Phase identification on the intermetallic compound formed between eutectic SnIn solder and single crystalline Cu substrate

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ABSTRACT

The intermetallic compound (IMC) formed between eutectic SnIn solder and single crystalline Cu substrate during reflow and solid-state aging was investigated precisely utilizing electron microscope. Two kinds of crystal structures with different morphologies were identified, which are Cu(In,Sn)2 at the solder side and Cu2(In,Sn) at the Cu substrate side. The Cu(In,Sn)5 layer with chunk-type morphology suffered spalling easily during slightly increased liquid soldering at 160 °C and Cu2(In,Sn) was in the form of duplex structure with coarse-grain and fine-grain sublayers. During solid-state aging at 60 °C, the morphology of fine-grain Cu2(In,Sn) kept granule-type, while that of the coarse-grain Cu2(In,Sn) was substrate-dependent with elongated morphology.

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1. Introduction

Sn–Pb solders have been widely used as a joining material for many years in modern microelectronic industry with good-wetting and low-temperature properties. However, due to the adverse effects of toxic Pb element on human health and its serious pollution to environment, the elimination of Pb usage in electronic components and devices is an inevitable trend [1]. Therefore, Sn-based lead-free solders have been widely focused on for electronic packaging applications, such as Sn–Bi [2], Sn–Ag–Cu [3, 4] and Sn–Cu [5] alloys, in which Sn element acts as the main species and reacts with the substrates to form intermetallic compound (IMC) layers for joining. Besides the above-mentioned Sn-based lead-free solders, the binary eutectic Sn–In solder has the advantages of lower melting temperature, better wettability, better ductile properties and longer fatigue life [6], and exhibits particular and different characters such as the phase species of IMC owing to the participation of In element in the interfacial reactions between solder and substrates.

During soldering process, the phase species of formed interfacial IMC can affect the properties and service life of solder joints. Over the past decades, the phase identification on the interfacial reaction between eutectic SnIn solder and Cu has been studied during reflowing as well as long-term solid-state aging. For example, Kim and Jung [7] found two possible phases in this system: Cu(In,Sn)2 adjacent to the solder and Cu2(In,Sn)5 at the substrate side, which was the dominant phase formed in the process of solid-state aging at a temperature range of 70–100 °C for 0–60 days. Chuang et al. [8] reported that Cu2(In,Sn) and Cu2(In,Sn)5 were the possible phases at the interface after soldering in the In–49Sn/Cu system during subsequent aging at 60–110 °C. More recent work was performed by Sommadossi et al. [9], who found that below 200 °C only the Cu–16In–27Sn (at.%.) phase grew alone showing two different morphologies: large coarse-grains grew into the liquid In–48Sn due to the diffusion of Cu from the substrate and fine-grains grew into the solid Cu due to In and Sn diffusion through the Cu–16In–27Sn (at.%) phase. It can be clearly seen that the results of phase identification are not absolutely in agreement with each other. One reason comes from the complexity of binary phase diagrams between Sn/In and Cu, because both Sn and In can react with Cu to form IMC with close atomic percentage, such as Cu2In, Cu2Sn and Cu11In5. Another reason is that the experimental methods used in previous studies mainly focused on the elemental analyses with electron probe microanalyzer (EPMA) or energy dispersive spectrometer (EDS), which are not very accurate to identify different crystal structures especially with similar compositions. Thus it is necessary to distinguish the IMC formed in SnIn/Cu solder joints more precisely using other method like electron microscopy.

2. Experimental procedures

The solder used in this study was eutectic In–48Sn alloy, and the substrate was single crystalline Cu. The (100) and (111) Cu plates (40 × 4 × 2 mm3) were commercially purchased with polished and clean surfaces (the roughness is below 0.5 nm). Wetting TEM samples were prepared by sandwiching eutectic SnIn thin
foil (~100 μm thick) into two copper sheets, while wetting SEM samples were prepared by putting eutectic SnIn thin foil on the polished Cu sheets. Then they were aligned, clamped together and heated to the reflow temperature to form a solder joint. The typical reflowing and aging temperatures are 160 °C and 60 °C, respectively. In order to clearly reveal the morphologies of the IMC formed between eutectic SnIn solder and Cu from the top, the unreacted solder should be removed completely. The surface excess solder was mechanically polished first, and then was carefully etched with the 20% H2O2 + 80% CH3COOH (vol%) etchant solution. All the clean samples were observed with a LEO super35 and Quanta600 scanning electron microscopes with an EDS system to study the morphologies of the IMC and to perform compositional analyses.

3. Results and discussion

3.1. Cross-sectional microstructure and phase identification

3.1.1. The composition and crystal structure of Cu2(In,Sn) compound
After reflowing at 160 °C for 5 s, the cross-sectional SEM image of the In–48Sn/Cu(111) interface was shown in Fig. 1. It could be seen that there are two distinct IMC layers on (111) Cu substrate, whose interface was indicated by horizontal arrows. Layer I is adjacent to Cu substrate, while layer II is at the solder side whose outer boundary was outlined with dashed line. The corresponding EDS analyses of these two layers were shown in Table 1, and layer I consists of 66.11%Cu, 15.53%In, and 18.36%Sn which could be described as 66Cu–16In–18Sn (at.%), while layer II consists of 33.05%Cu, 51.66%In, and 15.29%Sn which corresponds to 33Cu–52In–15Sn (at.%). The thickness of these two layers was measured from a wide range with an image analyzing software as depicted in detail by Shang et al. [10]. It was found that both layers are in thickness of around 1 μm after soldering, with a thickness ratio of about 1:1 between them. It is worth noticing that some grains with composition of 33Cu–52In–15Sn was observed within the solder as shown in Fig. 1 (top-left corner), which should come from the spalling of layer II during liquid reaction in reflowing.

As SEM observations could not provide sufficient information besides composition to determine the IMC species, the interfacial microstructure was investigated further using TEM (also equipped with EDS system). Fig. 2(a) shows a typical bright field image of the detailed interfacial microstructures between eutectic SnIn solder and (111) Cu. Different from the double-layer morphology in Fig. 1, three layers could be observed on Cu substrate: a fine-grain layer A, a coarse-grain layer B (B1, B2, and B3 are different grains in the same layer), and a large-grain layer C. Elemental analyses using EDS revealed that layers A and B have similar composition of 66Cu–16In–18Sn (at.%), while layer C has a composition close to 33Cu–52In–15Sn (at.%). It implies that layer I in Fig. 1(a) is made of two sublayers A and B in Fig. 2(a), and layer II corresponds to layer C. Besides the similar composition, electron diffraction also revealed that sublayers A and B have the same crystal structure. The SAED patterns of these two sublayers were shown in Fig. 2(b and c) respectively, both of them can be indexed with the hexagonal Cu2In structure with lattice constants of a = b = 0.4292 nm, c = 0.5232 nm, α = β = 90°, and γ = 120° [11]. The extra or scattered spots in Fig. 2(b) come from surrounding fine-grains in layer A, while Fig. 2(c) shows a perfect diffraction pattern from only one coarse-grain in sublayer B with the same zone axes of [110]Cu2In. Therefore, the IMC species of layer I (including sublayers A and B) can be identified as Cu2In(In,Sn) that has a hexagonal Cu2In lattice dissolved with some Sn atoms for substituting In atoms, which agrees well with those observed on polycrystalline Cu substrate [12].

Many theoretical and experimental works have been tried to consummate the Cu–In–Sn ternary phase diagram [13,14]. Liu and his coworkers [13] studied the Cu–In–Sn isothermal section at 110 °C, which is the lowest available temperature in the literature for this ternary system. In their study, they pointed out that the η phase, which represents Cu2Sn5 and CuIn phases, continuously existed from the Cu–In to the Cu–Sn system. Lin et al. [14] studied the Cu–In–Sn isothermal section at 250 °C and found that η’(Cu2Sn5, CuIn) phase formed a continuous solid solution. However, they cannot distinguish the crystal structures between Cu2Sn5 and CuIn clearly, noticing that the η’-Cu2Sn5 has a NiAs B8 crystal structure with dimensions of a = b = 0.4200 nm, c = 0.5090 nm, α = β = 90°, γ = 120° [15], which is similar to the crystal structure of Cu2In. It is well known that η'-Cu2Sn5 can exist stably above the temperature of 189 °C [15]. When the temperature is below 189 °C, the η’-Cu2Sn5 will transform into η”-Cu5Sn5, which has a monoclinic structure with lattice constants of a = 1.1033 nm, b = 0.7294 nm, c = 0.9830 nm, α = 90°, β = 98.82°, γ = 90° [16,17]. In this study, the reflowing temperature (160 °C) is much lower than 189 °C, and none of three- or five-modulated superstructures were observed according to TEM investigations. Precise electron diffraction confirmed that neither η’-Cu2Sn5 nor η”-Cu5Sn5 was formed during reflowing eutectic SnIn/Cu solder joint at 160 °C. The resulted IMC at substrate side is undoubtedly determined as Cu2(In,Sn) with hexagonal crystal structure.

3.1.2. The composition and crystal structure of Cu2(In,Sn)2 compound
According to the EDS analyses in TEM, layer C in Fig. 2(a) has a similar composition to that of layer I in Fig. 1, which is about 33Cu–52In–15Sn (at.%). To identify its crystal structure, series of SAED patterns from the same grain in layer C were taken as shown in Fig. 2(d–g). These diffraction patterns can be indexed exactly with

![Fig. 1. Cross-sectional SEM images taken at the interface between eutectic SnIn solder and single crystalline (111) Cu after reflowing at 160 °C for 5 s.](image-url)

<table>
<thead>
<tr>
<th>IMC layer</th>
<th>Content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer I</td>
<td>66.11 15.53 18.36</td>
</tr>
<tr>
<td>Layer II</td>
<td>33.05 51.66 15.29</td>
</tr>
</tbody>
</table>

Table 1

The content (at.%) of element in I and II IMC layers (see Fig. 1).
tetragonal CuIn₂ crystal structure that has dimensions of \( a = b = 0.6645 \text{ nm}, \ c = 0.5376 \text{ nm}. \) \( \alpha = \beta = \gamma = 90^\circ, \) and their zone axes are \([001]_{\text{CuIn}_2}, [111]_{\text{CuIn}_2}, [101]_{\text{CuIn}_2}, \) and \([313]_{\text{CuIn}_2} \) respectively (see Fig. 2(d–g)). Moreover, a comparison of the intersecting angle of each pair of rotated zone axes between the experimental measurement and the theoretical calculation was made, as given in Table 2. It is found that the experimental results of the rotation angle between each pair of zone axes agree well with the theoretical value. Thus it can be concluded that the 33Cu–52In–15Sn (at.%) IMC in layer C has CuIn₂ tetragonal crystal structure.

Keppner et al. \cite{18,19} studied the compound formation at Cu–In interface using X-ray diffraction measurement, and identified that after isothermal annealing the formed CuIn₂ film also has a tetragonal crystal structure. As Sn can substitute In atoms due to the similar atomic radius during interfacial reaction, the IMC species of layer C (or layer II) should be described as Cu(In,Sn)\(_2\), which corresponds well to the composition of 33Cu–52In–15Sn (at.%).

In the previous works on the interfacial microstructure between In–48Sn and Cu, the Cu(In,Sn)\(_2\) phase was seldom observed and reported \cite{12}. One reason is that the Cu(In,Sn)\(_2\) phase has a similar contrast with the \( \gamma \)-InSn\(_4\) phase in the solder during SEM investigations. Another reason should be related to the spalling phenomenon of Cu(In,Sn)\(_2\) during liquid soldering for longer time, as shown in Fig. 3. When refloved at 160 °C for 5 s, a continuous Cu(In,Sn)\(_2\) layer was formed on Cu\(_2\)(In,Sn) layer in Fig. 3(a), whose interface was indicated by horizontal arrows. The formed Cu(In,Sn)\(_2\) IMC prefers adjoining to the Sn-rich \( \gamma \) phase in solder with similar light contrast. However, after 20 s refloving as shown in Fig. 3(b), some Cu(In,Sn)\(_2\) grains spalled into the solder as indicated by arrows, leaving discontinuous Cu(In,Sn)\(_2\) layer at the interface as marked with dashed line. After refloving at 160 °C for 60 s in Fig. 3(c), it was found that the spalling of continuous

### Table 2

Comparison of experimentally tilted and theoretically calculated angles between different pair of zone axes in Cu(In,Sn)\(_2\) crystal structure (see Fig. 2).

<table>
<thead>
<tr>
<th>Zone axis 1</th>
<th>Zone axis 2</th>
<th>Experimental angle (°)</th>
<th>Theoretical angle (°)</th>
</tr>
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<tr>
<td>[111]</td>
<td>[101]</td>
<td>37.5</td>
<td>37</td>
</tr>
<tr>
<td>[111]</td>
<td>[313]</td>
<td>24</td>
<td>23</td>
</tr>
<tr>
<td>[101]</td>
<td>[313]</td>
<td>14</td>
<td>13.5</td>
</tr>
</tbody>
</table>

![Fig. 2. TEM bright field image showing the interfacial microstructure between eutectic SnIn and single crystalline (111) Cu after soldering at 160 °C for 5 s (a), and the corresponding SAED patterns from grains in region A (b), region B (c) and region C (d–g) at different zone axes.](image1)

![Fig. 3. Interfacial SEM images of Cu(In,Sn)\(_2\) and duplex structure Cu\(_2\)(In,Sn) layers formed on (100) Cu during liquid soldering at 160 °C for 5 s (a), 20 s (b), and 60 s (c), showing the spalling process.](image2)
Cu(In,Sn) layer also took place, while most of the Cu(In,Sn)$_2$ grains has spalled into the solder and less of them could be observed at the interface area. Therefore, after long-term liquid soldering Cu$_2$(In,Sn) phase is seemed to be the only IMC at the interface, and Cu(In,Sn)$_2$ phase can be easily omitted.

The spalling phenomenon of IMC often occurs during soldering process. Kim and Tu [20] found that ripening-assisted spheroidal Cu$_6$Sn$_5$ grains spalled into the molten Sn–Pb solder, which exerted a lifting force to the Cu$_6$Sn$_5$ grains due to gravity or density difference. Sohn et al. [21] and Lin and Duh [22] concluded that the spalling of Ni$_3$Sn$_4$IMC was caused by the Ni–Sn–P layer formed between the solder and the P-rich layer. According to the study of Ronnie Teo and Sun [23] on the Sn–3.5Ag–0.7Cu system based on finite element analysis, it was found that the spalling phenomenon was caused by two factors: one was the interface structure change of IMC, and the other was cyclic shear stresses and strains induced during temperature cycling. It can be seen that there exist many mechanisms responsible for the IMC spalling phenomenon.

As the spalled Cu(In,Sn)$_2$ and coarse Cu$_2$(In,Sn) grains show elongated morphology (see Fig. 3) but not spheroidal one as reported Cu$_6$Sn$_5$ grains. According to the study of Shewmon [24], who found that the IMC grains liquefied and broke off preferentially at the grain boundary, the diffusivity of In atoms through the grain boundary is much faster than that in the lattice. Moreover, grain boundary diffusion, grain boundary grooving, grain coarsening and dissolution into the molten solder, were also observed during the growth of Ni$_3$Sn$_4$ that suffered from certain reflow cycles and thermal aging [25]. In this study, it is believed that the grain boundaries and their grooves among the frontier IMC grains also play an important role in the spalling process, which is accompanied by Cu atoms dissolution into the liquid In–48Sn solder. A schematic diagram is shown in Fig. 4 to illustrate the spalling process of IMC grains, where the bottom distance between two adjacent grain boundaries or grain boundary grooves of the extruding IMC grains was denoted as $d$ with arrows. Since spalling phenomena occurs during liquid–solid reaction, here we only focus on the IMC grains at the frontier of the liquid/solid interface, but not the whole IMC grains. As some IMC grains extrude into the liquid solder as shown in Fig. 4(a), the interface between IMC layer and liquid solder is uneven, and the grain boundaries and their grooves between these extruding frontier grains will act as quick diffusion path for reacting species in the process of liquid reaction. Hence the grain boundary grooves among extruding IMC grains will grow laterally to let the melted solder fill in, and the value of $d$ decreases as shown in Fig. 4(b). Accompanying the increased liquid soldering, more and more Cu atoms are dissolved, the lateral size $d$ of grain boundary grooves of IMC decreases, and only a small amount of junction exist between the IMC grains and the bottom IMC layer (see Fig. 4(c)). When the bottoms of some IMC are completely surrounded by the melted species, they would spall away from the adjoining IMC layer into liquid solder as shown in Fig. 4(d). The same phenomenon or behavior was also observed for the spalling of coarse-grain Ni$_3$Sn$_4$ phase due to the lateral grain boundary grooving during Ni/Sn liquid soldering, and the corresponding mechanism has been discussed in detail [26].

### 3.2. Top-view microstructure and morphology characterization

According to the cross-sectional TEM investigation as shown in Fig. 2, the Cu(In,Sn) layer is made up of a fine-grain and a

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**Fig. 4.** Schematic diagram illustrating the spalling process of elongated coarse IMC grains.

**Fig. 5.** Top-view SEM images of different IMC layers formed on single crystalline (111) Cu substrate, showing the chunk-type Cu(In,Sn)$_2$ grains after soldering (a), three IMC sublayers with different morphologies after solid-state aging at 60°C for 1 day (b), the duplex structure Cu$_2$(In,Sn) layer with inhomogeneous etching after aging at 60°C for 2 days (c), and fine-grain Cu(In,Sn) grains with granular morphology solid-state aged for 2 days (d).
coarse-grain sublayers, which was named as “duplex structure” in previous study. Beek et al. [27] reported coarse- and fine-grain duplex structural FeSn phase in Fe-Sn system, while Neijmeijer and Kolster [28] observed duplex structural Nb3Sn phase in Nb–Sn system. In this work, statistical results show that the average grain sizes of fine- and coarse-grain Cu2(In,Sn) are about 50 nm and 200 nm respectively (refers to the lateral size for coarse Cu2(In,Sn) grains), while Cu2(In,Sn) grains have the largest grain size in micrometer scale. In order to reveal and expose the morphologies of these different IMC, the top-view microstructures were investigated on reflowed (160 °C) and solid-state aged (60 °C) samples.

By etching off top solder alloy after reflowing, the microstructure of Cu2(In,Sn) sublayer formed on (111) single crystalline Cu surfaces was given in Fig. 5(a), which shows chunk-type morphology with large grain size. After further corrosion, it can be clearly seen that besides chunk-type Cu2(In,Sn) sublayer, elongated and granule grains were exposed, which corresponds to the coarse-grain and fine-grain Cu2(In,Sn) respectively as shown in Fig. 5(b). The microstructure of this duplex structure Cu2(In,Sn) layer was shown in Fig. 5(c) after aged at 60 °C for 2 days. It is found that the coarse-grain Cu2(In,Sn) grains on the top of fine-grain Cu2(In,Sn) grains display growth regularity, which will be studied later. By further etching off the coarse-grain Cu2(In,Sn) sublayer, the grain-type fine-grain Cu2(In,Sn) grains were presented clearly in Fig. 5(d), which distribute homogeneously on the entire substrate surface.

The top-view investigations verified the sequence and three morphologies of IMCs formed during reflowing at 160 °C for 5 s, that Cu2(In,Sn) sublayer is on top of duplex structure Cu2(In,Sn) layer. It was found that on single crystalline Cu substrate, chunk-type Cu2(In,Sn) and granule-type fine-grain Cu2(In,Sn) grains grew homogeneously without obvious regularity, while coarse-grain Cu2(In,Sn) grains had elongated morphology displaying special growth directions. Concerning the grain size of these IMCs, chunk-type Cu2(In,Sn) has the largest grain size, while coarse-grain Cu2(In,Sn) is in between. According to our recent investigations, the distribution of coarse Cu2(In,Sn) grains on (100) and (111) Cu substrates is different, showing preferential growth with various orientation relationships [29]. From this point of view, it is believed that coarse-grain Cu2(In,Sn) is formed first between liquid SnIn and solid Cu substrate during soldering, while Cu2(In,Sn) is the result of interfacial reaction between liquid SnIn and solid coarse-grain Cu2(In,Sn), and fine-grain Cu2(In,Sn) comes from the solid interfacial reaction between coarse-grain Cu2(In,Sn) and Cu substrate. Further study is still going on to clarify the growth behavior of Cu–Sn/In IMCs, which will be summarized and reported later.

4. Conclusions

The species of intermetallic compounds at the interface between eutectic SnIn solder and single crystalline Cu substrate were systematically investigated using SEM and TEM, and the following conclusions were drawn:

(1) After reflowing at 160 °C for 5 s, two kinds of IMC were formed in three sublayers from solder to substrate side, which are Cu2(In,Sn) layer with tetragonal crystal structure, coarse-grain Cu2(In,Sn) sublayer and fine-grain Cu2(In,Sn) sublayer with hexagonal crystal structure.

(2) The morphology of Cu2(In,Sn) layers is chunk-type with the largest grain size. In the process of increased liquid soldering, this Cu2(In,Sn) layer is prone of spalling into solder leaving duplex structure Cu2(In,Sn) as the dominating IMC, which should be paid attention to during phase identification.

(3) The fine-grain Cu2(In,Sn) shows granule-type morphology with the smallest grain size, which distributes homogeneously on the entire Cu substrates. However, coarse-grain Cu2(In,Sn) is substrate-dependent with elongated morphology on single crystalline Cu surfaces, whose grain size is in between.

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