Bi-induced voids at the Cu$_3$Sn/Cu interface in eutectic SnBi/Cu solder joints

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Transmission electron microscopy evidence was obtained to elucidate the mechanism for Bi-induced interfacial void formation in solder joints. After thermal aging, Bi segregated to the Cu$_3$Sn/Cu to form fine particles on the interface in SnBi/Cu solder joints. Interfacial voids were found near the interfacial Bi particles.

Keywords: Eutectic SnBi alloy; Soldering; Interface; Segregation; Transmission electron microscopy (TEM)

In the microelectronics industry, solder interconnects have been extensively used for many years to provide electrical connections as well as mechanical and physical connections [1,2]. With the trend towards miniaturization and functionality in modern consumer electronics, a large number of input/output (I/O) connections are needed to improve the packaging density on high circuit density device chips. As the density of solder bumps rises, the individual solder joints are being scaled to ever smaller dimensions. Therefore, the microstructural defects in the small solder joints, such as impurity atoms and voids at the interfacial region, become increasingly important for component reliability between solder and metallization [3,4].

Interfacial voids have been widely observed in eutectic SnPb/Cu solder joints [4–6]. They are often associated with the growth of Cu$_3$Sn intermetallic compound (IMC) and are attributed to the Kirkendall effect. Recently, another type of void was found in the interconnect made from Pb-free eutectic SnBi alloy [3], which is a potential candidate to replace eutectic SnPb solder in some applications due to its lower melting temperature and better mechanical properties [7,8]. This type of void is different from the Kirkendall void in that they appear along the Cu$_3$Sn/Cu interface only after the necessary segregation of Bi to that interface [3,9]. However, since the Bi segregation was analyzed by a scanning Auger microprobe (SAM), the structural and morphological relationships between Bi and interfacial voids remain uncertain.

In this work, a transmission electron microscopy (TEM) study was carried out to characterize the microstructures of reflowed and aged eutectic SnBi/Cu and pure Sn/Cu solder joints. After segregation, Bi was found as fine particles along the Cu$_3$Sn/Cu interface. Near the Bi particles, interfacial voids were observed. The mechanism for interfacial void formation is discussed by examining the relationship between Bi segregation and void formation in eutectic SnBi/Cu solder joints.

The substrate used in this study was oxygen-free high conductivity (OFHC) Cu sheet 10 mm × 7 mm × 2 mm. After surface cleaning and polishing, two copper sheets covered with a commercial eutectic SnBi solder paste were placed face to face, and several fine brass wires (diameter less than 20 μm) were sandwiched between these plates to control the thickness of solder. The samples were heated on a heating plate (about 443 K) until the solder paste was completely melted for about 3 s. Then they were cooled in air as reflowed samples. Aging of samples was conducted in silicone oil bath at 393 K for different periods. For comparison, pure Sn/Cu solder joints were reflowed and aged in the same way.

To prepare TEM foils, a cross-sectional specimen 300 μm thick was cut from the solder joint by spark...
erosion. It was then mechanically ground to a final thickness of 40 μm, and ion-milled (Gatan model 691 PIPS) at 5.0 keV and 5 μA with a low milling angle (<6°). An FEI Tecnai F30 electron microscope equipped with energy dispersive X-ray spectroscopy (EDS) was used for conventional TEM observations as well as high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) analysis.

In reflowed eutectic SnBi/Cu sample two distinct IMC layers have already been identified: a thick Cu₆Sn₅ layer at the solder side, and a thin Cu₃Sn layer at the Cu side, as shown in Figure 1a. The average grain size of Cu₃Sn was about 100 nm. The thickness of Cu₃Sn layer was not uniform along the Cu substrate, and the interface between Cu₃Sn and Cu₆Sn₅ was rough. Inside the Cu₆Sn₅ layer, there were channels (grain boundaries) for atomic diffusion, which terminated at the Cu₃Sn/Cu₆Sn₅ interface as indicated by the arrows. Figure 1b shows a high-resolution electron microscopy (HREM) image of the interface between Cu and Cu₃Sn viewed along the Cu₃Sn [100] orientation. The interface is relatively smooth, but there is no orientation relationship between Cu and Cu₃Sn in this direction.

After the eutectic SnBi/Cu sample had been aged for 24 h at 393 K, the average thickness of Cu₃Sn layer at the interface increased from 100 nm to more than 200 nm (see Fig. 2a). As the Cu₃Sn layer thickened, voids appeared at the interface between Cu₃Sn and Cu as indicated by arrows in Figure 2a. The thicker the Cu₃Sn layer, the greater the number of the voids at the interface. After 48 h of aging at 393 K, the interface in the eutectic SnBi/Cu solder joint became highly porous, as shown in Figure 2b. There were no voids at the Cu₆Sn₅/Cu₃Sn interface, even after prolonged aging.

For the reflowed pure Sn/Cu solder joint, there was only one layer of Cu₆Sn₅. The Cu₃Sn phase was still absent even for the sample aged for 24 h at 393 K in Figure 2c, where the large grains of Cu₆Sn₅ were in direct contact with Cu. After 48 h of aging (see Fig. 2d), the Cu₃Sn layer grew quickly, at a higher growth rate than that in eutectic SnBi/Cu joint. For all the Sn/Cu samples, no voids were found at any interfaces among Cu₆Sn₅, Cu₃Sn, and Cu as shown in Figure 2c and d. Therefore, Cu₃Sn formed earlier in SnBi/Cu solder, and voids presented at its Cu₃Sn/Cu interface during thermal aging.

The different growth behavior of Cu₃Sn in these two samples can be understood from the difference in Sn diffusion. It is well known that in interfacial reactions, high fluxes of diffusing species control the formation of phases, and can even suppress the other phases or consume previously formed phases [10]. In the Sn-containing/Cu couple, the scallop-type Cu₆Sn₅ is the first phase to form during the reflowing process. As Sn is in equilibrium with Cu₆Sn₅ in the phase diagram, sufficient Sn can diffuse through the scallop-type Cu₆Sn₅ to react with Cu to keep up with the growth of Cu₆Sn₅ [11]. Thus the formation of Cu₃Sn in pure Sn/Cu solder joint is delayed. On the other hand, in eutectic SnBi alloy the concentration of Bi is 58 wt.%. As Bi does not form any IMC with Cu, such non-reactive alloying elements in Sn-based eutectic solder would influence the concentration of Sn and the growth rate of IMC by changing the interfacial equilibrium constant [12]. The addition of Bi up to 58 wt.% would decrease the concentration of Sn from 0.0613 to 0.0310 mol cm⁻³. Moreover, the Bi-rich phase may also aggregate at the Cu₆Sn₅/solder interface as a diffusion barrier due to the consumption of Sn during reflow [13]. Thus there would be not enough Sn from the solder side to supply to the Cu₆Sn₅/Cu interface, thus creating a favorable condition for Cu₃Sn to nucleate and grow early in eutectic SnBi/Cu joints.

Bi in Sn solder alloy not only promotes the reaction of Cu₆Sn₅ + Sn → Cu₃Sn at the initial stage, but also induces interfacial voids at the Cu₃Sn/Cu interface during thermal aging as shown in Figure 2a and b. It was found that the voiding process was directly related to Bi segregation in Cu₃Sn. Figure 3a is a HAADF image of the SnBi/Cu sample aged for 24 h, showing two IMC layers.
on Cu. The area marked by a red square, which covers both Cu3Sn/Cu and Cu6Sn5/Cu3Sn interfaces, was analyzed by elemental mapping in STEM. The maps of elemental Cu, Sn and Bi are shown in Figure 3b–d, respectively. Bi particles were clearly detected as indicated by arrowheads in Figure 3d. Some of Bi particles were located at the exact Cu3Sn/Cu interface, and others embedded within the Cu3Sn phase near the interface. As the Bi particles were as small as <50 nm at this stage, they were difficult to observe by conventional TEM. When the sample was further aged, at 393 K for 240 h, small Bi particles agglomerated to form large particles of up to 200 nm, as shown in the HAADF image in Figure 4a. Bi particles (indicated by white arrowheads) show up as bright contrast at the interface, while voids (indicated by black arrowheads) are dark. The corresponding EDS spectrum of these particles is shown in Figure 4b, in which Cu peaks came from the substrate. For the Sn/Cu solder joint, which is Bi-free, the interface was completely smooth without particle segregation or void formation even after 240 h aging at 393 K. In the SnBi/Cu solder joint, it was observed that Bi segregation only took place at the Cu3Sn/Cu interface. The interface between Cu3Sn and Cu6Sn5 is free of Bi particles. Based on the fact that voids only existed at the Cu3Sn/Cu but not the Cu3Sn/Cu6Sn5 interfaces, it is evident that the interfacial voids were induced by Bi segregation.

It was previously assumed that Bi would segregate as a monolayer at the Cu3Sn/Cu interface [3], as has been observed at Cu grain boundaries [14,15]. According to the TEM investigations in this study, Bi segregation was found not to be homogeneous. Extra Bi precipitated as particles at the interface. This particle morphology of Bi has also been observed in the voids at the grain boundary of slowly cooled Cu–Bi alloy [16]. As shown in Figures 3 and 4, Bi appeared not only along the interface but also inside Cu3Sn near the interface. The Bi particles formed first, followed by void formation. It is interesting to see that at the Cu3Sn/Cu interface, Bi particles always locate on the solder side, while voids are generally on the Cu side (see Fig. 4a). It implies that once Bi particles precipitated, they acted as a barrier to Cu diffusion. During solid-state reaction, Cu atoms have to diffuse around Bi particles, creating Cu vacancies in between Bi particles and Cu. These vacancies then condense to form voids on the Cu side. Between the Bi particles, the Cu flux becomes highly concentrated. When the Cu supply to the interface cannot keep up with the high Cu flux, additional vacancies are generated. Further condensation of the vacancies leads to void formation at the interface. In the early stage of Bi segregation, Bi atoms can fill up the vacancy sinks at interfacial dislocations, leaving excess vacancies at the interface. Bi atoms and particles can also pin down interfacial dislocations and thus limit the Cu supply to the interfacial reaction. As suggested by Liu and Shang [9], the combination of inadequate Cu supply and excess vacancies then leads to void formation.

In conclusion, the microstructure of eutectic SnBi/Cu solder joints during reflow and thermal aging was compared to that of pure Sn/Cu solder joints by TEM investigations. The Cu3Sn phase nucleated early in SnBi/Cu solder joints, but grew slowly in the following solid-state aging process. Segregation of Bi occurred at the Cu3Sn/Cu interface in eutectic SnBi/Cu solder joints during aging. Bi precipitated as particles whose size increased with prolonged aging. Following Bi segregation, interfacial voids were induced around Bi particles, and these voids generally located on the Cu side.

Figure 3. Elemental mapping of the interface showing the segregation of Bi in eutectic SnBi/Cu solder joint aged for 24 h at 393 K: (a) HAADF image; (b) Cu mapping; (c) Sn mapping; (d) Bi mapping.

Figure 4. (a) Low-magnification HAADF cross-sectional image and (b) corresponding EDX result of Bi particle showing interfacial voids and Bi particles after the sample was aged for 240 h at 393 K.
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