Synchrotron Micro-XRF Measurements of Trace Element Distributions in BGA Type Solders and Solder Joints

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Abstract

Trace elements are increasingly being incorporated into lead-free solder compositions. This paper analyses the distribution of trace elements in solder joints when commercial purity Sn-based alloys are soldered onto Cu substrates. Analysis techniques include μ-XRF (X-ray fluorescence) mapping performed at the SPring-8 synchrotron radiation facility. The mapping results indicate that Ni is present in the Cu₆Sn₅ intermetallic reaction layer, and is distributed in a relatively homogeneous fashion as (Cu,Ni)₆Sn₅. In alloys containing trace levels of Ge (60 ppm), this element is comparatively concentrated within the oxide at the solder surface, and a lower concentration is distributed homogeneously in the solder matrix and the intermetallic reaction layer. In Sn–Pb alloys, the Pb was found to segregate to the boundaries between adjacent Cu₆Sn₅ grains.

Keywords: Lead-free Solder, Intermetallics, Synchrotron Micro-XRF, Trace Elements

1. Introduction

In microelectronic assembly, the intermetallic layers in the reaction zone between the solder and substrate are crucial to the mechanical and electrical integrity of soldered joints. Cu₆Sn₅ is the most commonly formed intermetallic in the reaction zone between the Sn-based solder and the Cu substrate. Recently, much attention has been paid to the effects of impurities and alloying additions on the Cu₆Sn₅ interfacial reaction layers between the Sn-based solders and Cu substrates.[1–6] Trace elements are categorised into two groups:[6] (1) elements that show marked solubility in the Cu₆Sn₅ intermetallic reaction layer such as Ni, Sb, Au, In, Co, Pt, Pd, and Zn, and (2) elements that are not extensively soluble in Cu₆Sn₅ such as Ag, Fe, Bi, Al, P, Ti, S, and rare-earth elements. The role of dissolved trace additions in Cu₆Sn₅ in determining the intermetallic layer growth and phase stability has been the subject of a range of recent studies.[1, 4–6] Cu₆Sn₅ has at least two crystal structures in the solid state, with an allotropically transformation at 186°C.[7, 8] At equilibrium, monoclinic eta-Cu₅Sn₅ (C2/c) is the lower-temperature phase while hexagonal eta-Cu₆Sn₅ (P63/mmc) is stable at higher temperatures.[7] In 2008, it was found[9] by TEM that the faceted eutectic (Cu,Ni)₆Sn₅ intermetallic containing around 9 at% Ni in hypo-eutectic Sn–0.7Cu–0.05Ni alloys remains in the hexagonal eta phase at room temperature in contrast to binary (Ni-free) Cu₅Sn₅ intermetallics which transform into the low-temperature monoclinic eta' phase under identical cooling conditions. Since then, DSC[10, 11] and synchrotron powder XRD[10, 12, 13] have shown that Ni additions suppress the eta to eta' transformation, and the intermetallic appears to remain as the eta phase at room temperature. In support of this, first principle calculations have shown that Ni additions reduce the energy difference between eta' and eta at 0 K.[14] It also has been reported that small amounts of Sb in Cu₅(Sn,Sb)₅ shift the thermal
stability range of high-temperature Cu₆Sn₅.[15] Further research is required to understand the role of impurities on solder joint reliability since impurities influence factors including the Cu₆Sn₅ grain size, the mechanical properties of Cu₆Sn₅, the thickness and growth of the IMC reaction layer, Cu₆Sn₅ phase transformations, and cracking in Cu₆Sn₅.[4, 6, 16] This report presents the results of a microanalysis of the distribution of various trace elements in solders of several common compositions. In particular, the distribution of the elements in the Cu₆Sn₅ phase is examined in an attempt to understand the relationship between microstructure, grain size, thickness of the IMC solder layer, and composition.

A method for elemental mapping using an X-ray fluorescence microscope technique (μ-XRF) has been developed at the synchrotron radiation light source, SPring-8 Japan.[17, 18] In the micro-XRF technique, elemental mapping is performed by detecting the characteristic X-rays of constituent elements. Since the intensity of the X-ray beam emitted from the undulator source at SPring-8 is extremely high, the X-ray fluorescence from a substance with a mass in the order of femtograms on the surface can be detected. This technique has been utilised to analyse the distribution of trace elements in the modified eutectic Si phase of commercial Al–Si alloys,[19, 20] to characterise the distribution of doping elements in a Mg–Ni alloy,[21] and to analyse the microstructures of lead-free solder Sn–Cu based alloys.[22] The spatial resolution is below 100 nm, which is comparable to the current resolution achievable by FE-SEM/EDX. In the current research, this technique was used to investigate the distribution of the trace elements Ni (500 ppm) and Ge (60 ppm) along with the major elements Sn, Cu, Ag and Pb in the region of the solder-substrate interface (and accompanying IMC Cu₆Sn₅ layer) for a variety of solder compositions.

2. Experimental procedure

Ball Grid Array (BGA) type soldered samples with Cu substrates were used in the experiments. Table 1 shows the chemical composition of the three solder alloys investigated, the soldering methods used and the solder temperatures. BGA type samples were obtained from 500 μm diameter solder balls on organic solderability protection (OSP) Cu boards using a common reflow process with RMA-type organic halogen-containing flux. This cycle was conducted twice for each BGA specimen. For micro-XRF experiments, all samples were embedded in epoxy resin and polished in cross-section to observe the solder joints. Figures 1(a) to 1(c) show cross-sectioned optical micrographs of a) Sn–0.7Cu–0.05Ni+Ge, b) Sn–1.2Ag–0.5Cu–0.05Ni and c) Sn–37Pb. Figure 2 shows a sample SEM micrograph of a BGA type Sn–0.7Cu–0.05Ni+Ge solder on a Cu substrate, which has been reported previously.[12] An EDS point analysis indicates around 4–5 at% Ni is present in the Cu₆Sn₅.

The micro-XRF experiments were performed at undula-
tor beamline 47XU at SPring-8, Japan. A schematic diagram of the experimental set-up for micro-XRF is available elsewhere.[17, 18] The undulator radiation was monochromatized at 6.1 and 15 keV by passing through a liquid-nitrogen-cooled Si 111 double-crystal monochromator. A Fresnel zone plate (FZP) was used as an X-ray focusing device to produce a fine probe. The FZP was fabricated using an electron-beam lithography technique at NTT Advanced Technology Co. Ltd. A zone structure with a 1 μm thick tantalum is deposited onto a 2 μm thick SiC membrane. The diameter is 155 μm and the focal length at the X-ray energy of 15 keV is 187.5 mm. The outermost zone width is 100 nm. In this setup, the beam size was 180 nm (vertical) × 150 nm (horizontal) and the total flux of the focused probe was 2 × 10^9 photons/sec. The focused X-ray beam was used as the probe. The samples were mounted on a translation scanning stage with a motion accuracy of better than 10 nm. The XRF spectra were measured with a Si drift diode detector (Rontec Xflash D301). The X-ray path between the sample and the detector was through helium gas in order to reduce the decrement of intensity by the absorption of air.

3. Results and Discussion

The XRF spectra corresponding to the sample of Sn–0.7Cu–0.05Ni+Ge are shown in Figure 3. The signal integration time for the acquisition of the XRF spectra was 200 s. Spectra are taken from a region in the middle of the BGA solder. Sn Lα₁ (3.444 keV), Fe Kα₁ (6.404 keV), Ni Kα₁ (7.478 keV), Cu Kα₁ and Kβ₁ (8.047 and 8.905 keV, respectively), and Ge Kα₁ (9.886 keV) are present. The X-ray energy of Ag Lα₁ is 2.984 keV and since Sn is the dominant element of the solder, it is expected to be difficult to measure trace levels of Ag in this experiment due to the overlapping with the Lα spectra of Sn. Table 2 shows the measured X-ray spectra for this experiment.

A μ-XRF elemental map of the Sn, Cu, Ni and Ge at the soldered-copper interface taken with high resolution scanning is shown in Figure 4(a) (scan pitch: 100 nm, integration: 0.2 sec) for BGA type Sn–0.7Cu–0.05Ni+Ge solders, and a map including the solder surface is shown in Figure 4(b) (scan pitch: 200 nm, integration time: 5 sec). In the elemental mappings, brighter regions indicate a higher concentration of a specific element. It is clear from the mapping results that Ni is present in the intermetallic region, and is distributed in a relatively homogeneous fashion throughout the IMC phase, Cu₆Sn₅.

Figure 4(a) shows that only trace levels (60 ppm) of Ge are present in the bulk solder or in the reaction layer IMC. However, Figure 4(b) shows that Ge is concentrated to a degree at the solder ball surface region. This measurement is consistent with past work on Sn–3.0Ag–0.5Cu–0.05Ge alloy solder balls after a five-time reflow as analysed using XPS.[23] This result suggests the trace Ge addition in the solder may influence the oxidation behaviour of the solder during melting and solidification but not the formation and growth of the IMC. At the resolution of this study, there is no discernable segregation or precipitation of Fe in the bulk solder or the IMC layer.

Table 2 X-ray spectra from Fig. 3.

<table>
<thead>
<tr>
<th>Element</th>
<th>X-ray Energy (keV)</th>
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<tbody>
<tr>
<td>Ag</td>
<td>Lα₁</td>
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<tr>
<td>Sn</td>
<td>Lα₁</td>
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<tr>
<td>Fe</td>
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<td>Ni</td>
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<td>Cu</td>
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<td>Pb</td>
<td>Lα₁</td>
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Fig. 2 SEM micrograph of a cross-sectioned BGA type Sn–0.7Cu–0.05Ni+Ge solder on a Cu substrate.

Fig. 3 XRF spectra of Sn–0.7Cu–0.05Ni+Ge solder.

Table 2 X-ray spectra from Fig. 3.
Figure 5 (scan pitch: 100 nm, integration time: 0.2 sec) shows the Sn, Cu, Ni and Ag distributions in the solder-substrate interface region for a BGA-type Sn–1.2Ag–0.5Cu–0.05Ni solder. The distribution of the 500 ppm Ni is homogenous in the IMC layer in the reaction zone, as was found in the Sn–0.7Cu–0.05Ni+Ge samples shown in Figure 4(a) and 4(b). Ag is expected to have very low solubility in Cu₆Sn₅, but trace Ag levels could not be examined here because the Sn Lα₁ and Ag Lα₁ elemental peaks overlap. However, Ag could be detected when present at high concentrations, such as in Ag₃Sn particles. Ag₃Sn was found in the solder matrix (Figure 5), as reported in past research,[3] but was not present between Cu₆Sn₅ grains in the reaction layer. Additionally, the Ni distribution in the IMC was not discernibly affected by Ag.

Previous work has shown that (Cu,Ni)₆Sn₅ has a wide solubility range of Ni[24–27] and around 4–5 at% Ni is measured in Cu₆Sn₅ solder joints of BGA-type Sn–0.7Cu–0.05Ni+Ge on Cu substrate by point analysis using SEM/EDS.[10, 12] Figures 6(a) and (b) schematically show how the distribution of Ni in the intermetallic may have significant implications for joint integrity. In the presence of a concentration gradient (a), a situation might arise where some regions of the IMC have Ni concentrations above the level required for stabilization of the hexagonal allotrope and other regions may have concentrations lower than that required. Temperature cycling can therefore result in a stress gradient within the IMC layer due to the associated...
volume changes occurring with the transformation.[12] In contrast, a homogeneous distribution of Ni in the IMC, such as that shown in (b), where the Ni concentration exceeds that required for the transformation will avoid stress concentrations. The micro-XRF mapping results shown in Figures 4 and 5 clearly indicate that the scenario of Figure 6(b) occurs and there is 4–5 at% Ni homogeneously distributed throughout the Cu₆Sn₅.

Previous research has shown that (Cu,Ni)₆Sn₅ containing 4–5 at% Ni remains as hexagonal eta at room temperature under cooling conditions that cause binary Cu₆Sn₅ to transform to monoclinic eta'.[9, 14] The influence of retarding or eliminating this solid-state phase transformation on the thermomechanical stability of solder joints is a continuing area of research.[10, 12] Recently Chung et al.[28] discussed the direct evidence for early stage Cu₆Sn₅ and Cu₃Sn growth between non-Ni-containing Sn–Cu solder and Cu substrates based on detailed TEM work. They claimed that the formation and growth of Cu₆Sn₅ is a two-stage process with (1) a first stage occurring during the ramping up of the temperature when the solder had not yet become molten, and (2) a second stage where Cu₆Sn₅ rapidly covers the entire interface and a thin layer of Cu₃Sn also forms. They concluded that the existence of Cu-enriched regions indicates that the grain boundary and phase boundary diffusion of Cu atoms was the dominant mechanism for the growth of Cu₆Sn₅ and Cu₃Sn in the early stages of the soldering reactions. Since our Ni-containing solder shows a homogeneous Ni distribution, it is expected that the Cu and Ni atoms responsible for the growth of (Cu,Ni)₆Sn₅ were supplied only from the Sn–Cu–Ni solder and did not originate from the Cu substrate.

It is suggested that the formation and growth mechanisms of the intermetallics at the interface of the Ni-containing Sn–Cu solder and Cu substrates might be different from that occurring between Ni-free Sn–Cu solders and Cu substrates. Very thin layers of Cu₃Sn formation on Cu substrates when using Ni-containing Sn–Cu solder also indicate a difference from Ni-free Sn–Cu solders.

Figures 7(a) and (b) show the Sn, Cu and Pb distributions in the IMC layer for BGA-type Sn–37Pb solders. High-magnification mapping of the Pb distribution in Figure 7(b) (scan pitch: 50 nm, integration time: 0.2 sec) clearly indicates that Pb precipitates between the Cu₆Sn₅ IMC grains, but is not present within the Cu₆Sn₅ grains. As

![Fig. 6 Significance of Ni distribution in (Cu,Ni)₆Sn₅ IMC, (a) inhomogeneous distribution of Ni in Cu₆Sn₅ (b) homogeneous distribution of Ni in Cu₆Sn₅. 4–5 at% Ni is homogeneously distributed throughout the Cu₆Sn₅. This level of Ni stabilises the hexagonal allotrope of (Cu,Ni)₆Sn₅ (eta) at room temperature, minimising stresses associated with phase transformation.

![Fig. 7 (a) Low magnification micro-XRF mapping of BGA Sn–37Pb. (b) High magnification micro-XRF mapping of BGA Sn–37Pb.](image)
shown schematically in Figures 8(a) and (b), this distribution of Pb may be more favorable in regards to the accommodation of stress in the IMC layer compared to a situation where no segregates are present. The solid solubility of Pb in Cu6Sn5 is very low and it is reasonable that Pb is found at the grain boundaries of Cu6Sn5. It is reported that Sn–Ag–Cu solder joints have a higher rate of interfacial failure than Sn–Pb joints.[29] Soft Pb distributions/seggregations between the Cu6Sn5 grains along the Cu6Sn5 grain boundaries in the reaction layer may inhibit cracking in the reaction zone.

4. Conclusions

This research utilised a μ-XRF trace element mapping technique at the SPring-8 synchrotron radiation facility for solder joint analysis. Three BGA-types of samples on Cu substrates were used in the experiments. All samples with a solder of base composition 500 ppm Ni had a homogeneous Ni distribution in the Cu6Sn5 IMC layer. Ge, when present in trace levels, is distributed homogeneously in the solder at a very low concentration but is also present at the solder surface at a higher concentration, where it contributes to the oxidation resistance of the joint. In the Pb-containing system, the Pb in the Sn–37Pb solder precipitates or is segregated to the Cu6Sn5 IMC grain boundaries. The variations in crystal structure and composition across the soldered interfaces have practical implications for the mechanical properties and propensity for damage accumulation within the IMC layer.

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