Intermetallic compound identification and Kirkendall void formation in eutectic SnIn/Cu solder joint during solid-state aging

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(Received 4 January 2011; final version received 21 March 2011)

Microstructural investigations were performed on the interfacial reactions between eutectic SnIn solder and Cu substrate during reflowing at 433 K and solid-state aging at 373 K. Cu2(In,Sn) was identified as the only intermetallic compound (IMC) at the interface, which consists of two sublayers with different morphology, a fine-grained sublayer at the Cu side and a coarse-grained sublayer at the solder side. During solid-state aging, voids were found between these two Cu2(In,Sn) sublayers but not at the substrate interface, which is also attributed to the Kirkendall effect considering the different diffusion fluxes of Sn or In and Cu atoms in different sublayers.

Keywords: diffusion; intermetallic compounds; SnIn solder; interfaces; Kirkendall void

1. Introduction

The usage of lead-free solder in microelectronic industry introduced two main reliability problems in the last decade. The first one is that most currently commercial lead-free solders, such as SnAg and SnAgCu, have higher melting temperatures ($T_m$ of SnAg and SnAgCu are 217 and 221°C, respectively) than that of the conventional eutectic SnPb solder (183°C) [1]. Therefore, the reflow temperature during electronic assembly must be raised, which will reduce the integrity, reliability and functionality of printed circuit board and components. The second problem is the quick reaction of lead-free solder with Cu substrate, resulting in a fast nucleation and growth of the intermetallic compound (IMC), especially when the component was used in a high temperature environment. Not only is the nature of IMC brittle, but also are defects, such as Kirkendall voids, easy to be formed in the IMC layer [2]. Thus the microstructural investigations on the interfacial reaction and IMC growth are necessary to understand reliability problems in solder joints.

The Kirkendall voids have been widely observed between Tin-containing solder and Cu substrate during solid-state aging, including SnPb/Cu, SnBi/Cu, SnAg/Cu

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and SnAgCu/Cu solder joints [2–5]. In the reflow process of the tin-containing solder/Cu system, Cu6Sn5 forms first at the interface, and then Cu3Sn will develop between Cu and Cu6Sn5 by solid-state reaction. The Kirkendall voids were formed at the Cu6Sn5/Cu interface with the growth of Cu3Sn phase, which will greatly degrade the solder joint reliability. It has been suggested that Kirkendall voids originated from the faster diffusion of Cu atoms than Sn atoms in Cu3Sn layer [2,6,7]. The measured diffusion rate of Cu is about 1.4 times at 493 K and three times faster at 398 K than that of Sn atoms in Cu3Sn phase [8,9]. However, all of the experimental results did not supported this standpoint. Laurila et al. [7] found that no void was formed using high-purity oxygen-free high-conductivity (OFHC) Cu and pure Sn or pure SnAgCu even if the sample was annealed at 398 K up to 1000 h. Therefore, they suggested that the impurities in different “quality” Cu substrate are the origin of interfacial voiding. Recently, Yu and Kim [9] found that S segregation at the Cu3Sn/Cu interface could reduce the free energy barrier for void nucleation and accelerate the void formation at the interface, which supports the standpoint of Laurila et al. [7]. Besides the residual impurities introduced from the substrate, some ingredients from solder itself, such as Bi in eutectic SnBi solder, can also segregate to the Cu/Cu3Sn interface and accelerate the formation of voids [3]. For all these reported Kirkendall voids in SnPb/Cu, SnBi/Cu, SnAg/Cu and SnAgCu/Cu solder joints, voids are always present at the interface between IMC (generally Cu3Sn) and Cu substrate. The Kirkendall effect in SnIn/Cu solder joint has not been investigated yet.

In this study, the interfacial microstructural evolutions of eutectic SnIn/Cu solder joint during reflowing and solid-state aging were investigated by transmission electron microscopy (TEM). The resulted IMC was identified as Cu2(In,Sn). It was first observed that Kirkendall voids did not form at the IMC/Cu interface, but generated in-between two Cu2(In,Sn) sublayers. The corresponding mechanism was discussed considering the different diffusion rate of reactive species in the joint.

2. Experimental procedure

The eutectic Sn48In52 solder used in this study was prepared by melting high-purity In and Sn into an ingot, cold rolled into a 1 mm thick foil and then cut into pieces in size of 10 × 2.5 mm². The oxygen-free high-conductivity (OFHC) polycrystalline Cu were cut by electro-discharge machining to the size of 10 × 2.5 × 2 mm³. Copper surfaces were grinded and carefully polished with 0.5 μm diamond paste, and then rinsed in acetone, methanol alcohol and distilled water in an ultrasonic bath. Two copper sheets were soldered together with the eutectic Sn48In52 alloy to form a copper-solder-copper sandwich. Before soldering, several brass wires with a diameter of 50 μm were placed between two copper sheets to control the solder thickness. Solder reflowing was performed at the temperature of 433 K for 5 s, and then solid-state was aged at 373 K for different days.

For microstructural analysis the soldered samples were cut cross-sectionally, then grinded and polished carefully by BUEHLER polishing suspension with 0.05 μm Al2O3 powder. Scanning electron microscopy (SEM) observations were carried out on an FEI Quanta 600 SEM equipped with an Oxford Link ISIS energy dispersive
X-ray spectroscopy (EDS) system. To prepare TEM foils, the cross-sectional slices were mechanically grinded to a final thickness of 40μm, and ion-milled (Gatan model 691 PIPS) under 5.0keV and 5μA at a low milling angle (less than 6°). A JEM-2100 electron microscope was used to carry out TEM observations.

3. Results and discussion

Figure 1a shows SEM cross-sectional morphology of the eutectic SnIn/Cu solder joint reflowed at 433 K for 5 s. The microstructure of Sn48In52 solder is composed of Sn-rich γ phase and In-rich β phase according to elemental analysis. TEM observations confirmed that the γ phase is InSn₄, while the β phase is In₃Sn.

![Figure 1. (a) SEM cross-sectional image showing the microstructure of eutectic Sn48In52/Cu solder joint after reflowing at 433 K for 5 s. (b) EDS result on the corresponding interfacial IMC layer.](image)
The reflow temperature was higher than the melting point of Sn48In52 solder (393 K), IMC layer in thickness of 2–3 μm was formed on Cu substrate. EDS analyses on different regions of the IMC layer revealed that it contains Cu, In and Sn elements with little compositional fluctuation which was less than 5 at.% for Cu, In and Sn elements. A typical EDS spectrum of IMC layer is shown in Figure 1b, which indicates that the atomic ratio of Cu:In:Sn is about 4:1:1. In order to characterize the IMC layer precisely, TEM observations were carried out. Figure 2 shows a cross-sectional bright-field image of the solder joint, in which the interface between IMC and Cu substrate was marked with black arrow heads. The grain contrast in IMC layer can be seen clearly. It was found that there are two kinds of grain morphologies, which divide the IMC layer into two sublayers: a fine-grained sublayer at the Cu side with average grain size of about 80 nm, and a coarse-grained sublayer at the solder side with the average grain size of about 400 nm. The interface between these two sublayers was marked by white arrow heads in Figure 2. Selected area electron diffraction (SAED) was used to identify the compounds in IMC layer. The SAED pattern of grain A in coarse-grained sublayer was inserted in the top-left corner of Figure 2, while that of grain B in fine-grained sublayer was inserted in the bottom-right corner. Among different Cu–In–Sn compounds, only the hexagonal Cu2In lattice \[a = b = 0.4292 \text{ nm}, c = 0.5232 \text{ nm}, \alpha = \beta = 90^\circ, \gamma = 120^\circ\] could be adopted to index these patterns, which are along [01T1] and [1453] zone axis, respectively. For identifying the phase crystal structure, the SAEDPs along the different zone axes of the sample were also taken when the sample was rotated in TEM, and the rotation angles measured in the experiment were accordant.

Figure 2. TEM bright field image of the IMC/Cu interface after reflow. The Cu2(In,Sn) IMC layer consists of a coarse- and a fine-grained sublayers. The top and bottom insets are corresponding SAED patterns from grain A and B, respectively.
with the theoretical values if the SAEDPs were indexed by the above hexagonal 
Cu$_2$In lattice parameters. Further investigations confirmed that although two 
sublayers present different grain morphologies, all the grains have Cu$_2$In crystal 
structure. That is to say, there is only one kind of IMC at the interface, which is 
accordant with the SEM observations. However, as this compound contains not only 
Cu and In but also Sn elements (Figure 1b), it is believed that Sn atoms dissolved in 
the Cu$_2$In lattice and took up the substitutional sites of In atoms, because Sn atom 
has a similar atomic radius with In atom. Hence, the IMC formed between eutectic 
SnIn solder and Cu during reflow at 433 K was finally identified as Cu$_2$(In,Sn).

For the phase identification of interfacial IMC between SnIn solder and Cu 
during soldering, the results are not entirely in agreement with each other in the 
literatures. Romig et al. [11] dipped Cu-based metal into the molten solder twice, and 
then aged in air at the temperature range of 333–383 K, and found two kinds of 
IMC – Cu$_2$(In,Sn) and Cu$_2$In$_3$Sn at the interface. Sommadossi et al. [12] drew a 
similar conclusion when the samples were experienced a diffusion soldering process 
in the range of 453–673 K. A recent work by Chuang et al. [13] reported that $\epsilon$-
Cu$_3$(In,Sn) and $\eta$-Cu$_6$(In,Sn)$_5$ were the possible interfacial compounds after 
soldering the In-49Sn/Cu system at 333–383 K. It must be noticed that all the 
above results were obtained through electron probe microanalyzer (EPMA) or 
Energy Dispersive X-Ray Spectrometer (EDS) methods. The detailed proof for the 
phase identification, especially the crystallographic structure of the IMC, was absent 
in earlier reports. In this study, Sn$_{48}$In$_{52}$ solder reacted with Cu at a reflowing 
temperature of 433 K for 5 s. According to the elemental analyses and crystal 
structure investigations, the resulted IMC was identified as only Cu$_2$(In,Sn) phase, 
which has a coarse-grained morphology at solder side and a fine-grained morphol-
ogy at Cu side. No other compounds like Cu$_2$In$_3$Sn, Cu$_3$(In,Sn)$_3$ or Cu$_6$(In,Sn)$_5$ were 
observed in IMC layer.

During the subsequent solid state aging at 373 K, the Cu$_2$(In,Sn) IMC layer grew 
thicker and thicker. It was found that many voids appeared in the IMC layer after 
seven days’ aging, which are indicated with small arrows in Figure 3a. TEM 
investigations revealed that the coarse-grained sublayer grew into eutectic SnIn 
solder and the fine-grained sublayer grew into Cu substrate. Voids were observed 
only at the interface between coarse- and fine-grained Cu$_2$(In,Sn) sublayers as 
shown in Figure 3b (indicated with small arrows), but the Cu$_2$(In,Sn)/Cu interface is 
completely void free (Figure 3c). However, in the compared experiments on eutectic 
SnBi/Cu solder joint, a large number of voids were formed at the Cu$_3$Sn/Cu interface 
after the sample was solid-state aged for two days [3,14]. Obviously, the location of 
the voids in SnIn/Cu solder joint is different from conventional ones which appeared 
at the Cu$_3$Sn/Cu interface in tin-containing/Cu solder joints [2–4,14]. The void 
formation within Cu$_2$(In,Sn) IMC layer in the solder joint has not been reported 
before.

In order to understand the origin of void formation between Cu$_2$(In,Sn) 
sublayers, atomic diffusion of reactive species and the growth of IMC should be 
considered. Figure 4 shows the schematic diagram of the interdiffusion process in the 
SnIn/Cu couple during solid-state aging. $J_{\text{In,Sn}}^1$ and $J_{\text{In,Sn}}^2$ represent the diffusing flux of 
(In, Sn) atoms in the coarse- and the fine-grained Cu$_2$(In,Sn) layers, respectively. 
$J_{\text{Cu}}^1$ and $J_{\text{Cu}}^2$ represent the diffusing flux of Cu atoms in the coarse- and the fine-
Figure 3. (a) SEM image of the interfacial microstructure after solid-state aging at 373 K for seven days. Small arrows indicate voids within IMC layer. (b) Corresponding TEM image showing Kirkendall voids at the interface between coarse- and fine-grained Cu₂(In,Sn) sublayers. (c) The image of Cu₂(In,Sn)/Cu interface which is free of voids.

Figure 4. The schematic diagram of the interdiffusion process in the SnIn/Cu couple during solid-state aging.
grained Cu$_2$(In,Sn) layers, respectively. It has been proved that the boundary between the two different microstructural Cu$_2$(In,Sn) layers corresponded to the original solder/Cu interface [11,15]. This implied that the coarse-grained Cu$_2$(In,Sn) layer grew thick by the Cu atoms through the IMC layer to react with the solder, while the fine-grained Cu$_2$(In,Sn) phase was formed by solid-state diffusion of Sn and In atoms through the coarse-grained Cu$_2$(In,Sn) phase to react with Cu substrate. In addition, the diffusing rate of Sn and In atoms in the coarse- and the fine-grained Cu$_2$(In,Sn) should be different, which can be understood by considering the grain boundary diffusion. The effective diffusion coefficient, $D_{\text{eff}}$, may be expressed by [16]

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

(1)

where $d$ is the average grain size, $\delta$ is the thickness of the grain boundary, $a$ is a shape constant ($a \approx 1$), $D$ is volume diffusion coefficient and $D_b$ is the grain boundary diffusion coefficient. Based on Equation (1), it was widely believed that the diffusing rate of Sn and In atoms in the fine-grained Cu$_2$(In,Sn) layer is faster than that in the coarse-grained Cu$_2$(In,Sn) layer ($J_{\text{In,Sn}}^f > J_{\text{In,Sn}}^c$). Therefore, there should be some Sn and In atom vacancies at the interface of the fine and coarse-grained Cu$_2$(In,Sn) layers during solid-state aging process. Generally, these vacancies could be consumed by two possible ways: first, the vacancies were consumed by the interfacial reaction between the fine- and coarse-grained Cu$_2$(In,Sn) layers or second, the Cu atoms from Cu substrate took up these vacancy sites. For the first type, it was proved that the boundary between the two different microstructural Cu$_2$(In,Sn) layers was immobile during solid-state aging. Therefore, the vacancies could only be consumed by the Cu atoms from Cu substrate. If there are no sufficient Cu atoms diffusing to the fine- and coarse-grained Cu$_2$(In,Sn) interface and taking up the Sn atom then vacancy sinks ($J_{\text{In,Sn}}^c - J_{\text{In,Sn}}^f > J_{\text{Cu}}^c - J_{\text{Cu}}^f$). It is reasonable to speculate that the consumption is not enough, because Cu can diffuse through IMC layer easily (the solder near IMC interface also contains some amount of Cu), and more Cu atoms are needed at solder side to form coarse-grained Cu$_2$(In,Sn) (the atomic ratio of Cu : Sn(or In) in the compound is 2 : 1). With the increase in solid-state aging, the vacancy density would increase and coalesce to form voids at the interface of the coarse- and fine-grained Cu$_2$(In,Sn) layers. This proposed mechanism of void formation in eutectic SnIn/Cu solder joint is different from that in eutectic SnBi/Cu solder joint [3,17–20], where Bi atoms segregated to the Cu$_3$Sn/Cu interface and acted as a barrier for Cu diffusion, hence accelerated the coalescence process of vacancy due to the different diffusing velocity of Cu and Sn in Cu$_3$Sn layer.

4. Conclusion

The interfacial microstructures of eutectic Sn$_{48}$In$_{52}$/Cu solder joint during reflow (433 K) and solid-state aging (373 K) were investigated by SEM and TEM. Both the liquid reaction during reflowing and solid reaction in aging resulted in the formation of Cu$_2$(In,Sn) compound with a hexagonal crystal structure. The Cu$_2$(In,Sn) IMC layer has two kinds of morphologies after reflow, a coarse-grained sublayer at the solder side and a fine-grained sublayer at the Cu side. During solid-state aging,
Kirkendall voids formed between these two interior sublayers in Cu$_2$(In,Sn), while the Cu$_2$(In,Sn)/Cu interface was completely void-free, which is different from the reported Kirkendall voids at the Cu$_3$Sn/Cu interface in other solder joints. The different diffusion fluxes of Sn or In and Cu atoms in fine- and coarse-grained Cu$_2$(In,Sn) sublayers were considered to be the origin of void formation in eutectic SnIn/Cu solder joint. It leaves vacancies at the interior interface of Cu$_2$(In,Sn), and the vacancies are increased and coalesced to voids during solid-state aging.

Acknowledgements
The authors gratefully acknowledge the financial support from the Hundred Talents Program of the Chinese Academy of Sciences, the National Basic Research Program of China (Grant No. 2010CB631006), and the Major National Science and Technology Program of China (Grant No. 2011ZX02602).

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