Evaluation of Solder Composition by Surface Analysis

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Solder composition was evaluated with several methods of surface analysis. Since solder is a heterogeneous alloy, ordinary surface analysis is not adequate for accurate determination of its composition. Recently however, a method of quantification with phase analysis has been introduced in EPMA for heterogeneous systems. In this paper, we examine the validity of phase analysis for Sn-Pb eutectic solder and Sn-3.0wt%Ag-0.5wt%Cu solder, and found that phase size needs to be considered when using phase analysis.

1. Introduction

Solder is an indispensable material for mounting microelectronic parts on a substrate. In recent years, as a result of the smaller scale and higher density in microelectronic packages, solder joint areas have decreased in size considerably. As a result, surface analytical techniques have become more important for failure analysis of small solder joint areas.

Since solder is a heterogeneous alloy, ordinary surface analysis is not adequate for accurate determination of its composition because quantification in surface analysis is made on the assumption that a specimen is essentially a homogeneous system. The use of the calibration line method or multi-point analysis might provide more accurate results, but these methods are not practical. Accordingly, the solder's bulk composition has been measured conventionally using wet analysis.

Recently however, a method of quantification with phase analysis has been introduced in EPMA (both EDX and WDX) for heterogeneous systems [1,2]. In this method, mapped areas of different composition are recognized as different phases, and the composition and area-ratio for each phase are used for the quantification.

In this study, we conducted quantitative analysis for Sn-Pb eutectic solder and a Pb-free solder (Sn-3.0wt%Ag-0.5wt%Cu) with surface analytical techniques. Specifically, we report on the applicability and validity of quantification using a phase analysis with EDX.

2. Experimental

Two kinds of solder were subjected to the following analyses, and the results were compared with their bulk compositions.

(a) Sn-37wt%Pb eutectic solder (foil form)

- The foil surface composition was measured by EDX, WDX, AES and XPS.
- The surface and cross-sectional compositions of the foil were measured using EDX for conventional quantification and phase analysis.
- Depth profiles were measured by XPS and AES.

(b) Sn-3.0wt%Ag-0.5wt%Cu solder (ball form)

- The cross-sectional composition of a solder ball was measured using EDX for conventional quantification and phase analysis.
- Phase structure was analyzed by XRD.

SEM-EDX technique was performed using HITACHI S-4500 and HORIBA EMAX-7000. WDX, AES, XPS and XRD techniques were performed using JEOL JXA-8600MX, JEOL JAMP-7100, SHIMADZU-KRATOS AXIS-HS3.5 and RIGAKU PSPC-MDG2000, respectively. Phase analysis was performed using HORIBA EMAX-7000 software.

3. Sn-Pb eutectic solder

3-1. Surface composition

The concentrations of Sn and Pb (to be Sn+Pb=100) on the foil surface were measured by EDX, WDX, AES and XPS, with three measurement area sizes, 30, 120, 300 μm ϕ (with XPS, an area of 300 $\times$ 700 μm was

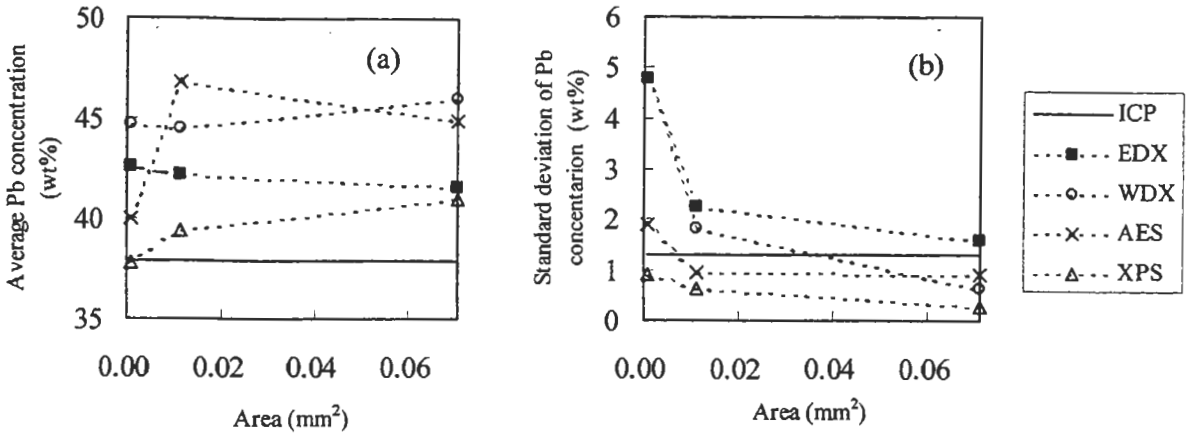

Figure 1. (a) Averages and (b) standard deviations of surface concentrations of Pb (to be Pb+Sn=100) for as-received surface of Sn-Pb eutectic solder foil. (Acceleration voltage was 20 kV and irradiation current was 2×10^{-10} A in EDX, 15kV and 3×10^{-8} A in WDX.)

Table 1. The concentrations of Pb and Sn (wt%).

Position	Bulk(Ref.)	Surface		Cross-section	
Method	ICP	Conventional	Phase	Conventional	Phase
Pb	37.9	41.6	49.9	26.2	38.1
Sn	62.1	58.4	50.1	73.8	61.9

substituted for the 300 μ m ϕ). The quantitative calculations of each technique were carried out using the ZAF method without standard specimens in EDX, the ZAF method with standard specimens (pure Sn and pure Pb) in WDX, and the relative sensitivity factor method in AES and XPS. They were measured 25 times per size, respectively, and the results were compared with the bulk composition as measured by ICP.

The averages and standard deviations of Pb concentrations are shown in Fig.1. The standard deviations in surface analyses decreased linearly with the size of measurement areas, but the averages in the surface analyses were inconsistent with the result of ICP, even for the largest measurement area of WDX.

3-2. Phase analysis with EDX

The surface and cross-sectional compositions of the foil were measured using EDX for conventional quantification and phase analysis. The cross-section was made by polishing the foil fixed in an embedding resin with abrasives.

In this paper, 'conventional' EDX refers to the quantification with EDX where the ZAF correction is applied to the intensity of characteristic X-ray emissions from the entire analytical area. On the other hand, in 'phase' EDX (the quantification using phase analysis with EDX), the ZAF correction is applied only to the individual phases [1].

The concentrations of Sn and Pb obtained with the four methods are shown in Table 1. A SEM image and a phase map of the cross-section are shown in Fig.2. The concentrations of Sn and Pb and the area-ratio for each phase obtained by phase analysis are shown in Table 2.

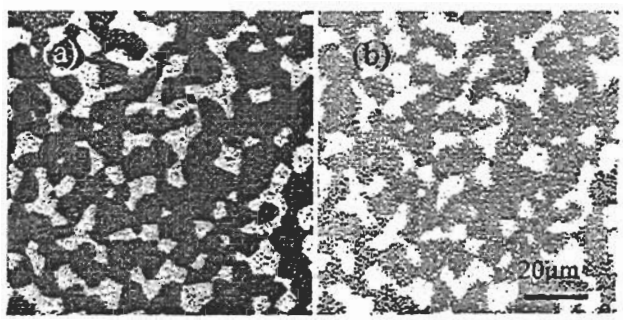

Figure 2. (a) SEM image and (b) phase map of the cross-section of Sn-Pb eutectic solder foil. In the map, the Pb-rich and Sn-rich phases are shown as the white and gray parts respectively.

Table 2. The concentrations of Sn and Pb in each phase from the cross-section of Sn-Pb eutectic solder foil.

	Concentration (wt%)		Area-ratio
	Sn	Pb	(%)
Pb-rich	15.6	84.4	31
Sn-rich	95.8	4.2	69

The following are deductive conclusions from Table 1.

- The result of cross-sectional 'phase' EDX was quite consistent with the bulk composition.
- 'Conventional' EDX showed a greater Sn concentration than 'phase' EDX.
- The surface was found to contain more Pb than the bulk.

3-3. Depth profiling with XPS and AES

Depth profiles using XPS are shown in Fig.3. Initially, solder surface was covered with Sn-oxides (Fig.3 (a)), and with further sputtering, surface segregation of Pb was observed (Fig.3 (b)). Similar depth profiles were given by AES.

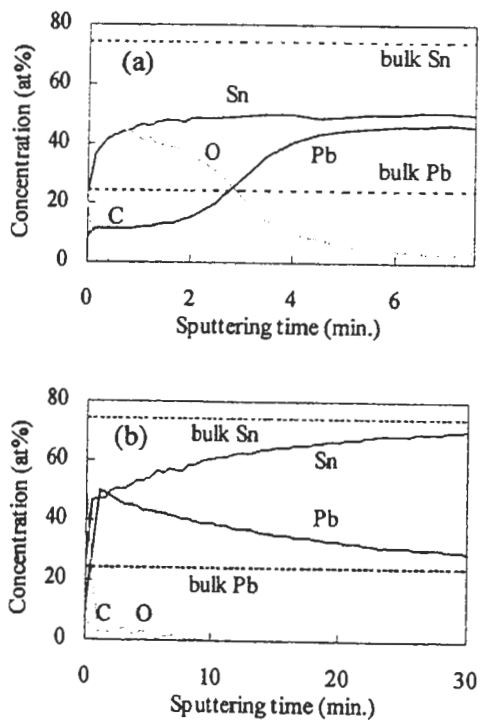

Figure 3. Depth profiles of Sn, Pb, O and C on surface of Sn-Pb eutectic solder foil for times up to (a) 7.5 min (10sec intervals) and (b) 30 min (30sec intervals). The sputtering rate is 3.4nm/min in SiO_2.

Generally, when a Sn-Pb alloy is sputtered, surface enrichment of Sn is observed due to preferential sputtering [3]. Even taking into account the preferential sputtering, Pb segregation was clearly observed, and this phenomenon was also revealed by EDX.

For long periods of sputtering, we observed that the Pb-rich phase was removed faster than the Sn-rich phase, and the presence of an uneven surface was confirmed (Fig.4). Thus, this means that the actual composition of solder cannot be determined accurately by XPS and AES.

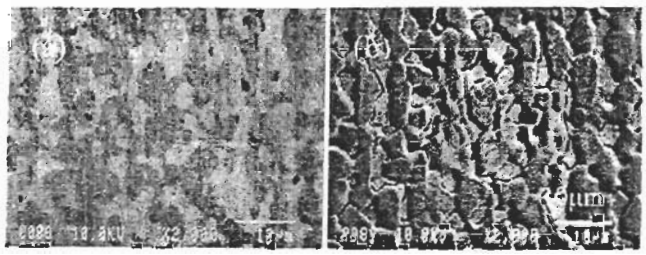

Figure 4. SEM images of Sn-Pb eutectic solder foil surface: (a) before and (b) after ion-sputtering.

4. Sn-3.0wt%Ag-0.5wt%Cu solder

4-1. Phase analysis with EDX

The cross-sectional composition of Sn-3.0 wt%Ag-0.5wt%Cu solder ball was measured using 'conventional' and 'phase' EDX. The cross-section was made by polishing the balls fixed in an embedding resin with abrasives.

The results of each method are compared in Table 3. A SEM image and a phase map are shown in Fig.5, and the concentrations of Sn, Ag and Cu and the area-ratio for each phase given by phase analysis are shown in Table 4.

As shown in Table 3, the result obtained by 'conventional' EDX was closer to that obtained by the wet analysis.

4-2. Phase structure with XRD

The cross-section of Sn-3.0wt%Ag-0.5wt% Cu ball was measured by XRD. The resulting X-ray diffraction pattern is shown in Fig.6. The specimen was found to consist of β-Sn, Ag_3Sn and Cu_6Sn_5.

In comparing Table 4 and Fig.6, the Ag-rich and the Cu-rich phases distinguished by 'phase' EDX are inconsistent with Ag_3Sn and Cu_6Sn_5 as the metal phases determined by XRD.

Table 3. The concentrations of Sn, Ag and Cu (wt%)

	Wet (ref.)	Conventional	Phase
Sn	96.5	96.9	96.0
Ag	3.0	2.7	2.9
Cu	0.5	0.4	1.1

Table 4. The concentrations of Sn, Ag and Cu in each phase and their area-ratio.

	Concentration (at%)			Area-ratio
	Sn	Ag	Cu	(%)
Sn-rich	100.0	0.0	0.0	71.0
Ag-rich	84.8	15.2	0.0	16.0
Cu-rich	81.0	4.3	14.7	13.0

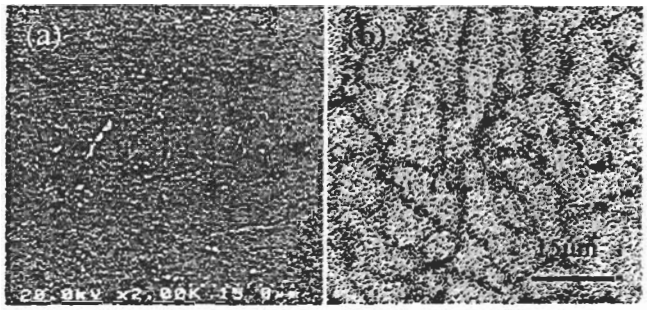

Figure 5. (a) SEM image and (b) phase map of the cross-section of Sn-3.0wt%Ag-0.5wt%Cu solder ball. In the map, the Sn-rich, Ag-rich and Cu-rich phases are shown as the light-gray, dark-gray and black parts respectively.

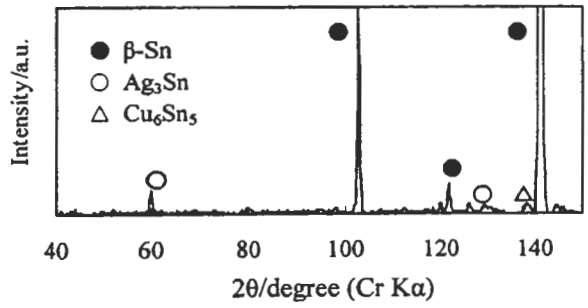

Figure 6. X-ray diffraction pattern of Sn-3.0wt%Ag-0.5wt%Cu solder ball.

In other words, the Ag-rich phase is composed of β-Sn and Ag_3Sn, and the Cu-rich phase is composed of β-Sn, Ag_3Sn and Cu_6Sn_5, because it is likely that the Ag_3Sn and Cu_6Sn_5 phases are sub-microns in size, which is below the spatial resolution of EDX.

'Phase' EDX thus was inadequate in quantification. Nevertheless the distribution of each phase can be recognized using the phase map with EDX for specimens including trace elements as in this case.

5. Conclusion

When a solder is subjected to surface analysis to determine its composition, we should take into account its heterogeneous nature and the variation between the surface and the depth compositions. In AES and XPS, the preferential sputtering poses an additional problem. Therefore, we realized that the discussion of the quantitative results needs careful consideration.

In EPMA, validity of the phase analysis depends on the sample. In Sn-Pb eutectic solder, the result of cross-sectional 'phase' EDX was quite consistent with its bulk composition. In Sn-3.0wt%Ag-0.5wt%Cu solder, however, 'conventional' EDX seemed better, at least in quantification, than 'phase' EDX.

If phase sizes are larger than a few microns, phase analysis should be used for quantitative analysis. While, if phase sizes are sub-microns and therefore approaching the spatial resolution of EPMA, 'conventional' quantification should be used.

Phase analysis can be improved by the use of standard sample consisting of an inter-metallic compound to obtain a more accurate phase separation [4].

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7. References

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