Composition Distribution Studies of Sn/Ag/Cu Solder Material using TOF-SIMS, XPS and EDX

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***Abstract*— Determination of compositional distribution for solder material is of particular interest in the area of failure analysis, specifically in the investigation of various solder alloy formations during the joining processes and interconnection failures. In this paper, we explored several advanced techniques such as time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX) for characterizing the composition of SnAgCu solder material. Each analysis technique has its advantages in the information attained, thus stimulating multi-technique approaches for material analysis in future.**

Keywords—SnAgCu solder material, TOF-SIMS, XPS, EDX, 3-D ion image

I. INTRODUCTION

Solder materials have been extensively used in various electronic products, especially for electronic interconnection, wire/interfacial bonding, solar cell and photovoltaic module applications. In the past, many studies have been conducted to understand the mechanical properties of solder materials due to their rapid development and important role in the design and manufacture of various electronic products. Typically, the mechanical properties of solder materials are not only directly related to their microstructures, such as grain size and grain orientation but also the homogeneity and distribution of their compositions [1-4]. Very often, the inhomogeneity and changes of solder composition distribution are mainly induced by high temperature reflow process and this can seriously affect products' reliability and failure. Therefore, the characterization of solder materials, particularly in the study of their microstructures and composition distributions are immensely important in order to understand the solder failure mechanisms.

Conventional chemical composition analysis technique using inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique can provide bulk chemical composition information of material, but it suffers from the limitation in revealing the actual distribution of composition within the material at a specific interested micro area [5]. Therefore, present study explored several techniques for determining the compositional distribution of SnAgCu solder material using several advanced tools such as time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDX). In particular, three dimensional (3-D) depth profile imaging technique through TOF-SIMS was found able to provide valuable information in terms of the distribution of surface and inner compositions of the investigated solder material.

II. EXPERIMENTAL PROCEDURE

SnAgCu solder material was obtained from commercial industry. The microstructure and bulk composition of the solder material were analyzed by FEI Helios Nanolab 600i field emission scanning electron microscopy (FESEM) and EDX, respectively. XPS spectra were recorded by PHI Quantera II spectrometer using mono Al-K_α radiation (1486.6 eV, 15 kV) with reference to C 1s line at 284.5 eV. An Ar^+ ion beam sputtering at 2 keV was used to investigate the depth profile of the solder material. The sputtering rate was calibrated based on SiO_2. TOF -SIMS was performed using an IONTOF TOF.SIMS 5 instrument configured with a 25 keV Bi^+ primary ion beam at 1pA. Depth profile analysis was investigated using 2 keV Cs^+ (40 nA) sputtering with a 100x100 μm analysis area.

III. RESULTS AND DISCUSSION

A. Microstructure Analysis

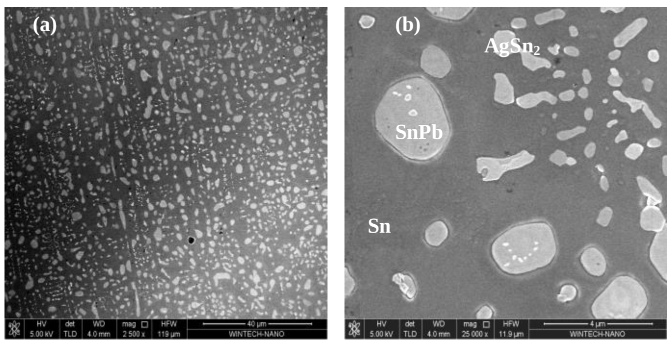

Fig. 1: FESEM images (a) low magnification and (b) high magnification for the investigated solder material at 5 kV.

FESEM is a very useful technique to investigate the microstructure and morphology of material. EDX is used in conjunction with FESEM for determining the bulk chemical composition and elemental information of material. The microstructure of the investigated solder material is shown in Fig.1 FESEM images and its bulk composition is provided in Table 1. FESEM images depicted that the material mainly consisted of different sizes of particles embedded in the matrix of the solder material. EDX analysis revealed that the solder material contained Pb (Table 1). The matrix of solder material was confirmed mainly Sn and the embedded particles can be SnPb or $AgSn_2$. Cu was the least element that detected in the solder material. EDX mapping further showed that Cu distributed throughout the solder material (Fig. 2). Ag and Pb were mostly detected at the embedded particles.

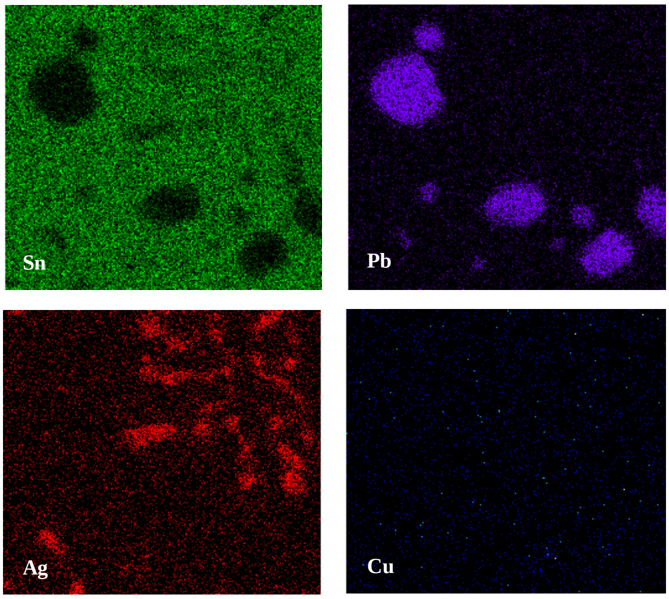

Fig. 2. EDX mapping of (a) Sn, (b) Pb, (c) Ag and (d) Cu distribution for the solder material at 15 kV

TABLE 1: EDX BULK COMPOSITION FOR THE INVESTIGATED SOLDER MATERIAL IN ATOMIC %

Element	Atomic %
Cu	2.3
Ag	3.8
Sn	91.2
Pb	2.7

B. TOF-SIMS Analysis

TOF-SIMS is a widely used technique to characterize the atomic and molecular composition of uppermost surface layers (~1-3 nm) for all organic and inorganic materials [6,7]. This technique is basically based on sputtering process where the sample surface is bombarded by primary ion beam and the atoms and molecule fragments (secondary ions) sputtered from the surface are analyzed through mass spectrometer. It has the capability of detecting all elements, including H and isotopes with sub ppm sensitivity which enable trace level element or contamination study. Another feature of TOF-SIMS is that the composition variation with depth below the surface can be analyzed through the depth profile analysis. Furthermore, it has the advantages of obtaining laterally resolved 2-D and 3-D elemental distribution images mapping for the investigated surface area.

Fig. 3 showed the depth profile analysis for the investigated solder material. The result showed that Sn^+ was the major element in the solder material. It also indicated high Pb^+ content at the surface of solder material. The Pb^+ content decreased after ~100 nm sputtering.

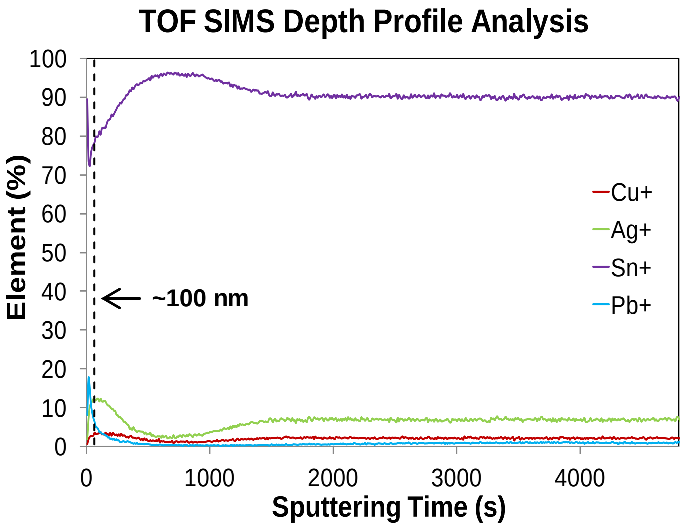

Fig. 3. TOF-SIMS depth profile analysis for the solder material

In addition, we explored the feasibility of TOF-SIMS technique to reveal the 3-D elemental information of the solder material. Fig. 4 shows the 3-D images of Sn^+, Ag^+, Cu^+ and Pb^+ distribution in the solder material. In this technique,

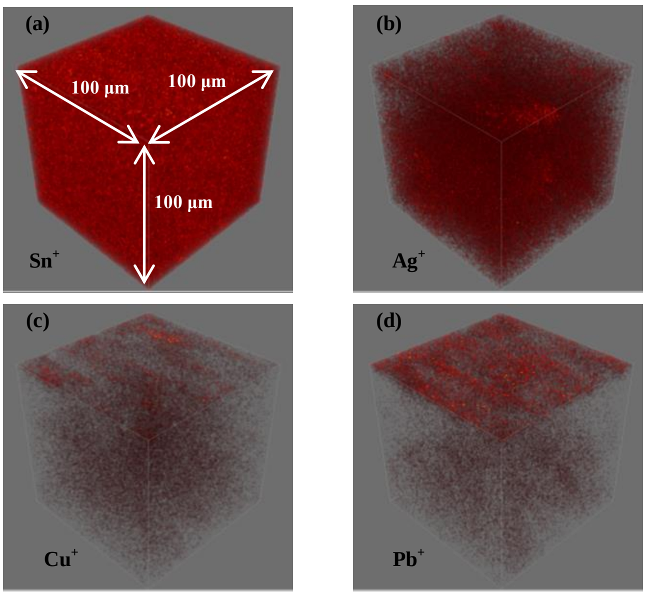

Fig. 4. TOF-SIMS 3-D images for (a) Sn^+, (b) Ag^+, (c) Cu^+ and (d) Pb^+ distribution in the solder material

primary ion beam was used to sputter the sample. With the increase in depth profiling or sputtering, a series of secondary ion images were acquired. The reconstruction of resulting ion images was used for mapping 3-D elemental distribution in the solder material. From Fig. 4, it can be observed that Sn^+ was the major element that distributed throughout the matrix of solder material followed by Ag^+. Pb^+ distribution at surface was higher than the inner part of the solder material. Unlike EDX analysis that only able to provide 2-D elemental mapping information, the unique feature of TOF-SIMS 3-D ion images obtained from the depth profile analysis will be very useful to reveal the internal elemental distribution and structure of various materials, for example layered thin film and composite materials. Furthermore, the feasibility in direct viewing the compositional distribution of materials in 3-D will be highly favorable in the field of material failure analysis.

C. XPS Analysis

XPS is applied for precisely determining the chemical composition of all types of material surfaces that are either conductive or insulative. It is a surface sensitive technique with resolution ~0.1-1 at% and information depth of ~2-10 nm [8,9]. Unlike TOF-SIMS, this technique has the advantages of providing both elemental and chemical state/bonding information for all elements except hydrogen and helium. In addition, XPS can be integrated with ion beam sputtering to provide the in-depth composition profile and chemical state information.

Fig. 5 showed the XPS elemental survey scan of the solder material. The solder material mainly consisted of Sn, Ag, Cu and Pb. Adventitious C and O were found on the surface of the investigated solder material and they were removed after sputtering.

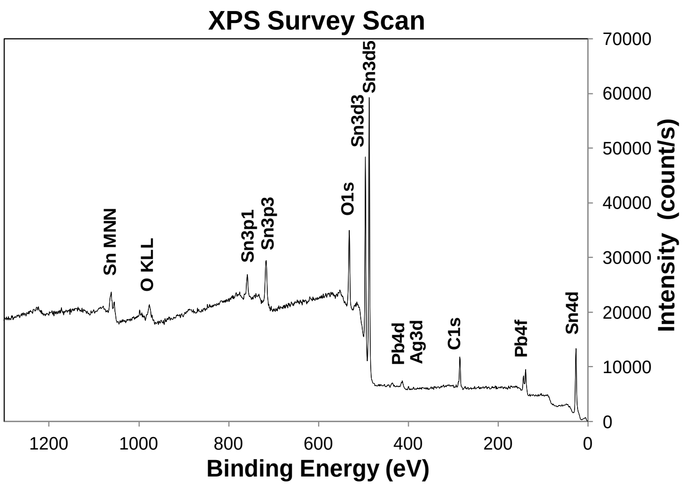

Fig. 5. XPS survey scan for the investigated solder material

The estimated composition in atomic% for the surface of the solder material is shown in Table 2. XPS depth profile analysis was also performed to investigate the inner composition of the solder material (Fig. 6). Similar to TOF-SIMS, Sn was found as the major element in the solder material. Pb showed higher concentration at the surface of the solder material. After 100 nm sputtering, no significant composition change was observed for Sn, Pb, Ag and Cu.

TABLE 2: XPS SURFACE COMPOSITION FOR THE INVESTIGATED SOLDER MATERIAL IN ATOMIC %

Element	Atomic %
Cu	2.2
Ag	0.6
Sn	91.2
Pb	6.0

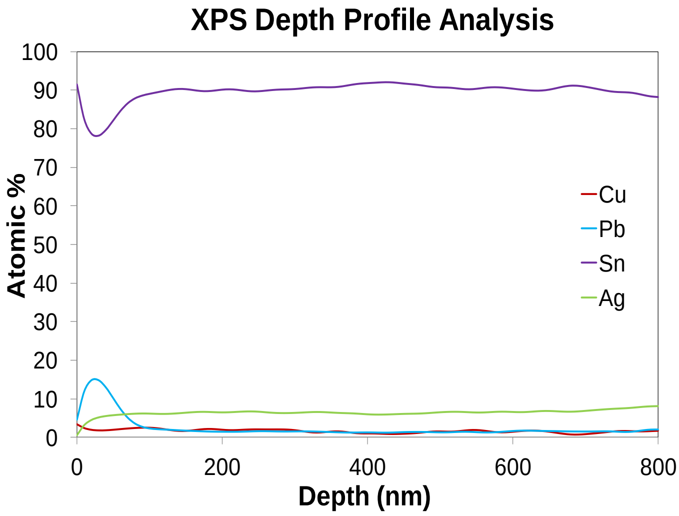

Fig. 6. XPS depth profile analysis for the investigated solder material

In realizing the importance of grain structures to the mechanical properties of solder materials, future study will explore electron backscatter diffraction (EBSD) technique in our laboratory to investigate the phases, crystal orientation and chemical composition within the grains of solder materials. EBSD is a unique technique for characterizing the microstructures of inorganic crystalline materials [10]. In this technique, electron beam is directed to a sample which is tilted at 70° from horizontal. The diffracted electron from the sample surface will produce a diffraction pattern which can be indexed. The band in the diffraction pattern represents the reflecting planes of the materials and this information can be used to identify the grain size, grain/crystal plane orientation, grain boundary and phase of the material.

IV. CONCLUSION

In this study, we have demonstrated the capability of TOF -SIMS, XPS and EDX to determine the chemical composition of solder material. TOF-SIMS, XPS and EDX have their own strength and they complement each other in material analysis.

The combination of TOF-SIMS, XPS and EDX analyses can be applied to obtain useful and complementary information regarding the composition distribution of solder materials. Significantly, present study can pave the way in enhancing the capability of integrating different surface analysis tools to reveal the microstructure and chemical composition distribution of various materials in future.

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