter of 760 μm was calculated to be below 0.22 wt. % when a 10 μm Cu-Zn layer dissolved completely and that Zn concentration was too small to transform into a Zn containing IMC.[26] The effect of Ag on IMC growth was ignorable because Ag does not participate in the interfacial reaction.[27]

The overall IMC thickness and Cu_3Sn IMC thickness on Cu and Cu-Zn layers was measured from the cross-section images divided by the length of the bottom side of the IMC and was plotted as a function of aging time in Fig. 3. Total IMC thickness increases with aging time. IMC growth on both Cu and Cu-Zn layers followed parabolic behavior, showing that IMC growth is controlled by bulk diffusion.[28] The IMC growth rate of the SAC/Cu interface was higher than that of SAC/Cu-Zn interface. The growth behavior of the IMCs has the same trend as that in the previous study.[19-21] The thickness of the Cu_6Sn_5 formed on both Cu and Cu-Zn substrates was almost equal for the same aging time. The disparity of the IMC growth rate on Cu and Cu-20 wt. % Zn wetting layer depends on the formation and growth of Cu_3Sn. The thermodynamic calculation showed that the driving force of the Cu_3Sn decreased in the SAC/Cu-Zn sys-

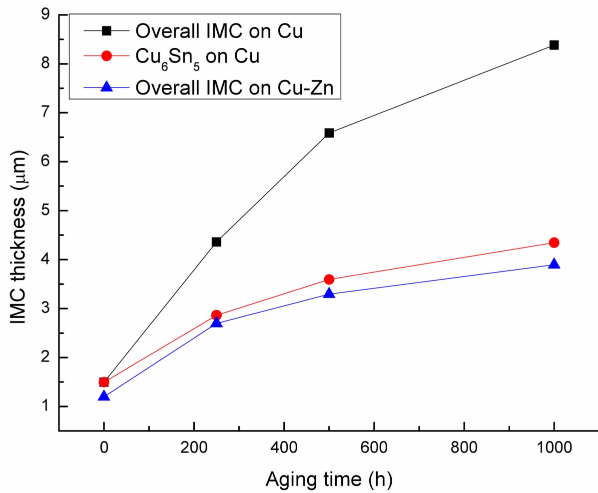

Fig. 3. Intermetallic compound (IMC) thickness of overall IMC (Cu_6Sn_5+Cu_3Sn) and Cu_3Sn on Cu layer and Cu_6Sn_5 on Cu-Zn layer after aging at 150°C for 1000 h.

tem with increasing contents of Zn in the Cu-Zn wetting layer.[29] Hence, the diffusion of Cu is retarded, and then the formation of Cu_3Sn IMC is retarded. Also, since the activity of Cu in the Cu-Zn alloy is lower than that in pure Cu,[29] Cu diffusion from the Cu-Zn layer to the solder could be difficult. Thus, the Cu_3Sn phase did not form at the SAC/Cu-Zn interfaces. Since the formation of microvoids is associated with the growth of Cu_3Sn,[8,25] it is reasonable to assume that microvoids did not form. This result clearly demonstrates that the growth of IMC was retarded by the Zn of the Cu-Zn layer. Moreover, the existing Zn in the Cu-Zn wetting layer should affect the diffusion of Cu elements so as to lead to the formation of the IMC layers.

Figure 4 shows FE-EPMA mapping results of the interface between SAC and the Cu-20 wt. % Zn layer aged for 1000 h. Elemental mapping results for Cu and Sn clearly show the presence of only one layer, Cu_6Sn_5 in the SAC/Cu-Zn system after aging. It is interesting to note that the Zn atoms accumulated at the interface between the Cu_6Sn_5 IMC and the Cu-Zn layer and the Zn accumulation forms the Zn-rich layer at the interface of Cu_6Sn_5/Cu-Zn. The thickness of the Zn-rich layer was about 1.5 μm. The composition of this Zn-rich layer was measured to be about 43-48 at. % Zn and 52-57 at. % Cu. The formation of the Zn-rich layer, the so called CuZn phase at the Cu_6Sn_5/Cu-Zn interface, acts as a diffusion barrier for Sn and Cu atoms.[22,23] The average composition of the Cu_6Sn_5 formed on the Cu-20 wt. % Zn layer was measured to be 54.2 at. % Cu, 43.6 at. % Sn and 2.2 at. % Zn, indicating that a small amount of Zn had been incorporated into the Sn sublattice of Cu_6Sn_5. Consequently, this compound should be more properly referred to as $Cu_6(Sn, Zn)_6$.[30] The Zn atoms substitute for Sn atoms in the Cu_6Sn_5 phase, however, the solubility of Zn in Cu_6Sn_5 was low, the Zn accumulated at the $Cu_6(Sn, Zn)_6$/Cu-Zn interface during aging, and consequently the CuZn phase was formed during aging.

The total amount of Zn supplied from the dissolving of the Cu-20 wt. % Zn wetting layer into the SAC/Cu-Zn system after reflow and aging for 1000 h was calculated based on the consumed Cu-20 wt. % Zn layer and was compared with the CuZn phase using the thickness of the CuZn phase measured. The calculated Zn concentration in the Cu-20 wt. % Zn layer, CuZn phase, $Cu_6(Sn, Zn)_5$ and solder were obtained from the density of each phase, volume, atomic weight and wt. % of Zn in each phase. The amount of Zn from the CuZn phase and $Cu_6(Sn, Zn)_5$ was calculated to be 2.06×10^{16} atoms and 1.84×10^{15} atoms, respectively. The value of Zn in the solder was ignorable because the concen-

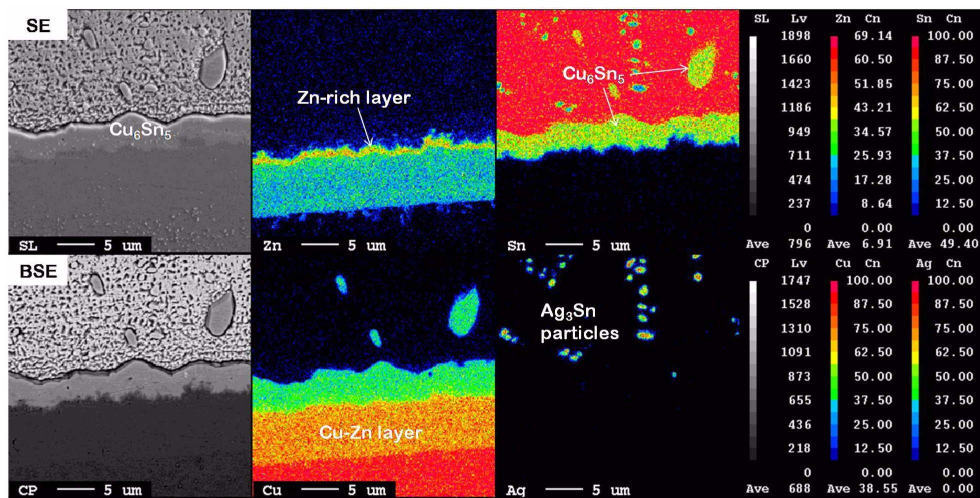

Fig. 4. Secondary electron (SE) image, back scattered electron (BSE) image of Sn-4.0Ag-0.5Cu/Cu-Zn interface after aging for 1000 h at 150°C and X-ray mapping images of Zn, Sn, Cu and Ag are shown.

tration of Zn measured by FE-EPMA was too low. The Zn content from the consumed Cu-20 wt. % Zn layer (~4.5 μm) was about 2.29×10^{16} atoms. These results show that the Zn supplied into the SAC/Cu-Zn system was almost equal to the Zn in the CuZn phase and in $Cu_6(Sn, Zn)_5$, which suggests that the concentration of Zn measured by FE-EPMA mapping data was quite accurate, as our expectation.

4. CONCLUSION

In this study, the delayed IMC growth mechanism on a Cu-20 wt. % Zn layer was investigated with thermal aging. The major contribution of the slow IMC growth on the Cu-Zn wetting layer was ascribed to the retardation of the formation of the Cu_3Sn layer at the Cu_6Sn_5/Cu-Zn interfaces because the driving force of the formation of the Cu_3Sn phase was reduced significantly by adding Zn into the Cu wetting layer. Also, the dissolution of Zn into the Cu_6Sn_5 was low on the Cu-Zn wetting layer due to the low activation energy. And the CuZn phase formed at the $Cu_6(Sn, Zn)_6$/Cu-Zn interface during aging plays the role of a barrier layer for Cu diffusion.

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