

Microstructural Study on Kirkendall Void Formation in Sn-Containing/Cu Solder Joints During Solid-State Aging

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Abstract: Kirkendall void formation at the solder/metallization interface is an important reliability concern for Cu conductors and under-bump metallization in microelectronic packaging industry, whose mechanism is still hard to be understood for different individual cases. In the present work, two typical solder/Cu-diffusing couples, eutectic SnIn/Cu and SnBi/Cu, were studied by scanning/transmission electron microscopy to investigate the microstructural evolution and voiding process after soldering and then solid-state aging. It was concluded that Kirkendall voids formed between two sublayers within $\text{Cu}_2(\text{In},\text{Sn})$ phase in eutectic SnIn/Cu solder joint, whereas they appeared at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface or within Cu_3Sn for eutectic SnBi/Cu solder joint. Besides the effect of impurity elements, the morphological difference within one intermetallic compound layer could change the diffusing rates of reactive species, hence resulting in void formation in the reaction zone.

Key words: lead-free solder, Kirkendall void, intermetallic compound (IMC), diffusion, interface, transmission electron microscopy (TEM)

INTRODUCTION

The Kirkendall voids have been widely observed between Sn-containing solders and Cu substrate during solid-state aging process, such as in SnPb/Cu, SnBi/Cu, SnAg/Cu, and SnAgCu/Cu solder joints (Zeng et al., 2005; Peng et al., 2007; Kim & Yu, 2008a; Shang et al., 2008). At present, the mechanism of void formation is widely considered to be due to the Kirkendall effect, which means that the Cu diffusion is faster than the Sn diffusion during solid-state aging, resulting in a net vacancy flux of Cu at the interface of intermetallic compound (IMC) or inside the Cu_3Sn (Laurila et al., 2005). However, it is still hard to understand the mechanism of void formation for different cases. van Dal et al. (2001) and Paul (2004) have predicted that the Kirkendall planes in a given solid-state diffusion couple need not be unique, which can be multiple, stable, or unstable. Following the theoretical predication, Laurila et al. (2005) reflowed the pure Sn or pure SnAgCu solder on oxygen-free high conductive (OFHC) Cu and then annealed the samples at 398 K up to 1,000 h and did not observe any voids using field-emission scanning electron microscope (SEM). Therefore, the void formation in Sn-containing solders and Cu interface was ascribed to the quality of Cu. Kim & Yu (2008b) recently designed systematic experiments to check the effects of impurity in Cu on the void formation during solid-state aging of Sn–3.5Ag solder and four types of Cu metallizations. The interesting results revealed that (1) no void was found in the joint made of pure Cu foil; (2) voids distributed uniformly in the matrix of Cu_3Sn phase in the joint made of electroplated Cu film without SPS (bis-

sodium sulfopropylidysulfide, $\text{C}_6\text{H}_{12}\text{O}_6\text{S}_4\text{Na}_2$); (3) in the joint made of electroplated Cu with SPS, voids nucleated and grew at the Cu/ Cu_3Sn interface because of the S segregation at the Cu/ Cu_3Sn interface, which reduced the free-energy barrier for void nucleation and accelerated void formation at the interface. These results are explicit evidences to confirm the influence of the compositions of the end members of the diffusion couple. Besides the residual impurities introduced from the substrate, some ingredients of the solder itself, such as Bi in eutectic SnBi solder, can also segregate to the Cu/ Cu_3Sn interface and accelerate the void formation (Shang et al., 2008).

Most recently, we observed void formation between two different morphological IMCs at the eutectic SnIn/Cu solder joint (Shang et al., 2011). It is quite different from the circumstances that occurred at the Cu/ Cu_3Sn interfaces in SnBi/Cu, SnPb/Cu, or SnAgCu/Cu diffusion couples. The motivation of this paper is to elaborate the mechanism of void formation at the SnIn/Cu interface, compared with that induced by impurities from the under-bump metallizations or from solder itself, using transmission electron microscopy (TEM).

MATERIALS AND METHODS

The solder alloys used in this study were prepared by melting high-purity In, Bi, and Sn into different ingots, and cold rolled into 1-mm-thick foils, and then cut into pieces of size $10 \times 2.5 \text{ mm}^2$. The OFHC polycrystalline Cu was selected as the substrate and then cut by electro-discharge machine into blocks of size $10 \times 2.5 \times 2 \text{ mm}^3$. Copper surfaces were grinded and carefully polished using $0.5 \mu\text{m}$ diamond paste, and then rinsed in acetone, methanol alco-

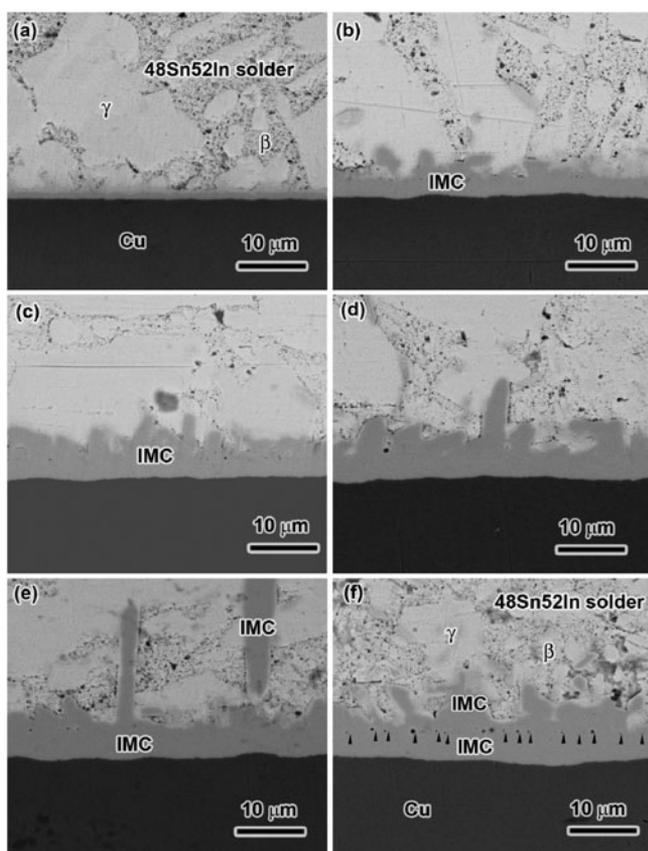


Figure 1. Cross-sectional SEM images of eutectic SnIn/Cu solder joint after (a) reflowing at 433 K for 5 s, and then solid-state aging at 373 K for (b) 1 day, (c) 2 days, (d) 4 days, (e) 5 days, and (f) 6 days. SEM, scanning electron microscope; IMC, intermetallic compound.

hol, and distilled water in an ultrasonic bath. Two copper sheets were soldered together with the eutectic SnIn or SnBi alloys to form a copper–solder sandwich, in which several brass wires with a diameter of 50 μm were placed in-between two copper sheets to control the gap thickness. Solder reflowing of SnIn joints was performed at the temperature of 433 K for 5 s, and then solid-state aged at 373 K for different days. For comparison, eutectic SnBi/Cu solder joints were reflowed at 443 K for 5 s and aged at 393 K up to 2 days.

The cross-sectional interface samples for microstructural analysis were prepared with the standard method. SEM observations were carried out on an FEI Quanta 600 SEM equipped with an Oxford Link ISIS energy-dispersive X-ray spectroscopy (EDS) system. An FEI Tecnai F30 electron microscope was used to carry out TEM/scanning transmission electron microscopy (STEM) observations at an accelerating voltage of 300 kV.

RESULTS

The typical interfacial images of the eutectic SnIn/Cu solder joint after reflowing and solid-state aging were shown in Figure 1. After reflowing at 433 K for 5 s, a thin uniform

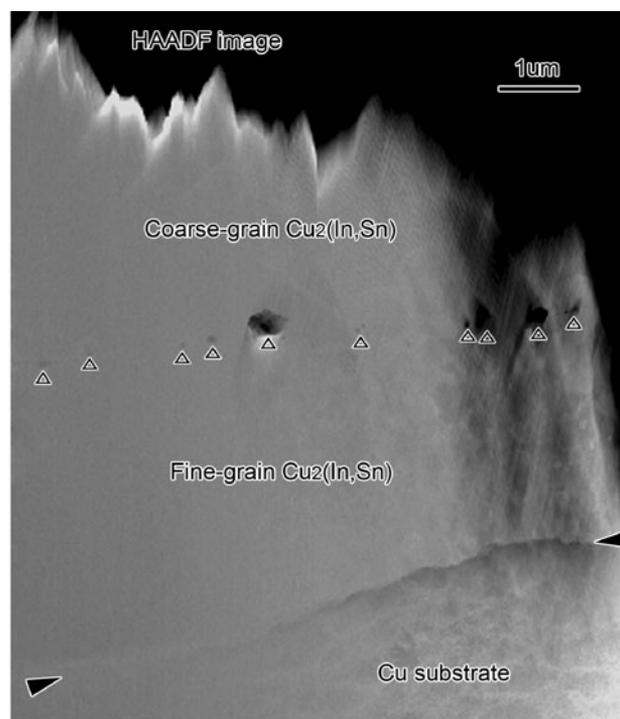


Figure 2. Low-magnification HAADF-STEM image showing the interfacial microstructure of eutectic SnIn/Cu after solid-state aging for 7 days at 373 K. The IMC/Cu interface was marked by black arrowheads, whereas white arrow heads indicate the voids within the IMC layer. HAADF, high-angle annular dark-field; STEM, scanning transmission electron microscopy; IMC, intermetallic compound.

IMC with a thickness of 1–2 μm was formed at the interface of eutectic SnIn/Cu as shown in Figure 1a. In the following solid-state aging process, the thickness of IMC increased quickly at the initial stage. It grew to more than 4 μm after only 1 day of aging in Figure 1b, and extended into the solder side gradually with a rod-like morphology after 2 days (see Figs. 1c–1e). However, in the late stage, the increase of IMC thickness was not distinct owing to the depletion of IMC from the interface into the solder. Six days later, some voids appeared inside the IMC layer, as indicated by arrowheads in Figure 1f, but no void was observed at the IMC/Cu interface. Although the size of voids is not uniform, they locate at the same plane. This was further verified by our high-angle annular dark-field-STEM (HAADF-STEM) observations. Figure 2 shows the typical low-magnification HAADF-STEM image of the sample that was solid-state aged for 7 days, and the voids ranging from tens to hundreds of nanometers (indicated by white arrowheads) were found within the IMC layer. However, the interface between IMC and Cu marked with black arrowheads in Figure 2 is completely void free, which is in complete accordance with SEM observations. It has been revealed that there was only one kind of IMC, $\text{Cu}_2(\text{In},\text{Sn})$, at the interface of eutectic SnIn/Cu solder joint after reflowing, which has two kinds of grain morphologies: a fine-grain sublayer at the Cu side and a coarse-grain sublayer at

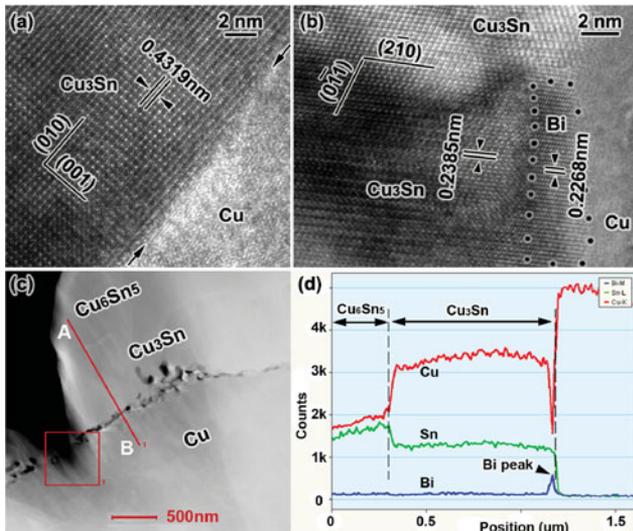


Figure 3. TEM images of $\text{Cu}_3\text{Sn}/\text{Cu}$ interface in eutectic SnBi/Cu solder joint after (a) reflowing at 443 K for 5 s, and (b) solid-state aging at 393 K for 1 day, as well as (c) interfacial HAADF image after solid-state aging at 393 K for 2 days, and (d) the corresponding EDS line scan inside the IMC layer. TEM, transmission electron microscopy; HAADF, high-angle annular dark-field; EDS, energy-dispersive X-ray spectroscopy; IMC, intermetallic compound.

the solder side (Shang et al., 2011). Our TEM observations confirmed that the voids formed exactly at the interface between coarse-grain and fine-grain $\text{Cu}_2(\text{In},\text{Sn})$ sublayers (see Fig. 2).

The interfacial microstructural change of the eutectic SnBi/Cu solder joint was also investigated. The $\text{Cu}/\text{Cu}_3\text{Sn}$ interface viewed along the Cu_3Sn [100] zone axis is shown in Figure 3a, where the interface (indicated by arrows) is relatively smooth and no void or atomic segregation took place after a short time of reflowing. After 1 day of aging at 393 K, voids began to appear at the $\text{Cu}/\text{Cu}_3\text{Sn}$ interface, and Bi segregation was also observed. Figure 3b shows a high-resolution TEM (HRTEM) image of a segregated Bi particle (about 5 nm) at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface. The crystallographic analyses on the HRTEM image revealed that there is a special crystallographic relationship between Cu_3Sn and Bi particle with a small lattice misfit of about 5%: $(2\bar{1}0)_{\text{Cu}_3\text{Sn}}//(\bar{1}\bar{1}0)_{\text{Bi}}$ and $[122]_{\text{Cu}_3\text{Sn}}//[771]_{\text{Bi}}$, in which Cu_3Sn has a basic orthorhombic lattice with dimensions of $a = 0.5514$ nm, $b = 0.4765$ nm, and $c = 0.4329$ nm, whereas Bi has a rhombohedral lattice with dimensions of $a = b = 0.4547$ nm and $c = 1.186$ nm. This gives explicit evidence that Bi precipitates from the Cu_3Sn phase to form segregated particles at the interface. Moreover, it is clear that the Bi segregation takes place before the void formation, because the boundary of the initial Bi particle is void free in Figure 3b. After 2 days of solid-state aging at 393 K, the interface in eutectic SnBi/Cu solder joint became highly porous, as shown in Figure 3c. The voids formed not only at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface but also within the Cu_3Sn phase, whereas at the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ interface there was no void even after a long duration of aging. The extensive TEM

observations revealed that two different morphological Cu_3Sn layers were formed between Cu_6Sn_5 and Cu during solid-state aging, a columnar grain layer at the Cu_6Sn_5 side and an equiaxed grain layer at the Cu side (Shang et al., 2009a, 2009b). Basing on Paul's prediction using the physicochemical approach, a Kirkendall plane in a diffusion zone should always be accompanied by a sharp change in morphology within a phase layer (Paul et al., 2004). Therefore, it is predicted that the Kirkendall plane within the Cu_3Sn layer in eutectic SnBi/Cu corresponds to the interface between the columnar grain sublayer and equiaxed grain sublayer, which could explain the void formation within the Cu_3Sn layer very well. On the other hand, the EDS line scan across the IMC/Cu interface revealed that a strong Bi peak appeared at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface on the Cu_3Sn side, as shown in Figure 3d. Thus, the segregated Bi particles at the $\text{Cu}/\text{Cu}_3\text{Sn}$ interface can act as a barrier for Cu diffusion and result in the void formation at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface.

DISCUSSION

On comparing the microstructural changes in both eutectic SnIn/Cu and SnBi/Cu solder joints, although the locations of void formation are different, one common feature of both diffusion couple system is that the void formation is always accompanied by a sharp morphological change within the same IMC layer. It could be a common phenomenon that occurs in many solder/UBM joints, such as $\text{Sn}-3.5\text{Ag}/\text{Ni}-\text{P}$ solder joint and so on (He et al., 2004). To understand its origin of void formation, atomic diffusion of reactive species across the interface of morphological change within an IMC layer should be considered, together with the growth of IMC itself. Driven by the concentration gradient in the solder joint, Cu and Sn atoms should diffuse toward solder and substrate sides, respectively, during solid-state aging process. However, the diffusing rates of reactive atoms in coarse-grain and fine-grain $\text{Cu}_2(\text{In},\text{Sn})$ sublayer should be different considering the contribution of grain boundaries. It is well known that the effective interdiffusion coefficient, D_{eff} , may be expressed as follows (Bader et al., 1995):

$$D_{\text{eff}} = D + a(2\delta/d)D_b$$

where d is the average grain size, δ is the thickness of the grain boundary, a is a shape constant (≈ 1), D is the volume diffusion coefficient, and D_b is the grain boundary diffusion coefficient. As the fine-grain sublayer has a smaller grain size (d) and more grain boundaries (δ), the atomic diffusing rate in fine-grain $\text{Cu}_2(\text{In},\text{Sn})$ sublayer should be faster than that in the coarse-grain $\text{Cu}_2(\text{In},\text{Sn})$ layer. Considering the diffusion of Sn (or In) atoms, when they go through the coarse-grain sublayer and arrive at the interface between coarse-grain and fine-grain sublayers, they will diffuse away faster through fine-grain sublayer to the Cu substrate side to form new $\text{Cu}_2(\text{In},\text{Sn})$ grains. Therefore, vacancies will be left at the interior interface of $\text{Cu}_2(\text{In},\text{Sn})$. Although these vacancies could be consumed by Cu atoms diffused from substrate, it is believed that the consumption is not

enough, because Cu can diffuse through the IMC layer easily, and more Cu atoms are needed at the solder side to form coarse $\text{Cu}_2(\text{In},\text{Sn})$ grain [the atomic ratio of Cu:Sn(or In) in the compound is 2:1]. As a result, more vacancies were left at the interior interface between $\text{Cu}_2(\text{In},\text{Sn})$ sublayers accompanying the growth of IMC. These vacancies will increase and coalesce during solid-state aging to form voids finally, which is also due to Kirkendall effect considering the different diffusion rates of Sn (or In) atoms in different $\text{Cu}_2(\text{In},\text{Sn})$ sublayers. This proposed mechanism of void formation is different from the impurity-induced void.

CONCLUSIONS

A compared experimental study of void formation in the eutectic SnIn/Cu and SnBi/Cu solder joints was conducted by SEM and TEM/STEM observations. At the eutectic SnIn/Cu interface, $\text{Cu}_2(\text{In},\text{Sn})$ was formed with two different morphologies during reflowing and solid-state aging. Kirkendall voids appeared exactly at the interface between coarse-grain and fine-grain sublayers. For the eutectic SnBi/Cu interface, voids were situated both inside the Cu_3Sn phase (between columnar and equiaxed grain sublayers) and at the exact $\text{Cu}_3\text{Sn}/\text{Cu}$ interface. It was found that if we excluded the impurity-induced voids at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface, the void formation was always accompanied by an obvious morphological change, which results in the different diffusing rate of reactive species in different sublayers, and hence leads to the formation of voids at the interface between different morphological sublayers within the same IMC phase layer.

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