The interfacial reaction between In-48Sn solder and polycrystalline Cu substrate during solid state aging

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A B S T R A C T
Intermetallic compounds (IMCs) with three different morphologies were formed through an interfacial reaction between In-48Sn solder and polycrystalline Cu substrate, which are chunk-type Cu2(In,Sn)2 and duplex structural Cu2(In,Sn). Two types of phase transformations between Cu2(In,Sn)2 and Cu(In,Sn) IMCs occurred during low temperature aging (20 °C and 40 °C) and high temperature aging (60 °C, 80 °C and 100 °C), respectively. At lower aging temperature, the duplex structural coarse-grain and fine-grain Cu2(In,Sn) transformed into Cu2(In,Sn)2, and a characteristic evolution model was provided. At a higher aging temperature, Cu(In,Sn)2 transformed completely into Cu2(In,Sn) within a very short time period. Based on the designed Cr-marker experiments, the growth kinetics of coarse-grain and fine-grain Cu2(In,Sn) sublayers at higher aging temperatures were investigated. It was concluded that the growth mechanism of Cu2(In,Sn) is temperature dependent, which is volume-diffusion-controlled at 60 °C to 80 °C, whereas grain boundary diffusion becomes rate-controlling at 100 °C. Through an elaborate design of aging test at 80 °C and 20 °C alternately, the reversible transformation between Cu2(In,Sn) and Cu(In,Sn)2 was observed and characterised.

1. Introduction
It is known that the intermetallic compound (IMC) layer acts as an important metallurgical bonding layer between soldering alloy and substrate metal, which has obvious effects on the mechanical properties of solder joints and their serving reliability [1–4]. Many researchers have systematically and widely investigated the interfacial reactions of Sn-based solders, such as SnBi [5], SnAgCu [6,7], Sn–Cu [8], mainly focusing on the nucleation and morphology of IMCs during soldering as well as the growth kinetics of IMC layers during the solid-state aging process. However, due to the complexity of In–Sn–Cu ternary phase diagram and the high cost of the In element, only few researchers and manufacturers have paid attention to In–48Sn/Cu system. The binary eutectic In–48Sn solder has the advantage of a low melting point and better mechanical properties [9–11], which can be utilized in many low-temperature fields, such as thermal sensitive components, multiple reflowing and low-temperature packaging. Hence, it is essential to study the interfacial reaction between In-48Sn solder and polycrystalline Cu substrate to clarify IMC formation and phase transformation therein.

Owing to the participation of the In element in interfacial reactions between solder and substrates, the In-48Sn solder joint exhibits specific characteristics such as the morphologies and phase species of IMC, which influence the mechanical property and service reliability of the interconnects in application. Moreover, the chemical reaction of IMCs often takes place at the interface in various systems during solid-state aging [12–15], which also plays an important role in a packaging structure’s life. In microelectronic applications, the solder joints suffer from different aging temperatures. Thus, the main diffusing species coming from the solder alloy or substrate metal may change as a function of temperature, to promote different chemical reactions at the interface. Hence, reversible chemical reactions between IMCs can take place, a subject which is seldom investigated.

In this study, the interfacial reaction between In-48Sn and polycrystalline Cu was studied systematically, mainly focusing on the IMC morphologies after reflowing, phase transformations
between Cu(In,Sn)\textsubscript{2} and Cu\textsubscript{2}(In,Sn) at different solid-state aging temperatures, as well as the growth kinetics of coarse-grain and fine-grain Cu\textsubscript{2}(In,Sn) sublayers. Considering the elemental diffusion during the interfacial reaction, a schematic diagram was proposed to elucidate the characteristic phase transforming process from duplex structural Cu\textsubscript{2}(In,Sn) into Cu(In,Sn)\textsubscript{2}.

### 2. Experimental procedures

#### 2.1. Cu substrate with Cr-marker preparation

The high purity, oxygen-free polycrystalline copper plates (>99.99%) were cut by an electro-discharging machine into sheets of size 40 × 4 × 2 mm\textsuperscript{3}. Then, the Cu surfaces were ground with grade SiC papers successively and polished carefully with 1 and 0.5 µm diamond paste. Thereafter, the Cu surfaces were rinsed in acetone and distilled water and then dried; half of these were later electroplated by a thin Cr layer to study the growth mechanism and growth kinetics of coarse- and fine-grain Cu\textsubscript{2}(In,Sn) sublayers after aging at 60 °C, 80 °C and 100 °C. A precise Cr-marker experiment\textsuperscript{[16]} was designed to distinguish the duplex structural Cu\textsubscript{2}(In,Sn) sublayers in In-48Sn/Cu system, as shown in Fig. 1. First, half of the polished Cu surface was masked by an electroplating tape (Fig. 1a). Then, a thin Cr layer was electroplated on the other polished Cu surface (Fig. 1b). Thereafter, the electroplating tape was removed, and the polished Cu surface was cleaned with distilled water and dried.

#### 2.2. In–48Sn solder foil preparation

The In–48Sn solder alloy was prepared using high purity In and Sn (>99.99%) according to weight ratio in a resistance vacuum furnace with vacuum degree 10\textsuperscript{–3} torr. The In–48Sn solder stripe was rolled into a thickness of about 200 µm by a manual rolling mill and cut into the size of 40 mm × 4 mm with scissors. Afterwards, the In–48Sn thin foil was cleaned ultrasonically in acetone and alcohol solvents respectively for 3–5 min to dissolve the remaining rosin mildly activated (RMA) on the sample surfaces. To observe the wetting front between the electroplated Cr layer and the solder joint, it is essential to carry out a second electroplating Cr layer as shown in Fig. 1d. Finally, the solder joint samples were cut into 4 × 4 mm\textsuperscript{2} pieces and then aged in thermal ovens at a temperature range of 20 °C–100 °C for different periods.

#### 2.3. Wetting sample preparation

Wetting samples were prepared by putting the In–48Sn thin foil on polished Cu substrates, whose half surface was electroplated by a thin Cr layer as a marker to distinguish the original liquid/solid interface of In–48Sn solder and Cu. The samples were then heated up to 160 °C for 5s on a heating plate; thereafter, the formed solder joint (Fig. 1c) was cooled in air up to an ambient temperature of 20 °C. Afterwards, the samples were cleaned ultrasonically in acetone for 5 min in order to dissolve the remaining rosin mildly activated (RMA) on the sample surfaces. To observe the wetting front between the electroplated Cr layer and the solder joint, it is essential to carry out a second electroplating Cr layer as shown in Fig. 1d. Finally, the solder joint samples were cut into 4 × 4 mm\textsuperscript{2} pieces and then aged in thermal ovens at a temperature range of 20 °C–100 °C for different periods.

#### 2.4. Microstructural observation

The cross-sectional samples for the scanning electron microscope (SEM) study were ground with SiC papers successively and then polished carefully with 0.05 µm Al\textsubscript{2}O\textsubscript{3} powder suspension. Top-view SEM samples first mechanically ground away the excess In–48Sn solder to about 100 µm thickness, following which the remaining solder alloy was carefully etched with 20% H\textsubscript{2}O\textsubscript{2} + 80% CH\textsubscript{3}COOH (vol%), which has the advantage of having a low etching rate and less effect on Cu substrate. The cross-sectional and top-view SEM samples were rinsed with distilled water in ultrasonic bath for 10 min to remove the residual etchant solution and Al\textsubscript{2}O\textsubscript{3} powder suspension, and then dried in air. All clean samples were studied using LEO super35 and Quanta 600 SEMs with energy-dispersive X-ray spectroscopy (EDS) system for compositional analyses.

#### 2.5. IMC thickness measurement

The thickness of IMC layers was measured using image analyses software as described earlier\textsuperscript{[17]}.

### 3. Results and discussion

#### 3.1. Morphology of interfacial IMCs after reflowing and their EDS analysis

After reflowing at 160 °C for 5s, the cross-sectional SEM image of the interface is shown in Fig. 2a, in which two distinct IMC layers—a continuous Cu(In,Sn)\textsubscript{2} layer next to In–48Sn solder and a Cu\textsubscript{2}(In,Sn)
layer adjacent to Cu substrate — were observed. The formed interfacial IMC species between In-48Sn solder and single crystalline Cu were investigated thoroughly utilizing electron microscopy after reflowing [18,19]; these were identified as Cu(In,Sn)₂ and Cu₂(In,Sn) IMCs. These formed IMC species are also formed in case of the polycrystalline Cu substrate under the same conditions according to microstructural characterization. However, the difference between the single crystalline Cu and polycrystalline Cu is the preferential orientation of the formed coarse-grain Cu₂(In,Sn) grains. There are orientation relationships during the nucleation and growth of coarse-grain Cu₂(In,Sn) compound on single crystalline Cu [18], but the formed coarse-grain Cu₂(In,Sn) grains display chaotic rod-type morphology and have no preferential orientation on polycrystalline Cu substrate. The Cu(In,Sn)₂ layer has a lighter SEM contrast than the Cu₂(In,Sn) layer, whose interface was indicated by arrows as shown in Fig. 2a. The average thickness of both of them is about 1 μm. By etching the solder joint from top to bottom, layer by layer, the exact morphologies of the formed IMCs could be revealed as shown in Fig. 2b–d. It was found that layer II contains Cu(In,Sn)₂ IMC (Fig. 2b) and has a chunk-type morphology. However, top-view SEM images show that layer I of Cu₂(In,Sn) IMC contains coarse-grain (Fig. 2c) and fine-grain (Fig. 2d) sublayers with rod-type and granular-type morphologies respectively, referred to as “duplex structure” in this study.

As SEM morphology observations could not provide sufficient information to determine the interfacial IMC species, composition analyses were further carried out using EDS, and the results are shown in Fig. 3. Elemental analyses using EDS revealed that the chunk-type, rod-type and granular-type IMCs have a composition close to 37Cu-46In-17Sn (at.%), 70Cu-12In-18Sn (at.%) and 67Cu-12In-21Sn (at.%), respectively, among which the rod-type and granular-type IMCs have similar compositions. Moreover, selected area electron diffraction (SAED) patterns using transmission electron microscopy (TEM) showed that chunk-type IMC had the tetragonal CuIn₂ type of crystal structure with unit cell dimensions of \( a = 0.6645 \) nm, \( c = 0.5376 \) nm. The rod-type and granular-type IMCs had hexagonal CuIn type of structure with unit cell dimensions of \( a = 0.4292 \) nm, \( c = 0.5232 \) nm [19]. Hence, two types of IMCs with three kinds of morphology were formed on polycrystalline Cu substrate after reflowing, which are Cu(In,Sn)₂, coarse-grain Cu₂(In,Sn) and fine-grain Cu₂(In,Sn).

### 3.2. Solid-state aging at higher temperatures of 60 °C, 80 °C and 100 °C

#### 3.2.1. Phase transformation from Cu(In,Sn)₂ into Cu₂(In,Sn) at higher aging temperature

When comparing Fig. 2a (after reflow) with Fig. 4, it can be clearly seen that the previous continuous Cu(In,Sn)₂ layer disappeared and duplex structural Cu₂(In,Sn) sublayers became the only dominantly growing IMC at the interface after solid-state aging at 60 °C, 80 °C and 100 °C for just 1 day. This is also the case for a higher aging temperatures and a longer aging time. Furthermore, the duplex structural Cu₂(In,Sn) sublayer grew thicker as the aging temperature increased. Thus, we conclude that the higher the aging temperature is, the thicker the formed IMC layer will be under the
Based on our earlier study [20] on phase transformation between Cu(In,Sn)₂ and Cu₂(In,Sn) compounds formed on single crystalline Cu substrate during the solid-state aging, chemical reactions took place between these compounds. It was found that both Cu(In,Sn)₂ and Cu₂(In,Sn) IMCs grew simultaneously and coexisted on (100)Cu and (111)Cu after aging at 60 °C [20]. However, on the polycrystalline Cu substrate, the Cu(In,Sn)₂ IMCs transformed into Cu₂(In,Sn); accordingly, the following partial chemical reaction should take place during the aging at 60 °C.

\[
3\text{Cu}_\text{diffuse} + \text{CuIn}_2 = 2\text{Cu}_2\text{In}
\] (1)

According to the theoretical model of chemical reactions at the interface [14,15], it can be derived that \(\frac{dx}{dt} > 0\) and \(\frac{dy}{dt} < 0\) at 60 °C; thus, the following two formulae can be obtained [19]:

\[
\frac{8}{3} \frac{k_{1\text{In}2} + k_{1\text{Cu}2}}{k_{1\text{In}2}} > \frac{x}{y}
\] (2)

\[
\frac{2}{3} \frac{k_{1\text{Cu}2}}{k_{1\text{In}2} + k_{1\text{Cu}3}} > \frac{x}{y}
\] (3)

Where \(k_{1\text{In}2}, k_{1\text{Cu}2}, k_{1\text{In}3}\) and \(k_{1\text{Cu}3}\) are the physical (diffusion) constants (m²/s) [14,15], indicating the IMC layer controlled by diffusion, \(x\) and \(y\) represent the thickness of Cu₂(In,Sn) and Cu(In,Sn)₂, respectively. It is known that the thickness of both Cu₂(In,Sn) and Cu(In,Sn)₂ is about 1 μm after reflowing. During solid-state aging at 60 °C, 80 °C and 100 °C for some days, Cu(In,Sn)₂ consumption and Cu₂(In,Sn) growth will eventually lead to \(x > y\) or even \(x \gg y\). Putting \(x = y\) into the inequality (3), it can be derived as:

\[
k_{1\text{Cu}2} > \frac{3}{2}(k_{1\text{In}2} + k_{1\text{Cu}3})
\] (4)

Owing to \(k_{1\text{Cu}3} \geq 0\), it can be further described as:

\[
k_{1\text{Cu}2} > \frac{3}{2} k_{1\text{In}2}
\] (5)

Therefore, the stronger diffusion ability of Cu than In and Sn atoms helps the chemical reaction (1) proceed, resulting in Cu(In,Sn)₂ consumption as well as Cu₂(In,Sn) growth. When
3.3. Solid-state aging at lower temperatures of 20 °C and 40 °C

3.3.1. Phase transformation from Cu2(In,Sn) into Cu(In,Sn)2 at lower-aging temperature

Fig. 6 shows the cross-sectional images of Cu(In,Sn)2 and Cu(In,Sn)2 layers on polycrystalline Cu substrate after aging at 40 °C for up to 90 days. In Fig. 6a, the interface between Cu(In,Sn)2 layer adjacent to the solder and Cu(In,Sn) layer next to Cu substrates after 5 days’ aging is indicated by horizontal arrows, at which some
coarse-grain Cu2(In,Sn) grains extrude into the Cu(In,Sn)2 layer. As shown in Fig. 6b, after 10 days’ aging, it was seen that the original, continuous Cu2(In,Sn) layer became discontinuous in region A. Furthermore, the thickness of the Cu(In,Sn)2 layer increased and that of the Cu2(In,Sn) layer decreased with increasing aging time. Fig. 6c shows the chemical reaction of IMC layers taking place after aging at 40 °C for 60 days. It can be clearly seen that with the increasing appearance of the discontinuous regions of the Cu2(In,Sn) layer, its thickness decreased dramatically due to its transformation into Cu(In,Sn)2. After 90 days’ aging at 40 °C, as shown in Fig. 6d, only very few Cu2(In,Sn) islands remained, while the rest of them had completely transformed into Cu(In,Sn)2 eventually. It was concluded that with increasing aging time, originally reflowing Cu2(In,Sn) eventually transformed into Cu(In,Sn)2, when aged at 40 °C. Moreover, it was also observed that the interface between Cu2(In,Sn) and Cu substrate changed from relatively even to uneven, and the interface concaved downwards to Cu substrate as shown in region B of Fig. 6d. According to the elemental analyses, new Cu(In,Sn)2 was formed in these regions. It meant that the original Cu2(In,Sn) layer transformed into Cu(In,Sn)2 completely, and the chemical reaction was still going on with Cu substrates due to the fast diffusion of In and Sn atoms. Such chemical reaction occurring on polycrystalline Cu substrate was also observed on (100)Cu and (111)Cu substrates at a long-term aging at 40 °C and on polycrystalline Cu substrate after the aging at 20 °C.

According to our previous study on (100)Cu and (111)Cu substrates [20], the following partial chemical reaction takes place when Cu2(In,Sn) transforms into Cu(In,Sn)2 during aging at 40 °C:

$$3 \text{In}_{\text{diffuse}} + \text{Cu}_2\text{In} \rightarrow 2\text{CuIn}_2 \quad (9)$$

According to the theoretical model of chemical reactions at the interface, it can be derived that $\frac{dx}{dt} < 0$ and $\frac{dy}{dt} > 0$; thus, the following two formulae can be obtained [19]:

$$3 \frac{k_{1\text{Cu}_2}}{k_{1\text{In}_2}} > \frac{y}{x} \quad (10)$$

$$3 \frac{k_{1\text{Cu}_2}}{8 k_{1\text{In}_1} + k_{1\text{Cu}_2}} > \frac{y}{x} \quad (11)$$

Where $k_{1\text{In}_1}$, $k_{1\text{Cu}_2}$, $k_{1\text{In}_2}$ and $k_{1\text{Cu}_3}$ are the physical (diffusion) constants (m$^2$/s), indicating that the IMC layer is controlled by diffusion; $x$ and $y$ represent the thickness of Cu2(In,Sn) and Cu(In,Sn)2, respectively. Putting $y = x$ into the inequality (11), it can be derived as:

$$k_{1\text{In}_2} > \frac{8}{3}(k_{1\text{In}_1} + k_{1\text{Cu}_2}) \quad (12)$$

Owing to $k_{1\text{In}_1} \geq 0$, it can be safely concluded that:

$$k_{1\text{In}_2} > \frac{8}{3}k_{1\text{Cu}_2} \quad (13)$$

It means that the diffusion ability of the In atom is at least several times stronger than that of Cu, making Cu2(In,Sn) to transform into Cu(In,Sn)2 with chemical reaction (9) taking the place when aged at 20 °C and 40 °C. After Cu2(In,Sn) transforms into Cu(In,Sn)2 completely, the following two partial chemical reactions take place at the interface to make Cu(In,Sn)2 grow continuously during aging at 20 °C and 40 °C on polycrystalline Cu substrate.

<table>
<thead>
<tr>
<th>Temperatures (°C)</th>
<th>coarse-grain Cu2(In,Sn)</th>
<th>fine-grain Cu2(In,Sn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.45</td>
<td>0.54</td>
</tr>
<tr>
<td>80</td>
<td>0.46</td>
<td>0.48</td>
</tr>
<tr>
<td>100</td>
<td>0.33</td>
<td>0.31</td>
</tr>
</tbody>
</table>
3.3.2. Evolution model of phase transformation from duplex structure Cu(In,Sn) into Cu(In,Sn)₂

As mentioned above, the transformation process of the duplex structure Cu₂(In,Sn) into Cu(In,Sn)₂ during aging at 20 °C and 40 °C shows its own characteristics, which have a close relationship with the special coarse- and fine-grain Cu₂(In,Sn) microstructures. Based on the experimental observations, an evolution model was elaborated and presented in Fig. 7. At the initial aging stage, as shown in Fig. 7a, some In atoms diffuse vertically from the solder into the top of the coarse-grain Cu₂(In,Sn) sublayer; subsequently, a partial chemical reaction (9) takes place and Cu(In,Sn)₂ IMC is formed. Here, Indiffuse is used to represent both In and Sn species considering the following two factors. On one hand, the atomic percentage of the In element in Cu(In,Sn)₂ is about 50% (more than that of Sn) and is nearly equivalent to the content of Sn element in Cu₂(In,Sn). On the other hand, Cu(In,Sn)₂ and Cu₂(In,Sn) are CuIn₂ and Cu₂In based crystal structures, respectively.

It is known that grain boundaries allow a much greater diffusion rate compared to the grain itself. As the grooves between the grain boundaries and also the grain boundaries of coarse Cu₂(In,Sn) grains can act as the straight and quick path for the diffusion of In and Sn atoms, chemical reaction (9) is promoted faster at grain boundaries than in coarse-grain Cu₂(In,Sn) itself, as shown in Fig. 6. Based on our previous TEM [19] and Cr-marker observations [16], there exists a distinct interface between the coarse- and fine-grain Cu₂(In,Sn) sublayers. When coarse-grain Cu₂(In,Sn) completely transformed into Cu(In,Sn)₂ in some regions, vertically diffusing along grain boundaries In atoms of coarse-grain Cu₂(In,Sn) reach the top of fine-grain Cu₂(In,Sn) sublayer, and the chemical reaction (9) between In atoms and fine-grain Cu₂(In,Sn) takes place. The In atoms diffusing through the fine-grain Cu₂(In,Sn) sublayer would diverge into two directions: one diffusing direction is vertical to Cu substrate and the other one is parallel to Cu substrate as shown by arrows in Fig. 7b. As the fine-grain Cu₂(In,Sn) sublayer has more grain boundaries, In atoms can diffuse towards the two directions mentioned above quickly through the grain boundaries and react with the fine Cu₂(In,Sn) grains to form new Cu(In,Sn)₂ IMC. However, the grain size of coarse-grain Cu₂(In,Sn) is larger and the quantity of grain boundaries in the layer is small. Thus, the transformation of coarse-grain Cu₂(In,Sn) sublayer is slow compared to that in fine-grain Cu₂(In,Sn) sublayer, as revealed in Fig. 7b.

When the fine-grain Cu₂(In,Sn) sublayer transforms into
Cu(In,Sn)2 completely, the regions are transformed into the Cu(In,Sn)2 IMC. Then, the diffusing In atoms migrate through the Cu(In,Sn)2 layer to reach the top of the Cu substrate and initiate a new partial chemical reaction (14), forming the Cu(In,Sn)2 IMC and making the Cu surface concave go down, as shown in Figs. 6d and 7c (region B). With the proceeding chemical reaction (9), the continuous duplex structure Cu2(In,Sn) sublayers were divided into certain discontinuous regions, and in some part of the microstructure, the duplex structure Cu2(In,Sn) becomes sandwiched between two Cu(In,Sn)2 layers to form a special layered structure of Cu(In,Sn)2/Cu2(In,Sn)/Cu(In,Sn)2. Moreover, some coarse Cu2(In,Sn) grains appear to be insulating islands surrounded by newly formed Cu(In,Sn)2 after a complete chemical transformation from fine-grain Cu2(In,Sn) into Cu(In,Sn)2, as clearly shown in Fig. 7c. After the duplex structure Cu2(In,Sn) sublayers were consumed, only the Cu(In,Sn)2 layer remained, as seen in Fig. 7d, but chemical reactions (14) and (15) still continued at the interfaces.

Due to the existence of coarse-grain and fine-grain duplex structures, the transformation process from Cu2(In,Sn) into Cu(In,Sn)2 is specific and different, considering the diffusion of In atoms. In other reaction diffusion systems, the consumption and growth of compound layers at the interfaces is uniform and no particular phenomenon is observed. For example, when Cu2(In,Sn) IMCs transforms into duplex structure Cu(In,Sn) sublayers completely, Cu(In,Sn) becomes the only dominant IMC without any IMC islands. As illustrated in Fig. 7, the fine-grain Cu2(In,Sn) sublayer with more diffusion paths has a great effect on the diffusion rate of In atoms, affecting the chemical reactions therein.

3.4. Reversible transformation between Cu2(In,Sn) and Cu(In,Sn)2

3.4.1. Phenomenon of reversible transformation during aging

Since the IMC transformation is different at higher and lower temperatures, as described in Sections 3.2 and 3.3, special aging experiments were designed to monitor the reversible transformation at different temperatures. The following samples suffering from the first aging process at 80 °C for 2 and 5 days are shown in Fig. 8a and b respectively; Cu(In,Sn)2 transformed completely into duplex structure Cu2(In,Sn), becoming the only dominant IMC at the interface. Then, these corresponding samples were aged at 20 °C for 2 years, and Cu(In,Sn)2 appeared again between the duplex structure Cu2(In,Sn) and In-48Sn solder as shown in Fig. 8c and d. As this transformation proceeded, Cu2(In,Sn) layer changed from being continuous to discontinuous, and some existing duplex structure Cu2(In,Sn) was sandwiched between the neighbouring two Cu(In,Sn)2 layers. For example, a thin unreacted fine-grain Cu2(In,Sn) sublayer lies vertically down in region A of Fig. 8c. Moreover, some other Cu2(In,Sn) grains were enveloped by Cu(In,Sn)2, similar to isolated islands, whose roots are adjacent to the Cu substrate, as indicated by horizontal arrowheads in Fig. 8c. The above transformation phenomena also appear in Fig. 8d. Besides, the interface between Cu2(In,Sn) and Cu substrate changed from relatively even to uneven and concaved downwards to Cu substrate, as shown in region B of Fig. 6d. In this concaved region B, Cu(In,Sn)2 penetrated into Cu substrate after a complete transformation from Cu2(In,Sn), and the interfacial reaction between Cu substrate and In-48Sn solder proceeded with the formation of a new Cu(In,Sn)2. Comparing Fig. 6 with Fig. 8a–d, we conclude that the same chemical reaction occurs between Cu2(In,Sn) and Cu(In,Sn)2 IMCs, and the evolution process from duplex structure Cu2(In,Sn) sublayers to Cu(In,Sn)2 is also similar when aged at 20 °C and 40 °C. From the above observation, the Cu(In,Sn)2 layer dominated over the whole IMC layer after long-term aging at 20 °C and 40 °C. Third, the corresponding samples after 2 years’ aging at 20 °C were further aged at 80 °C for just 1 day, and it was observed that the transformed Cu(In,Sn)2 in Fig. 8c and d almost completely converted into Cu2(In,Sn) again as revealed in Fig. 8e and f. From Fig. 8, it can be clearly seen that a reversible transformation between Cu2(In,Sn) and Cu(In,Sn)2 took place when samples were subjected to a series of aging treatments at different temperatures. Moreover, it was found that the thickness of the interfacial IMC layers in Fig. 8c and d was larger than that in Fig. 8a and b and did not change when compared to that in Fig. 8e and f.

As discussed in the above section, transformation from Cu2(In,Sn) into Cu(In,Sn)2 or from Cu(In,Sn)2 into Cu2(In,Sn) has a direct and close relationship with the main diffusing species of Cu or In/Sn atoms at different aging temperatures. When the diffusion ability of In atoms is stronger than that of Cu, Cu2(In,Sn) transforms into Cu(In,Sn)2; however, when the diffusion ability of Cu atoms is stronger than that of In, Cu(In,Sn)2 transforms into Cu2(In,Sn), leading to a reversible transformation between Cu2(In,Sn) and Cu(In,Sn)2.

3.4.2. Verification of reversible transformation by theoretical calculations

The above chemical reactions were quantitatively described considering IMC growth. Table 2 shows the thickness of IMCs on polycrystalline Cu as a function of aging time during a series of solid-state aging process, representing the evolution process of reversible transformations at the interface. According to the chemical reaction (9), the following equation can be derived:

\[ x_{CuIn} = 2.58x_{CuIn} \]  

(16)

It means when 1 μm of duplex structure Cu2(In,Sn) is consumed, 2.58 μm of Cu(In,Sn)2 grows. According to the image analyses software, the thickness of the transformed Cu(In,Sn)2 layer from the duplex structure Cu2(In,Sn) is about 4.3 μm. Putting the value of 4.3 μm of Cu(In,Sn)2 into equation (16), it can be derived that about 1.67 μm of Cu2(In,Sn) was consumed. Thus, it is concluded that:

\[ \ell_{total-second} = \ell_{dup-first} - 1.67 + 4.3, \text{ this is } \ell_{total-second} = \ell_{dup-first} + 2.63 \]  

(17)

Among which, \( \ell_{dup-first} \) represents the thickness of duplex structure Cu2(In,Sn) sublayers after the first aging at 80 °C for different time and \( \ell_{total-second} \) indicates the thickness of all the IMC layers of the considered above samples (consisting of unreacted duplex structure Cu2(In,Sn) and transformed Cu(In,Sn)2 layer) after aging at 20 °C for 2 years. The values of \( \ell_{dup-first} \) after the first aging at 80 °C and \( \ell_{total-second} \) after the second aging at 20 °C for 2 years of the corresponding samples are listed in Table 2. Putting the above values into (17), it can be found that the results are in a good agreement. It means that the duplex structure Cu2(In,Sn) layer after the first aging at 80 °C indeed transformed into Cu(In,Sn)2 after the second aging at 20 °C, due to the Cu atom’s faster diffusion rate as compared to In.

On the other hand, according to the chemical reaction (1), the following equations can be derived:

\[ x_{CuIn} = 1.54x_{CuIn} \]  

(18)

It means when 1 μm of Cu(In,Sn)2 is consumed, 1.54 μm of Cu(In,Sn) will grow. According to equation (16), the thickness of the transformed Cu(In,Sn)2 layer after the second aging at 20 °C for 2 days is about 4.3 μm, which should make 6.6 μm of Cu2(In,Sn) grow after the third aging at 80 °C. The measured thickness of Cu2(In,Sn) from the phase transformation of Cu(In,Sn)2 after the third aging at 80 °C and the unreacted Cu2(In,Sn) after second aging at 20 °C for 2 days is smaller than the calculated value.
the equation (18) after the third time aging at 80°C. This means that most of Cu(In,Sn)2 has transformed into Cu2(In,Sn) leaving only a few grains of un-reacted Cu(In,Sn)2, just as shown by the dotted regions in Fig. 8e and f, thus making Cu2(In,Sn) to grow continuously and become the dominant IMC after aging at 80°C for a longer time.

From the above observations and analysis, we can conclude that the chemical reactions dependent on the aging temperature indeed occurred at the interfaces between In-48Sn solder and polycrystalline Cu substrate, as summarized in Table 3. As presented in Table 3, all chemical reactions can be classified into two types: the Cu(In,Sn)2 layer grows while the Cu2(In,Sn) layer is consumed, and when the Cu(In,Sn)2 layer is consumed, the Cu2(In,Sn) layer grows.

4. Conclusions

In summary, the interfacial reaction between In-48Sn solder and polycrystalline Cu substrate was studied systematically in this paper and the following conclusions were drawn, focusing on the morphologies of IMCs after reflowing, the growth kinetics of coarse-grain and fine-grain Cu2(In,Sn) sublayers, as well as the phase transformations between Cu(In,Sn)2 and Cu2(In,Sn) at different aging temperatures.

1) After reflowing at 160°C for 5s, two kinds of IMCs were formed in three sublayers from solder to substrate side; these are as follows: a Cu(In,Sn)2 layer with tetragonal crystal structure, coarse-grain Cu2(In,Sn) sublayer and fine-grain Cu2(In,Sn) sublayer with hexagonal crystal structure. The morphology of the Cu(In,Sn)2 grains is a chunk-type with the largest grain size.
coarse-grain Cu$_2$(In,Sn) is chaotic and rod-like, whose grain size is medium, while fine-grain Cu$_2$(In,Sn) shows granule-type morphology with the smallest grain size.

2) Kinetics analyses reveal that the growth of both coarse- and fine-grain Cu$_2$(In,Sn) is controlled by a bulk diffusion at lower temperatures of 60 °C and 80 °C, while at the high temperature of 100 °C, the grain boundary diffusion dominates over their growth mechanisms.

3) When solid alloys are aged at 20 °C and 40 °C, Cu$_2$(In,Sn) gradually transforms into the Cu(In,Sn)$_2$ compound. At this temperature, the diffusion rate of In and Sn atoms is higher than that of Cu atoms, $k_{1\text{In}_2} > 8/3k_{1\text{Cu}_2}$, making the Cu(In,Sn)$_2$ layer grow and Cu$_2$(In,Sn)$_2$ layer to be continuously consumed. Considering the duplex structure of coarse- and fine-grain Cu$_2$(In,Sn), a characteristic evolution model was proposed to describe the transformation of Cu$_2$(In,Sn) into Cu(In,Sn)$_2$ at 20 °C and 40 °C.

4) At the aging temperatures of 60 °C, 80 °C and 100 °C, Cu(In,Sn)$_2$ can transform into Cu$_2$(In,Sn) quickly within just 1 day. Under these conditions, the diffusion ability of the Cu atom is much stronger than that of the In atom, $k_{1\text{Cu}_2} > 3/2 k_{1\text{In}_2}$, causing the Cu$_2$(In,Sn)$_2$ layer to grow and the Cu(In,Sn)$_2$ later to be continuously consumed.

5) The reversible transformation between Cu$_2$(In,Sn) and Cu(In,Sn)$_2$ IMCs was first discovered through the special designs of three-step aging experiments performed at different temperatures. Its occurrence is closely related to the diffusion ability of the main reaction species (In/ Sn or Cu atoms) at different aging temperatures, which was verified by quantitative analyses of IMC growth.

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