Effects of reflow on the interfacial characteristics between Zn nanoparticles containing Sn-3.8Ag-0.7Cu solder and copper substrate
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1. Introduction

Due to the inherent toxicity of lead (Pb), environmental regulations around the world such as the European Commission's (EC) Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) Directives have restricted the use of Pb-bearing solders in electronic assembly. This has prompted the development of Pb-free solders. Currently, Pb-free solders are increasingly being used in interconnection systems for electronic packages. The common lead-free solder alloys that are being investigated and used in the electronics industry include Sn-Ag-Cu, Sn-Ag, Sn-Ca and Sn-Bi, all of which have a relatively high Sn content in comparison to the traditional Sn-Pb alloy varieties (Li et al., 2005). Among the various lead-free solders, the alloy families of Sn-Ag and Sn-Ag-Cu solders are generally regarded as the most promising compositions for the replacement of Sn-Pb solders (Chen et al., 2003). This is because they have superior mechanical properties such as strength, elongation, high shear strength at ambient temperature and resistance to thermal aging and thermal mechanical fatigue during temperature excursions up to about 150°C, which is the current maximum operating temperature limit of “under the hood” automotive electronics.

However, problems in using the Sn-Ag-Cu solder alloys have been reported. These include the formation of large intermetallic compounds (IMC) such as Ag₃Sn and Cu₃Sn, which may have a negative effect on the mechanical properties, formation of voids at the interface of a substrate and a large degree of undercooling during the solidification (Cho et al., 2007). Due to their inherently brittle nature, IMC layers which are too thick at the solder-substrate interface may degrade the reliability of solder joints (Launila et al., 2005). Recent studies have also revealed several reliability problems with the Sn-Ag-Cu alloy system. One of the most critical problems is the formation of Kirkendall voids. The correlation between drop test performance and interfacial voiding has also been reported in the literature (Kim et al., 2003). Excessive void formation will cause brittle interfacial fracture, raising reliability concerns. In addition, solder joints may experience multiple reflows during multi-level packaging, assembly and rework (Yao et al., 2008) operations. Following the first reflow, multiple reflows are sometimes introduced to the solder joints with similar reflow profiles. In other circumstances, a hierarchy of reflows with decreasing...
temperature profiles is necessary (Pander and Pachamuthu, 2010). Therefore, the characteristics of the interfacial IMC of solder joints during multiple reflows become critically important when it is necessary to obtain a required service life. However, in the literature, melting up to 6x is considered as the standard for investigating the effect of multiple reflow cycles (Yao et al., 2008).

A few approaches have been taken to improve the performance of Sn-based solders. One of the approaches is adding minor alloying elements such as Zn, Mn, Ni, Fe, Co and rare earth elements to Sn-Ag-Cu solder. Zn (Zn) is one of the potential elements offering a number of advantages. It can, for example, reduce the size of Ag3Sn thus suppressing fatigue crack propagation (Song and Lin, 2003), result in void free, thinner interfacial intermetallic layers and superior impact strength retention (Anderson and Harringa, 2006), enhance the resistance of Cu atoms to electromigration due to strong binding of Zn with Cu (Yu and Duh, 2010) and reduce the amount of undercooling required for β-Sn solidification (Kang et al., 2006). However, despite all the advantages of Zn, Huang et al. (2000) reported that Zn had an adverse effect on the wettability of solder joints.

Another approach to improve the reliability of Sn-based solder is the addition of micro or nanosized reinforcement particles (Lin et al., 2003; Mavoori and Jin, 1998; Haseeb and Tay, 2011). Both metallic nanoparticle such as Co (Haseeb and Tay, 2011) and Mo (Ararat et al., 2011) and non-metallic particles, e.g. TiO2 (Li, 2003) and Al2O3 (Mavoori and Jin, 1998) have been investigated. Reinforcement particles have been found to be effective in improving the creep resistance by being distributed at the grain boundaries to limit grain boundary sliding (Kumar and Tay, 2004).

Currently, no information is available on the effect of Zn nanoparticles on Sn-based solders. Therefore, in this study, the effects of the addition of Zn nanoparticles to Sn-3.6Ag-0.7Cu (SAC) solder alloys were investigated during 1 and 6x reflow. Wettability properties, melting characteristics and interfacial microstructures of the composite solders were studied.

2. Experimental procedures

The size of the as-received Zn nanoparticles was measured under a high resolution field effect scanning electron microscope (FESEM, Zeiss Ultra-60). More than 500 particles were measured to determine the size distribution of the Zn nanoparticles. Nanocomposite solder paste was prepared by manually mixing Zn nanoparticles (Sigma Aldrich, USA) with Sn-3.6Ag-0.7Cu (SAC) solder paste (Indium Corporation) at a nominal percentage of 1 and 2wt.%. The mixture was manually stirred for 30 minutes at a moderate speed and strength to ensure a uniform distribution of Zn in the SAC matrix. Samples of the solder paste mixtures with added nanoparticles were subjected to differential scanning calorimetry (DSC) analysis in order to investigate the melting behaviour of the composite solder alloys. Five samples were investigated by DSC for each composition. The onset melting temperature of the nanocomposite solder was recorded from DSC curves. Polycrystalline Cu sheets, 30 mm x 30 mm x 0.3 mm, were used as substrates for solder joint preparation. The substrates were washed and cleaned with detergent before rinsing with deionized water to remove any oily stains present on the surface. After that, any oxide layer on the Cu surface was removed by immersing the substrates in 10 vol.% of sulphuric acid for 30 seconds. This was followed by rinsing with deionized water and drying with acetone. Then 0.2 g of solder paste was printed on the pre-cleaned Cu substrate using a jig with an opening of 6.5 mm diameter and a height of 1.24 mm following the Japanese Industrial Standard (JIS 23198-3, 2003). The solder paste was reflowed on a hotplate at 250°C for 45 seconds. After first reflow (1x), the flux residues were removed by acetone.

After soldering, a bulk solder sample was collected from the joint by scraping and was analyzed for Zn content by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Wetting behaviour was characterized by contact angles, which were measured using a video tool software under an optical microscope, whereas spreading rates were calculated according to the Japanese Industrial Standard (JIS 23198-3, 2003). The solder joint was also subjected to reflow at 250°C for 45 seconds for 6x. The cross-sectional specimens after 1 and 6x reflows were prepared by standard metallographic techniques. Top views of interfacial IMCs were revealed by deep etching with a solution of 93 vol.% methanol, 5 vol% nitric acid and 2 vol% hydrochloric acid (Yen et al., 2008). The cross-section and top morphology of intermetallic compound layers were investigated under field emission scanning electron microscope (FESEM, Zeiss Ultra-60). For each cross-sectional sample, the thicknesses of the IMCs were measured on four different FESEM images taken at magnifications of 4,000× and 8,000×. The average thickness of the IMCs was calculated by dividing the area of the IMC by its length (Haseeb and Tay, 2011). Elemental compositions of the IMC were characterized by energy dispersive X-ray spectroscopy (EDAX-Genesis Utilities).

3. Results and discussion

Figure 1(a) shows a FESEM micrograph of the as-received Zn nanoparticles. It can be seen from the FESEM micrographs that the Zn nanoparticles have a spherical shape with facets formed on the surface. The size of the nanoparticles was found to vary. Figure 1(b) shows the histogram of the size distribution of the Zn nanoparticles. A total of 560 particles were measured from the FESEM micrographs to calculate the average particle size of the Zn nanoparticles. The particle size was found to lie in the range of < 20 nm to about 300 nm. The particle size peak was in the range 40-60 nm. From the histogram, the average particle size was calculated to be 100 nm.

Figure 2 shows an FESEM micrograph and elemental mapping of the composite solder paste after mechanical mixing at a nominal content of 2wt.% of Zn nanoparticles. Mixing of Zn nanoparticles into SAC solder paste was done manually for 30 minutes. It can be seen from Figure 2(a) that the diameter of the SAC solder balls was about 45 μm. In between the solder balls the flux appears to be darker in contrast. In addition, very minute particles are visible on the solder ball surface as well as in the flux. EDX elemental mapping (Figure 2(c) and (d)) reveals that these minute particles were the Zn nanoparticles. The Zn nanoparticles are seen to be distributed homogeneously in the mixture.

Table 1 shows the actual Zn content of nanocomposite solders as determined after first reflow by ICP-OES. For the nominal addition of 1 and 2wt.% of Zn, only 0.3 and 0.8 wt.% of Zn remain in the solder, respectively. After reflow, only some of the Zn nanoparticles were successfully embedded.
Figure 1 (a) FESEM micrographs of Zn nanoparticles at a magnification of 50k and (b) histogram of the size distribution of the Zn nanoparticles.

Figure 2 (a) FESEM images of solder paste after the mixing of Zn nanoparticles at a nominal content of 2 wt.%, and elemental mapping of (b) Sn, (c) Zn and (d) combination of Sn, Ag, Cu and Zn.

Table 1: Actual Zn content in solders analyzed by ICP-OES after first reflow.

<table>
<thead>
<tr>
<th>Nominal content of Zn addition (wt.%)</th>
<th>Actual content of Zn by ICP-OES (wt.%)</th>
<th>Retained Zn content after reflow (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>40</td>
</tr>
</tbody>
</table>
into the solder mass, while the rest were carried away by flux residues. Hence, the content of Zn in the SAC solder is reported to be 0.3 and 0.8 wt. % of Zn are denoted as SAC-0.3Zn and SAC-0.8Zn, respectively.

It was reported by Haseb and Tay (2011) that, for the nominal Co contents of 0.5 and 1.5 wt. %, the actual contents of Co incorporated into the solders were 0.18 and 0.75 wt. %, respectively. It was suggested that because of the higher interfacial energy between Co and the liquid solder, Co nanoparticles were pushed by the particle-liquid solder interface to a greater extent. A similar phenomenon could operate in the case of Zn nanoparticles as well. However, further investigation is necessary to confirm this.

The melting characteristics of SAC and nanocomposite solders were investigated using DSC. The onset melting temperature was taken to report the melting temperature of the solders. The onset melting temperature of SAC was measured to be 217.2°C as shown in Figure 3. The addition of Zn nanoparticles into the SAC solder did not appear to cause any significant change in the onset melting temperature. The average melting temperatures for SAC-0.3Zn and SAC-0.8Zn were found to be 216.7°C and 217.0°C, respectively. These results are in good agreement with the reported values by Moon et al. (2000) and Kang et al. (2006), where the addition of a small amount of Zn as an alloying addition did not cause much change in the melting temperature.

The extent of wetting of the prepared solder was measured by the contact angle that formed at the solder junction. From Figure 4(a), it can be seen that the wetting angle increased with an increase in Zn content. Figure 4(b) shows that the spreading ratio of SAC nanocomposite solder decreased as the Zn content increased. The possible explanation for this behavior is that Zn is an active element and is easily oxidized during the soldering. Oxide accumulation tends to increase the surface tension of the solder, which then deteriorates the wetting behavior (Hao et al., 2007). This could also be due to the inhibited flow of the molten solder by nanoparticles resulting in increased viscosity. The nanoparticles are believed to "pin" the leading edge of the molten solder from further spreading (Shen and Chan, 2009).

Figure 5(a)-(c) shows cross-sectional FESEM micrographs of SAC and nanocomposite solder after 1 × reflow. It is seen that a scallop shaped Cu3Sn5 intermetallic compound formed in the SAC solder after 1 × reflow (Figure 5(a)). Similarly, upon the addition of 0.3 wt. % of Zn, the scallop shaped Cu3Sn5 IMC formed after 1 × reflow (Figure 5(b)), but the thickness of the Cu3Sn5 was much lower compared with that of SAC. Further addition of Zn nanoparticles to 0.8 wt. % resulted in the formation of two IMC layers at the interface (Figure 5(c)). The IMC layer close to the substrate had a lighter contrast, while that on the solder side had a darker contrast. In addition, some darker phase was also seen in the solder matrices.

Figure 5(d)-(f) shows the cross-sectional FESEM micrographs of the samples after 6 × reflows. Figure 5(d) shows the two distinct layers of IMCs in SAC after 6 × reflow. The inner Cu2Sn layer is very thin and <1 μm in thickness, even after 6 × reflows, but the outer Cu3Sn5 layer has grown much thicker. Upon addition of 0.3 wt. % Zn nanoparticles, the growth of Cu3Sn5 was suppressed and only scallop type Cu3Sn5 formed (Figure 5(e)). The thickness of the Cu3Sn5 was much lower compared to that of SAC. In the case of SAC-0.8Zn (Figure 5(f)), two IMC layers, one lighter and the other darker in appearance, were formed, as in the case for a single reflow. The thickness of both layers had increased after 6 × reflow. The darker phase was also seen to be present in the solder matrix. Identification of the IMC layers was performed by EDX analysis. Table II shows the composition and the phases present in the composite solders after 1 × reflow and 6 × reflow. It can be seen that the lighter layer in SAC-0.8Zn was Cu3Sn5 whereas the outer darker layer was Cu2Zn5Sn. The dark phase in the solder matrices of SAC-0.8Zn was also identified as Cu3Zn5.

EDX elemental mapping was performed to reveal the distribution of different constituents across the interface. Figure 6(a) shows a cross-sectional FESEM micrograph of SAC-0.8Zn after 6 × reflow, while the elemental maps for Sn, Zn, Cu and Ag are shown in Figure 6(b)-(e), respectively. The distribution of the individual elements in Figure 6(b)-(e) is consistent with the compositional analysis from the EDX result shown earlier in Table II. The distribution of the elements clearly shows that the copper-zinc based IMCs, Cu2Zn5Sn and Cu3Zn5Sn, forms both at the solder side of the interface as well as in the solder matrix in the SAC-0.8Zn sample after 6 × reflow.

The thickness of the individual IMC layers is plotted against the Zn content of the SAC in Figure 7. It can be seen in Figure 7(a) that, after 1 × reflow, the Cu3Sn5 IMC thickness decreased as the Zn content increased. The Cu3Sn5 IMC thickness decreased from 1.79 μm in SAC to 1.16 μm in SAC-0.3Zn and to 0.67 μm in SAC-0.8Zn. The Cu2Zn5Sn layer did not form in the SAC-0.3Zn sample. However, the Cu2Zn5Sn layer was found to have a thickness of 1.93 μm in SAC-0.8Zn. No CuSn layer was detected in any sample after 1 × reflow. After 6 × reflow (Figure 7(b)), it was found that the Cu2Zn5Sn thickness decreased progressively as the Zn content increased. For SAC, the thickness of the Cu2Zn5Sn was 4.11 μm. With the addition of 0.3 wt. % of Zn, it decreased to 1.22 μm and further to 0.97 μm in SAC-0.8Zn. The Cu2Zn5Sn IMC, which was found only in the SAC-0.8Zn solder, was 1.72 μm thick after 6 × reflows. So the increase in the thickness of the Cu2Zn5Sn layer with reflow time was not that large. Cu2Zn5Sn was
Figure 4 (a) Wetting angle and (b) spreading rate of SAC composite solder as a function of Zn content

Figure 5 Cross-sectional FESEM micrographs of a solder/Cu interface

Notes: (a) SAC; (b) SAC-0.3Zn; (c) SAC-0.8Zn after 1 × reflow; (d) SAC; (e) SAC-0.3Zn; (f) SAC-0.8Zn after 6 × reflow

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