TIO2 NANOPARTICLES REINFORCED LEAD-FREE 96.5SN–3.0AG–0.5CU SOLDER PASTE FOR ULTRA-FINE PACKAGE ASSEMBLY IN REFLOW SOLDERING PROCESS

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ABSTRACT: Ultra-fine package assembly using TiO2 nanoparticle reinforced lead-free solder paste was carried out in the reflow soldering process. TiO2 nanoparticles were mixed with the SAC solder paste at 0.01, 0.05 and 0.15 wt.%. The ultra-fine package (passive capacitor) was mounted on PCB with a thickness of 2.0 mm using the nanocomposite solders. Voids, microstructure and TiO2 nanoparticle distributions were inspected through the X-ray, SEM and HRTEM. The ultra-fine solder joints were formed perfectly without any void formation. The TiO2 nanoparticles are distributed homogenously in the solder joint. The mechanism of IMC reaction during the reflow soldering process is also discussed. Homogeneous mixing of nanoparticle plays a significant role for the distribution of the nanoparticle in the solder joint.

KEYWORDS: *Titanium Dioxide Nanoparticle; SAC305; Composite Solder; Ultra-fine Package*

1.0 INTRODUCTION

The current trend in integrated circuit (IC) packaging is moving towards miniaturization and diversification. The miniature IC package demands reliable solder joint to sustain the performance and overall product reliability. Current advancement of the electronics industries had resulted on the miniaturization of electronic components, simultaneously with the addition of new features and functionality of these devices.

By maintaining the service performance and joint reliability of an ultra-low solder joint volume on microelectronics packaging such as for 01005, 0.3 mm CSP nanotechnology can provide a satisfactory solution on these issues. In order to achieve this goal, various types of nanoparticles are often added to the lead-free solder to reinforce the solder joint resulting in improvement in their mechanical, material and thermal characteristics [1-2]. In order to achieve the most quality characteristics of solder joint, the optimization of Taguchi method has been widely used to improve the reflow soldering process [3].

Numbers of studies had been implemented to examine the effects of adding nanoparticles to the lead-free solder alloy such as Sn-3.5Ag-0.7Cu (SAC), SnAg, SnCu, and SnZn. Moreover, the melting temperature of the lead-free solder had affected by adding the nanoparticles [4-5]. The addition of aluminum oxide (Al2O3) [5], zirconia (ZrO3) [4] and rhodium [6] nanoparticles to the solder alloy slightly increased the melting temperature. Besides, various types of nanoparticles such as NiO [7], Fe2NiO4 [8], diamond [9] and TiO [10] had been considered to optimize the mechanical properties and microstructure of lead-free solder during the reflow soldering process. Recently, the solder joint micromechanical properties had been examined on the Electroless Nickel Immersion Gold (ENIG) surface finished with Cu substrate [11-12] at different high temperature storages.

However, the study on application of nano reinforced solder paste for the ultra-fine package assembly during the reflow soldering process is still limited. Therefore, this research is performed to investigate the significance of TiO2 to the voids formation on the ultra-fine solder joint and the morphology of the microstructure and their distribution of the nanoparticle after the reflow soldering process. TiO2 nanoparticle was considered due to its excellent characteristics, which could enhance the mechanical properties of the lead-free solder [1].

2.0 EXPERIMENTAL

2.1 Preparation of the ultra-fine package assembly using lead-free Sn-3.0Ag- 0.5Cu-TiO2 composite solders

The ultra-fine package that has been investigated in this study was 01005 passive capacitor (Figure 1). The dimension of this ultra-fine-package is 0.4 × 0.2 mm. The nanocomposites were prepared by adding TiO2 nanoparticles (Aldrich, 99.7% trace metals basis, particle size: <25 nm) into 96.5Sn–3.0Ag–0.5Cu solder paste (Alpha OM-353) at a nominal percentage of 0.01, 0.05 and 0.15 wt.% using a mechanical stirrer (Fritsch Planetary Mill PULVERISETTE 5) for approximately 10 minutes (300 rpm) to achieve homogeneity prior to assembly. The average particle size of 96.5Sn–3.0Ag–0.5Cu was 15 – 25 μm (Type 5, -500/+635 mesh designation as per ASTM B214).

Then, the ultra-fine package was mounted on PCB with a thickness of 2.0 mm (PCB Organic Solderable Preservative (OSP) surface finish) using lead-free Sn-3.0Ag-0.5Cu-TiO2 composite solders. The lead-free Sn-3.0Ag-0.5Cu-TiO2 composite solder paste was printed (DEK Horizon) with a thickness of 0.127 mm and using a stainless steel stencil laser cut (nano coated with 1:1 aperture – 0.2 × 0.2mm) and a steel squeegee. The robotic Fuji NXT with customized nozzle was used to mount the ultra- fine package onto the printed lead-free Sn-3.0Ag-0.5Cu-TiO2 composite solder paste. The soldering process was carried out with a lead-free reflow profile in a full convection reflow oven (Vitronics Soltec XPM2) under a nitrogen atmosphere. The reflowed PCBs (Figure 2) were cleaned using an aqueous cleaning machine (Electrovert Aquastorm 200). In order to heat up the mounted boards to suitable temperature in a specified period of time, a reflow furnace was used.

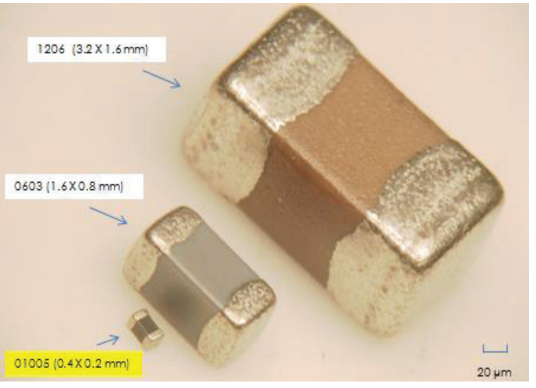

Figure 1: Ultra-fine package component (01005)

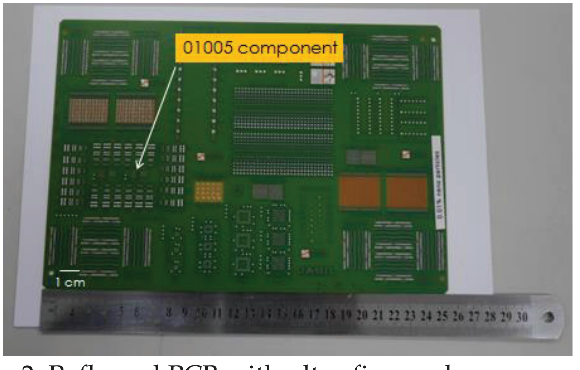

Figure 2: Reflowed PCB with ultra-fine package component

2.2 Characterization of the lead-free Sn-3.0Ag-0.5Cu-TiO2 Composite Solder Joints

X-Ray Inspection

Nikon XT V 160, an X-ray inspection system was used to examine the voids formation in the ultra-fine solder joint.

High Resolution Transmission Electron Microscopy (HRTEM) Analysis

FEI Helios NanoLab 650 Dual Beam systems have both "High Resolution Electron Beam" and "Finely Focused Ion Beam" that was used to prepare the HRTEM lamella. The HRTEM lamella was taken from the bulk sample and attached onto the molybdenum (Mo) grid finger by using Omni probe needle with in-situ lift out technique. Then, the thickness was reduced until electron transparency of less than 100 nm. The HRTEM characterization was carried out using High Resolution Transmission Electron Microscope system (FEI Tecnai G2 F20) with an Energy Dispersive X-ray Spectroscopy (EDS) for investigating the present of nanoparticles in the ultra-fine joint as well as elemental identification.

Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy Analysis

Since the ultra-fine package assembly is smaller, the neighbouring its location (0603; 1.6 × 0.8mm) has been chosen (similar lead-free Sn-3.0Ag-0.5Cu-TiO_2 composite solders) to be investigated. The reflowed samples were cross-sectioned and mounted in the cold epoxy and ground down to 240, 320, 600, 800, 1000, and 2000-grit sizes by using a silicon carbide paper cooled with flowing water to investigate the microstructure uniqueness. Then, it surfaces were polished with 1μm - Al_2O_3 (alumina) suspension followed by 0.3 and 0.05 μm. After complete polishing the cold-mounted samples, an ultrasonic cleaner was used to remove the existing polishing agent prior to few seconds etching on the surface in a mixture of 2% HCl, 5% HNO3, and 93% methanol.

The samples' morphology was observed using Scanning Electron Microscope (SEM) complete with Energy Dispersive X-ray Spectroscopy (EDS, Hitachi S-3400N). The etched surface was sputter-coated with Au prior to SEM analysis to avoid the charging effect. The solder microstructure and intermetallic elements were analyzed via SEM with Backscattered Detector (BSD).

3.0 RESULTS AND DISCUSSION

3.1 Solder Voids

The void areas of the ultra-fine joints were evaluated. X-ray images were illustrated the ultra-fine joints (Figures 3). Confirmed that no void was present in the ultra-fine-joints. According to Industry Standard requirements [13], the allowable level and size of non-BGA solder voids need to be specified by the customer agreement. However, M. Yunus et al. [14] reported that voids size > 50% of the solder joint area could lead to 25% till 50% reduction in reliability of the product. The observation indicates that the addition of TiO2 nanoparticle to the lead-free solder paste does not lead to the void formation in the solder joint.

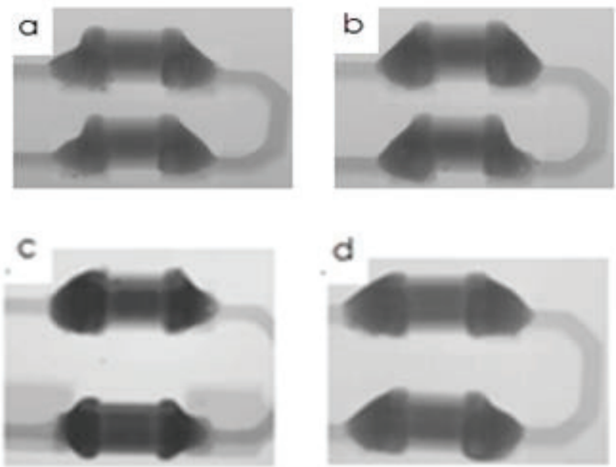

Figure 3: Laminography X-ray images (400×) of ultra-fine joints: (a) lead-free Sn-3.0Ag-0.5Cu- 0.01TiO2, (b) lead-free Sn-3.0Ag-0.5Cu-0.05TiO2, (c) lead-free Sn-3.0Ag-0.5Cu- 0.15TiO2 and (d) plain lead-free Sn-3.0Ag-0.5Cu only

3.2 TiO2 Nanoparticles Examination

HRTEM revealed that there was an evidence of nanoparticles presence in the ultra-fine joint. Figure 4 shows the HRTEM micrographs of an ultra-fine solder joint (lead-free Sn-3.0Ag-0.5Cu-TiO2 composite solder). The TiO2 nanoparticles were evenly distributed in the solder joint. This applied to the homogeneous mixing during the preparation of the lead-free Sn-3.0Ag-0.5Cu-TiO2 composite solders. Besides, no accumulation of TiO2 particle was observed in the solder joint. In addition, EDS confirmed the presence of titanium and oxygen content of TiO2 (Figure 5).

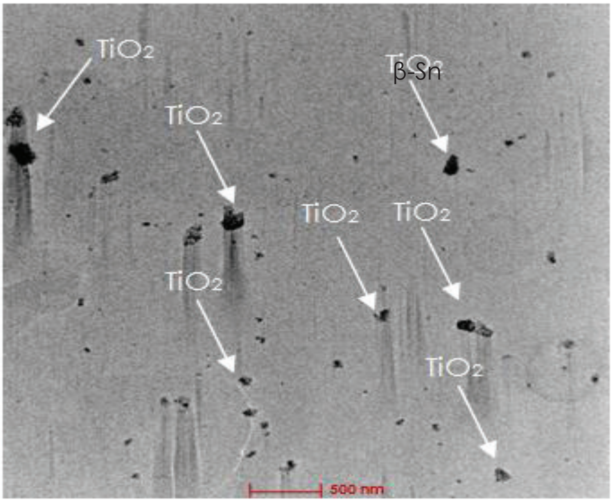

Figure 4: HRTEM micrographs of an ultra-fine solder joint

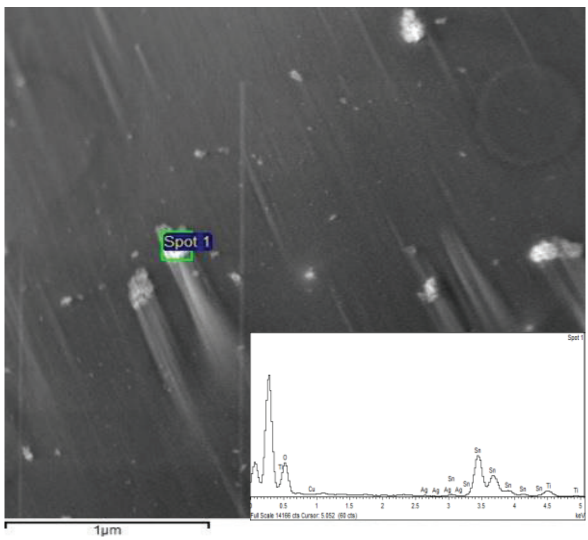

Figure 5: HRTEM micrographs of an ultra-fine solder joint (lead-free Sn-3.0Ag-0.5Cu-TiO_2 composite solder) and EDS pattern results that indicated in the spot region (Spot 1)

3.3 Cross-sectional Morphologies of Cu/Ag-Intermetallic Compounds in Lead-free Sn-3.0Ag-0.5Cu-TiO2 Composite Solder Joints

During the reflow soldering of the lead-free 96.5Sn–3.0Ag–0.5Cu-TiO2 composite solder on the OSP substrate, the copper starts to dissolve promptly to the molten solder after the oxide layer being removed by flux properties and allowed metallurgical bond between solder and copper pad. Ag atoms and also Cu atoms will react with Sn to form an Ag3Sn phase as well as Cu6Sn5 in the molten solder. The reaction of intermetallic formations are described in three consecutive stages [16]: (a) Dissolution, (b) Chemical reaction and (c) Solidification.

In addition, schematic diagrams of the IMC reaction stages under reflow process are illustrated in Figure 6. The schematic diagram of typical eutectic Sn-Ag-Cu structure is illustrated in Figure 7. The solidification structures of the lead-free Sn-3.0Ag-0.5Cu-TiO2 composite solders are shown in Figures 8a-8d. The β-Sn dendrite arms (lighter area) and eutectic structure (darker area) in form of network-like regions with dense arrays of IMC particulates (Cu6Sn5 and Ag3Sn) was observed. Moreover, Ag3Sn IMC was dispersed uniformly in the solder matrix after reflow [15] and the solder joint characteristics fulfilled the IPC standards [13]. EDS result confirmed the presence of elements that corresponding to the Ag3Sn and Cu6Sn5 phases.

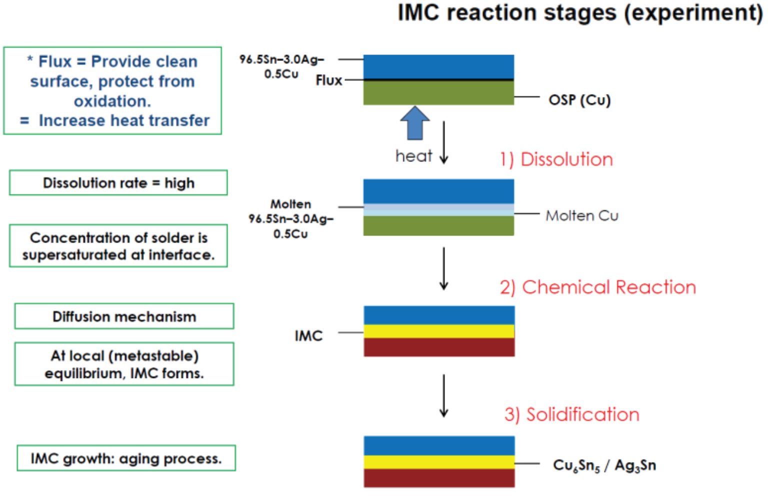

Figure 6: Schematic diagram of the IMC reaction stages under reflow process

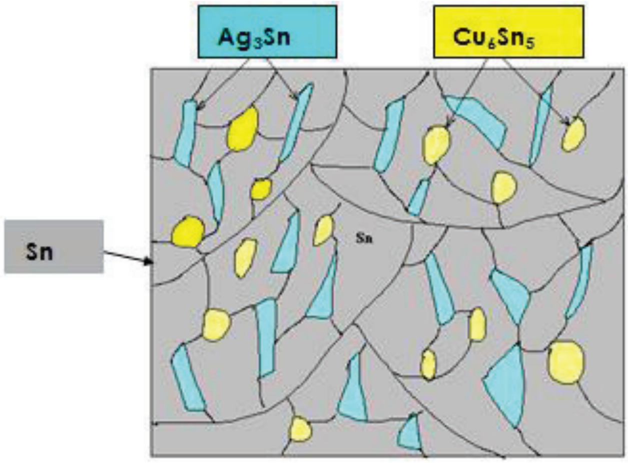

Figure 7: Schematic diagram of typical eutectic Sn-Ag-Cu structure

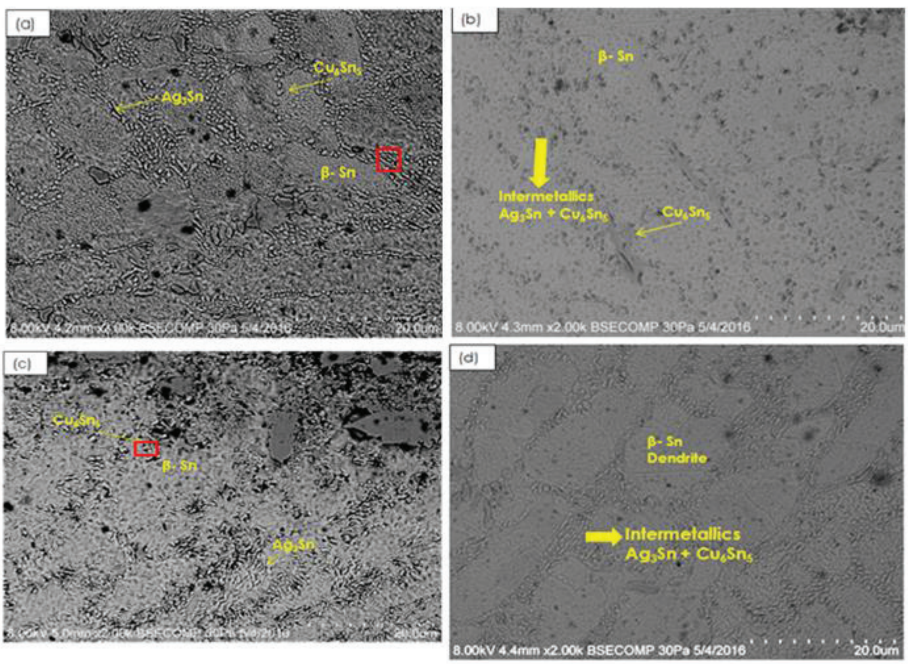

Figure 8: Scanning electron microscope backscattered electron of the cross-sectioned matrix for (a) lead-free Sn-3.0Ag-0.5Cu- 0.01TiO_2 , (b) lead-free Sn-3.0Ag-0.5Cu-0.05TiO_2, (c) lead-free Sn-3.0Ag-0.5Cu-0.15TiO_2 and (d) plain lead-free Sn-3.0Ag-0.5Cu

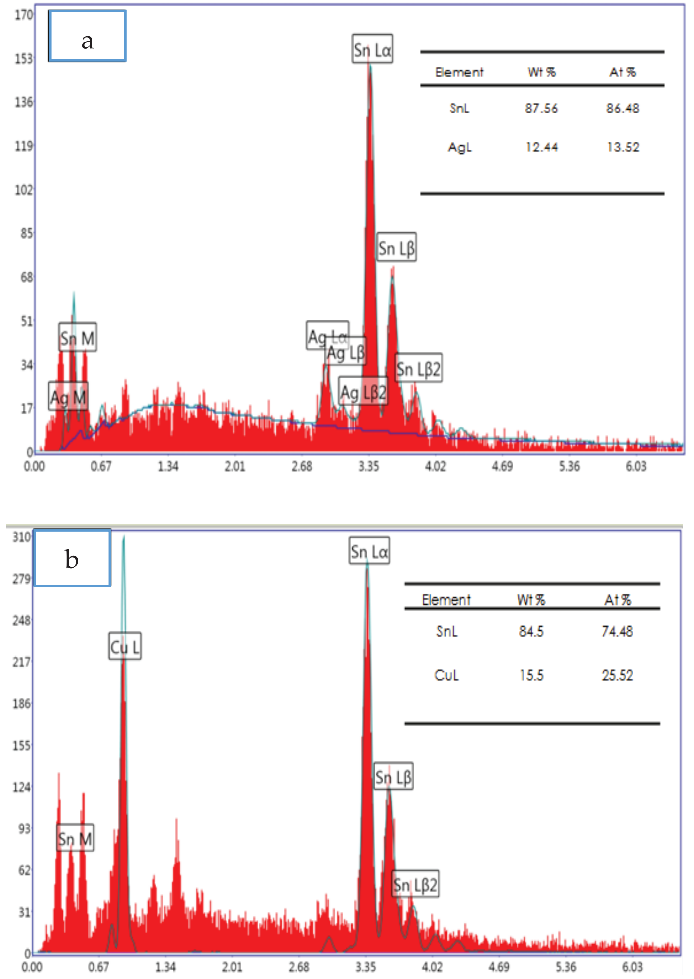

Figure 9: (a) EDS pattern for Ag_3Sn and (b) EDS pattern for Cu_6Sn_5 in the scan area

4.0 CONCLUSION

The TiO2 nanoparticle reinforced lead-free solder composites were successfully applied to the ultra-fine package assembly using the reflow soldering process. Various weighted percentages of TiO2 nanoparticles were considered in this study. The experimental results indicate that the presence of TiO2 nanoparticle in the solder paste retard the void formation during the reflow process. The ultra-fine solder joints were formed successfully using different weight percentages of TiO2 nanoparticle and fulfilled the IPC standards. HRTEM revealed the nanoparticles distributed evenly in the solder joint without any accumulation of the nanoparticle. TiO2 nanoparticle mixed uniformly as the tiny precipitation in the solder matrix. Hence, homogeneous mixing of nanoparticle is significance for the distribution of the nanoparticle in the solder joint.

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