Phase transformation between Cu(In,Sn)$_2$ and Cu$_2$(In,Sn) compounds formed on single crystalline Cu substrate during solid state aging

Feifei Tian, Zhi-Quan Liu, and Jingdong Guo
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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Interfacial reactions between eutectic SnIn and single crystalline Cu during solid-state aging at low temperature were investigated systematically. Three types of phase transformations between Cu(In,Sn)$_2$ layer and Cu$_2$(In,Sn) layer were observed, which are Cu(In,Sn)$_2$ grows and Cu$_2$(In,Sn) consumes at 40°C, Cu(In,Sn)$_2$ and Cu$_2$(In,Sn) grow simultaneously at 60°C, as well as Cu(In,Sn)$_2$ consumes and Cu$_2$(In,Sn) grows at 80 and 100°C. According to physicochemical approach, the chemical reactions at Cu/Cu$_2$(In,Sn)/Cu(In,Sn)$_2$/SnIn interfaces were discussed in detail. It was concluded that the diffusion ability of Cu and In atoms dominated different phase transformations. When diffusion constants $k_{1\text{In}2} > \frac{8}{3}k_{1\text{Cu2}}$ Cu(In,Sn)$_2$ will grow, and if $k_{1\text{Cu2}} \gg k_{1\text{In}2}$ Cu$_2$(In,Sn) will grow. Both Cu(In,Sn)$_2$ and Cu$_2$(In,Sn) can grow in the condition of $k_{1\text{In}2} \approx k_{1\text{Cu2}}$. The values of $k_{1\text{Cu2}}$ and $k_{1\text{In}2}$ at different temperatures on (100)Cu and (111)Cu substrate were also calculated or estimated by analyzing the growth kinetics of the compound layers. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4863336]

I. INTRODUCTION

The mechanical and serving properties of solder joints have close relation with their interfacial microstructure. As an important metallurgical bonding layer between a soldering alloy and the substrate metal, intermetallic compound (IMC) layer takes obvious effect on the reliability of solder joints.1–3 Till now, many researchers have worked on lead-free solders and investigated the nucleation and formation of IMCs during soldering4–8 as well as the growth kinetics of IMC layers during solid-state aging process.9–11 It is known that the growth of IMC layers plays an important role in the life of a packaging structure in microelectronic applications.

For solid-state growth kinetics of chemical compound layers in binary heterogeneous systems, numerous theoretical and experimental works have been carried out. These works can be divided into two distinct theoretical groups, diffusion model and physicochemical approach, which dominated over each other alternately in their development. The diffusion-based theory takes mainly account of the diffusing effect of reacting species that cross over the bulk of a growing chemical compound layer to the reaction site, but neglects the chemical reactions taking place at the interfaces. For example, Wagner12 established the pioneering diffusion theory based on Fick’s diffusion laws. He calculated the parabolic growth constant of a single-phase oxide on metal and derived the parabolic law of growth of a chemical compound layer, and developed a relationship between the interdiffusion coefficients with the parabolic growth rate constants in multiphase diffusion growth under quasi-steady-state local equilibrium conditions. Meanwhile, many other researchers13–18 were also devoted to the diffusion-based theory in many binary systems. On the other hand, the physicochemical theory in binary system, which paid attention to not only the diffusing transport of the reacting species but also the subsequent chemical reactions occurring at the interfaces, was also developed by many investigators at the same time. Evans19 first took account of the comparative effect of chemical and physical phenomena on the growth rate of a chemical compound layer and proposed an equation to prove this point. Recently, Paul et al.20 elucidated the role of the Kirkendall effect in the morphogenesis of Co-Si interdiffusion system. Moreover, Ghosh and Paul21 developed a physicochemical theory, which could be used in binary system for any end-member condition to explain the diffusion-controlled growth of single-phase or multiphase and to determine the diffusion parameters of product phases with a wide or narrow homogeneity range. The reported theoretical analyses matched very well with the experimental results in Ni-Al and Ag-Zn systems. More works in this area had been fulfilled by Dybkov,22–24 who studied the reaction diffusion and single-phase and multiphase solid-state growth of the chemical compound layers at the interface between two mutually insoluble substances in heterogeneous binary systems using physicochemical theory.

Based on previous studies, it was known that both the physicochemical theory and the diffusing theory led to the same results in determining diffusion parameters of product phases and calculating the thickness of chemical compound layers with a narrow homogeneity range. However, physicochemical approach has advantages of clearly clarifying the chemical reactions taking place at the interfaces and easily understanding without any speculative suppositions over diffusion approach. Line intermetallic compound with a narrow homogeneity range formed in heterogeneous binary system after soldering can be classified into chemical compound, and chemical reactions often occur in this system during
solid-state interdiffusion. Therefore, physicochemical theory seems to be more adequate than the diffusion theory in the study of interfacial reaction within solder joint. Though many researchers have done a lot of theoretical works based on the experimental results, few of them observed different reactions simultaneously. For example, one chemical compound consumed and the other grew, both of them grew simultaneously, as well as one chemical compound grew and the other consumed. The above-mentioned three conditions taking place in one and the same system are extremely rare, which has not been studied according to our knowledge.

In this study, physicochemical theory was utilized to elucidate chemical reactions taking place at the interfaces between two nearly mutually insoluble elementary substances In-48Sn solder and (100) and (111) single crystalline Cu during solid-state aging. Three kinds of phase transformations were observed, including Cu(In,Sn)2 layer grows and Cu2(In,Sn) layer consumes, Cu(In,Sn)2 and Cu2(In,Sn) layer grow simultaneously as well as Cu(In,Sn)2 layer consumes and Cu2(In,Sn) layer layer grows. Theoretical analyses revealed that the uniform and direct-view parameters $k_{Cu2}$ and $k_{In2}$ are responsible for different chemical reactions.

II. EXPERIMENTAL PROCEDURES

The solder used in this study was eutectic In-48Sn alloy, which was prepared by melting high purity Sn and In (>99.99%) in a carbon crucible, and the resulted eutectic composition was confirmed by X-ray diffraction. High purity single crystalline Cu (>99.999%) was selected as substrate. The (100) and (111) Cu single crystalline plates (40 × 4 × 2 mm²) were commercially purchased with polished and clean surfaces in roughness of below 0.5 nm, and the deviation of crystallographic orientation is within ±0.5°. Wetting scanning electron microscope (SEM) samples were prepared by reacting eutectic In-48Sn thin foil on single crystalline Cu substrates and reflowed at 160°C for 5 s, then cooled in air to ambient temperature. Afterwards, the samples were cleaned ultrasonically in acetone for 5 min to dissolve the remaining rosin mildly activated (RMA) on the sample surfaces. The samples were cut into 4 mm³ pieces and then aged in thermal ovens at a temperature range of 40–100°C for different times. SEM cross-sectional samples were ground successively with SiC papers and polished carefully with 0.05 μm Al2O3 powder suspension. All clean samples were observed with a LEO super35 and Quanta 600 scanning electron microscopes with energy-dispersive X-ray spectroscopy (EDS) system for compositional analyses. The thickness of IMC layers was measured using the image analyses software as described before.25

III. EXPERIMENTAL RESULTS

A. Interfacial reactions during aging at 40°C on (100) and (111) single crystalline Cu substrates

Based on our previous study,26 it was found that two crystal structural IMC layers with three different morphologies were formed after soldering at 160°C for 5 s, which are Cu(In,Sn)2 and duplex structure coarse-grain and fine-grain Cu2(In,Sn) being in thickness of about 1 μm, 0.5 μm, and 0.5 μm, respectively, from solder to substrate. As the coarse-grain and fine-grain Cu2(In,Sn) have the same Cu2In hexagonal crystal structure, it is reasonable to regard that chemical reactions take place between Cu(In,Sn)2 and Cu2(In,Sn) layer.

Fig. 1 shows the cross-sectional images of Cu(In,Sn)2 and Cu2(In,Sn) layer on (100)Cu substrate after aging at 40°C up to 90 days. In Fig. 1(a), the interface between Cu(In,Sn)2 layer adjacent to the solder and Cu2(In,Sn) layer next to Cu substrates after soldering was indicated by horizontal arrows, at which some coarse-grain Cu2(In,Sn) grains extruding into the Cu(In,Sn)2 layer. After 10 days aging of Fig. 1(b), it was seen that Cu2(In,Sn) layer changes from continuous to discontinuous as shown in region A. Furthermore, the thickness of Cu(In,Sn)2 layer increased and that of Cu2(In,Sn) layer decreased with elongated aging time. Fig. 1(c) shows the chemical reaction of IMC layers taken place after aging at 40°C for 60 days. It can be clearly seen that more discontinuous regions of Cu2(In,Sn) layer appeared and its thickness decreased dramatically due to its transformation into Cu(In,Sn)2 IMC. After 90 days aging at 40°C as shown in Fig. 1(d), only some Cu2(In,Sn) IMC islands remained, and the rest of which has transformed into Cu(In,Sn)2 completely. It was concluded that with increasing aging time, original Cu2(In,Sn) IMC after reflowing will
transform into Cu(In,Sn)$_2$ IMC eventually when aged at 40°C. Moreover, it was also observed that the interface between Cu$_2$(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. 1(c) and region C of Fig. 1(d). According to elemental analyses, new Cu(In,Sn)$_2$ IMC was formed in these regions. It means that original Cu$_2$(In,Sn) layer has transformed into Cu(In,Sn)$_2$ IMC completely, and the transformation is still going on with Cu substrates due to the fast diffusion of In and Sn atoms. Such chemical reaction taking place on (100)Cu substrate was also observed on (111)Cu substrate for long-term aging at 40°C.

To verify the above chemical reactions at the interfaces, EDS compositional analyses were carried out as shown in Fig. 2. Figs. 2(a) and 2(c) show the SEM cross-sectional images of the eutectic SnIn/(100)Cu solder joint aged at 40°C for 45 and 60 days, respectively, while Figs. 2(b) and 2(d) are the corresponding EDS line profiles. The EDS lines 1, 2, and 3 represent the intensity of Cu, Sn, and In, respectively, which is directly proportional to the content of the elements. From Figs. 2(a) and 2(b), it is clearly seen that in region 1 the content of Cu element in IMC layer keeps stable at some value, so do the contents of In and Sn elements. In region 2, the content of Cu is higher than that in region 1 but the intensity of In element shows an inverse phenomenon, which means the species of IMC in region 2 is different from those in region 1. EDS compositional analyses revealed that there exists a dramatic change in composition of IMC layers from 34.21Cu-51.71In-14.01Sn (at. %) in region 1 to 64.36Cu-15.21In-20.43Sn (at. %) in region 2. In the images of Figs. 2(c) and 2(d), region 1 corresponds to the eutectic SnIn solder, while region 2 is IMC layer. The contents of In, Sn, and Cu elements in IMC layer keep stable at certain values, which is consistent well with 34.21Cu-51.71In-14.01Sn (at. %). Thus, the only predominant IMC in region 2 becomes Cu(In,Sn)$_2$ without original Cu$_2$(In,Sn) after long-term aging at 40°C. Therefore, Fig. 2 shows the transitional process of IMCs from Cu$_2$(In,Sn) to Cu(In,Sn)$_2$, verifying the phase transformation from Cu$_2$(In,Sn) into Cu(In,Sn)$_2$. The uneven surface of Cu substrate implies that the interfacial reaction between SnIn solder and Cu has initiated, resulting in the IMC of Cu(In,Sn)$_2$. Same chemical reaction also takes place on (111)Cu substrate for long-term aging at 40°C.

B. Interfacial reactions during aging at 60°C on (100) and (111) single crystalline Cu substrates

When aged at 60°C, the interfacial microstructure of eutectic SnIn/Cu solder joint was shown in Fig. 3, in which the interface between Cu(In,Sn)$_2$ and Cu$_2$(In,Sn) was indicated by horizontal arrows. Being different from those observed in Fig. 1 aged at 40°C, it was found that the
continuous Cu(In,Sn)$_2$ layer (indicated with inclined arrows) was still existing and kept growing simultaneously with Cu$_2$(In,Sn) layer on both (100) and (111) single crystalline Cu substrates after aging for 6 and 10 days or even up to 15 days. Based on thickness measurement, it is found that the thickness of Cu$_2$(In,Sn) layer is nearly the same with that of Cu(In,Sn)$_2$ on both two single crystalline Cu substrates. However, the thickness of Cu$_2$(In,Sn), Cu(In,Sn)$_2$, and the total IMC layers on (100) single crystalline Cu plane is larger than that on (111) single crystalline Cu plane at the same aging conditions.

C. Interfacial reactions during aging at 80°C and 100°C on (100) and (111) single crystalline Cu substrates

For comparison, the interfacial reactions during aging at 80°C and 100°C on (100) and (111) Cu substrates were also investigated, and the images after 1 day aging were shown in Fig. 4. Compared with nearly the same thickness of continuous Cu(In,Sn)$_2$ and Cu$_2$(In,Sn) IMC layers after soldering as shown in Fig. 1(a), Cu$_2$(In,Sn) became the dominated IMC layer in Fig. 4, and there nearly does not exist any Cu(In,Sn)$_2$ IMC on (100) and (111) Cu substrates after aging at 80°C and 100°C for only 1 day. It indicates that chemical reaction between Cu(In,Sn)$_2$ layer and Cu$_2$(In,Sn) layer has taken place. Long-term solid-state aging at 80°C and 100°C can result in the phase transformation from Cu(In,Sn)$_2$ into Cu$_2$(In,Sn). Measured by image analyses software, the thickness of Cu$_2$(In,Sn) layer formed on (100)Cu is larger than that formed on (111)Cu substrate under the same aging temperature and time. Moreover, the thickness of Cu$_2$(In,Sn) layer aged at 100°C is larger than that aged at 80°C under the same substrate and aging time. After the complete phase transformation from Cu(In,Sn)$_2$, Cu$_2$(In,Sn) layer kept continuous growth, which can be attributed to the chemical reaction between eutectic SnIn solder and Cu substrate.

Concluded from Figs. 1–4, chemical reactions indeed took place at the interfaces between eutectic SnIn solder and single crystalline Cu substrates, which is dependent on aging temperature as summarized in Table I. The IMC on the leftward of the arrow represents the reactant in chemical reaction, while the rightward one acts as product, and the sign “+” means that both two IMCs can grow simultaneously. As presented in Table I, all chemical reactions can be classified into three types: Cu(In,Sn)$_2$ layer grows and Cu$_2$(In,Sn) layer consumes, Cu(In,Sn)$_2$ and Cu$_2$(In,Sn) layers grow simultaneously, as well as Cu(In,Sn)$_2$ layer consumes and Cu$_2$(In,Sn) layer grows. Which type of phase transformation will occur has a close relationship with aging temperatures. As SnIn/Cu solder joint was less studied, no one has observed the above chemical reactions before. In order to describe these
TABLE I. Summary of phase transformations between Cu(In,Sn)2 and Cu2(In,Sn) compounds at different temperatures on (100) and (111) single crystalline Cu substrates.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Temperature (°C)</th>
<th>Layer Interface</th>
<th>Partial chemical reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) Cu</td>
<td>40</td>
<td>Cu2In → CuIn2</td>
<td>Cu2In + CuIn2, CuIn2 → Cu2In</td>
</tr>
<tr>
<td>(111) Cu</td>
<td>60</td>
<td>Cu2In → CuIn2</td>
<td>Cu2In + CuIn2, CuIn2 → Cu2In</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

chemical reactions quantitatively, physicochemical theory model was introduced to retrieve a uniform and direct-view parameter for different kinds of interfacial reactions.

IV. DISCUSSIONS

A. Theoretical model of chemical reactions at the interfaces

To understand and explain the different conditions for chemical reactions, efforts were made to give a uniform and direct parameter for quantitative description. Dybkov22–24 had studied far and deeply on the reaction diffusion in heterogeneous binary systems focusing on the growth of one compound layer, two compound layers, and multiple compound layers at the interface between two mutually insoluble substances. However, the observed three conditions that took place in one and the same system in this study are extremely rare. As both Cu(In,Sn)2 and Cu2(In,Sn) IMCs are Cu-In based crystal structure, in which part of In atoms are substituted with Sn atoms due to their close atomic radius, the eutectic SnIn/Cu solder joint agrees with the mutually insoluble substances system and is adapted to the physicochemical reaction theory. To illustrate the thickness change or the interfacial movement among SnIn/Cu(In,Sn)2/Cu2(In,Sn)/Cu layers, a schematic diagram is given in Fig. 5 at an infinitesimal period of time $dt$, and four partial chemical reactions taking place at the different interfaces can be given as follows:

1. Layer Interface Partial chemical reactions
   - Cu2In: In$_{\text{diffuse}}$ + 2Cu$_{\text{surface}}$ = Cu2In, (1)
   - CuIn2: 3In$_{\text{diffuse}}$ + CuIn2 = 2Cu2In, (2)
   - Cu2In: 2In$_{\text{diffuse}}$ + Cu2In = 2CuIn2, (3)
   - Cu2In: Cu$_{\text{diffuse}}$ + 2In$_{\text{surface}}$ = CuIn2, (4)

![Fig. 5. Schematic diagram illustrating the thickness change of Cu(In,Sn)2 and Cu2(In,Sn) layer growing between elementary substances Cu and SnIn solder at the expense of diffusion of both components.](image)

According to the theory, all above four chemical reactions proceed only at the interfaces, which are regarded as transition regions of the interacting phases. No chemical reactions take place within Cu(In,Sn)2 and Cu2(In,Sn) layer, which are only transport paths for diffusing Cu and In atoms. It should be pointed out that here $In_{\text{diffuse}}$ is used to delegate both In and Sn for simplicity, because the atomic percentage of In element in Cu(In,Sn)$_2$ is about 50% and that in Cu2(In,Sn) is nearly equivalent to Sn element, and Cu(In,Sn)$_2$ and Cu2(In,Sn) are CuIn$_2$ and Cu2In based crystal structure, respectively.

Basing on these four formulæ, it is known that both Cu(In,Sn)$_2$ layer and Cu2(In,Sn) layer can grow and consume at different chemical reactions. For example, partial chemical reaction formulæ (1) and (2) make the Cu2(In,Sn) layer grow due to the diffusion and reaction of In, Sn, and Cu atoms at the interface 1 and 2, while partial chemical reaction formulæ (3) proceeding at interface 2 consumes Cu2(In,Sn) layer due to the formation of Cu(In,Sn)$_2$ layer. Inversely, partial chemical reaction formulæ (3) and (4) make the thickness of Cu(In,Sn)$_2$ layer increase due to the diffusion and reaction of In, Sn, and Cu atoms at the interface 1 and 2, while partial chemical reaction formulæ (1) and (2) make the Cu2(In,Sn) layer decrease. Therefore, the total change in thickness of Cu(In,Sn)$_2$ layer and Cu2(In,Sn) layer during the time $dt$ is comprised of three terms considering different interfacial reactions as illustrated in Fig. 5:

$$dx = dx_{\text{In1}} + dx_{\text{Cu2}} - dx_{\text{Cu}}, \quad (5)$$

$$dy = dy_{\text{In2}} + dy_{\text{Cu1}} - dy_{\text{Cu}}. \quad (6)$$

According to the growth kinetics of IMC layers, an infinitesimal change in thickness $dx$ of Cu(In,Sn)$_2$ and Cu2(In,Sn) layer during the infinitesimal time $dt$ could be described with following differential equations:

$$\frac{dx}{dt} = \frac{k_{\text{0In1}}}{1 + \left(\frac{k_{\text{0In1}}/k_{\text{1In1}}}{k_{\text{0Cu2}}/k_{\text{1Cu2}}}\right) + \frac{k_{\text{0Cu2}}}{1 + \left(\frac{k_{\text{0Cu2}}/k_{\text{1Cu2}}}{k_{\text{0In1}}/k_{\text{1In1}}}\right)}, \quad (7)$$

$$\frac{dy}{dt} = \frac{k_{\text{0In2}}}{1 + \left(\frac{k_{\text{0In2}}/k_{\text{1In2}}}{k_{\text{0Cu3}}/k_{\text{1Cu3}}}\right) + \frac{k_{\text{0Cu3}}}{1 + \left(\frac{k_{\text{0Cu3}}/k_{\text{1Cu3}}}{k_{\text{0In2}}/k_{\text{1In2}}}\right)}, \quad (8)$$

where $k_{\text{0In1}}$ is the chemical constant (m/s), indicating that the MC growth is controlled by chemical reaction. In the subscript of $0In1$, 0 represents the chemical reaction mechanism of the Cu2(In,Sn) layer, while $In1$ indicates that In atoms diffuse through the bulk IMC layers to interface 1 and proceed chemical reactions with Cu atoms. $k_{\text{1In1}}$ is the physical (diffusion) constant (m$^2$/s), which shows the MC layer is controlled by diffusion and identifies the reaction-diffusion coefficient of element In in the lattice of Cu2(In,Sn) IMC. In the subscript of $k_{\text{1In1}}$, 1 represents that diffusion mechanism controls the growth of the Cu2(In,Sn) layer, and the other...
signs have analogous meanings as described above. The signs \( p, q, r, \) and \( s \) correspond to 2, 1, 1, and 2 in \( \text{Cu}_2\text{In} \) and \( \text{CuIn}_2 \) IMCs, and \( g \) stands for the ratio of molar volume of \( \text{Cu}_2\text{In} \) and \( \text{CuIn}_2 \) compounds. Owing to the very close density and molecular weight between In and Sn atoms, it is proper to replace \( \text{Cu}_2\text{(In,Sn)} \) and \( \text{Cu(In,Sn)}_2 \) with \( \text{Cu}_2\text{In} \) and \( \text{CuIn}_2 \) during discussion, so the value of \( g \) could be obtained as about 3/4.

From formulae (7) and (8), it is known that three group of factors will affect the thickness change of \( \text{Cu}_2\text{(In,Sn)} \) and \( \text{Cu(In,Sn)}_2 \) layers: \( k_0 \) and \( k_1 \) (chemical and physical constants of elements), \( g \) (the ratio of molar volume of \( \text{Cu}_2\text{In} \) and \( \text{CuIn}_2 \) IMCs), and the signs \( (p, q, r, \) and \( s) \). In this study, only the values of \( k_0 \) and \( k_1 \) are unknown. Here, we focused on the growth kinetics of \( \text{Cu(In,Sn)}_2 \) and \( \text{Cu}_2\text{(In,Sn)} \) layers after soldering, whose thickness all reached at several hundreds of micrometers eventually. It is well known that the rate-limiting step is controlled by diffusion mechanism within the range of thickness, this is to say, \( k_{1\text{In}_2} \gg k_{1\text{Cu}_2} \gg k_{1\text{Cu}_2\text{In}_2} \), \( k_{0\text{Cu}_2} \gg k_{1\text{Cu}_2\text{In}_2} \), \( k_{0\text{Cu}_2} \gg k_{1\text{Cu}_2\text{In}_2} \), \( k_{1\text{Cu}_2} \gg k_{1\text{Cu}_2\text{In}_2} \). Thus, differential equations (7) and (8) can be further derived as follows. If \( dx/dt > 0 \) or \( dy/dt > 0 \), the IMC layer grows, while if \( dx/dt < 0 \) or \( dy/dt < 0 \), the IMC layer consumes

\[
\frac{dx}{dt} = \frac{k_{1\text{In}_2}}{x} + \frac{k_{1\text{Cu}_2}}{x} - \frac{3k_{1\text{In}_2}}{8y}, \tag{9}
\]

\[
\frac{dy}{dt} = \frac{k_{1\text{In}_2}}{y} + \frac{k_{1\text{Cu}_2}}{y} - \frac{2k_{1\text{Cu}_2}}{3x}. \tag{10}
\]

**B. Chemical reactions between \( \text{Cu(In,Sn)}_2 \) and \( \text{Cu}_2\text{(In,Sn)} \) layers during solid-state aging**

1. **\( \text{Cu(In,Sn)}_2 \) and \( \text{Cu}_2\text{(In,Sn)} \) layers grow simultaneously**

For better understanding, the condition of both IMC layer growth was discussed first. Fig. 6 shows the dependence of the thickness of the \( \text{Cu}_2\text{(In,Sn)} \) and \( \text{Cu(In,Sn)}_2 \) IMCs formed on (100) and (111) Cu substrates as a function of aging time at \( 60^\circ\text{C} \). It is obviously that \( \text{Cu}_2\text{(In,Sn)} \) and \( \text{Cu(In,Sn)}_2 \) layers grow simultaneously on (100) and (111) single crystalline Cu substrates. Thickness increase of both IMC layers will change their growth mechanism from chemical reaction to diffusion-controlled, which means that only partial chemical reactions (2) and (3) between diffusing In, Sn atoms and \( \text{Cu}_2\text{(In,Sn)} \) IMC as well as diffusing Cu atoms and \( \text{Cu}_2\text{(In,Sn)} \) IMC can take place, while partial chemical reactions (1) and (4) cannot proceed. That is to say, the terms of \( k_{1\text{In}_2}/x \) and \( k_{1\text{Cu}_2\text{In}_2}/y \) can be omitted and only partial chemical reactions (2) and (3) proceed at interface 2. Thus, the following differential equations can be obtained from formulae (9) and (10)

\[
\frac{dx}{dt} = \frac{k_{1\text{Cu}_2}}{x} - \frac{3k_{1\text{In}_2}}{8y}, \tag{11}
\]

\[
\frac{dy}{dt} = \frac{k_{1\text{In}_2}}{y} - \frac{2k_{1\text{Cu}_2}}{3x}. \tag{12}
\]

From Fig. 6, it can be clearly seen that the thickness of both IMC layers increases with aging time and the growth regime is controlled by diffusion. Thus, it is concluded that \( dx/dt > 0 \) and \( dy/dt > 0 \), which means

\[
\frac{k_{1\text{Cu}_2}}{x} > \frac{3k_{1\text{In}_2}}{8y}, \tag{13}
\]

\[
\frac{k_{1\text{In}_2}}{y} > \frac{2k_{1\text{Cu}_2}}{3x}. \tag{14}
\]

Hence, a range of the thickness ratio between \( \text{Cu}_2\text{(In,Sn)} \) and \( \text{Cu(In,Sn)}_2 \) layers can be derived

\[
\frac{2k_{1\text{Cu}_2}}{3k_{1\text{In}_2}} < \frac{x}{y} < \frac{8k_{1\text{Cu}_2}}{3k_{1\text{In}_2}}. \tag{15}
\]

It is obtained that the thickness ratio of \( \text{Cu}_2\text{(In,Sn)} \) and \( \text{Cu(In,Sn)}_2 \) layer depends on the values of the diffusion constants \( k_{1\text{In}_2} \) and \( k_{1\text{Cu}_2} \) on single crystalline Cu at \( 60^\circ\text{C} \). Fig. 6 shows that the longer the aging time goes on, the closer the
value of $x/y$ becomes, and the value of $x/y$ is slightly greater than 1 and very close to 1 after aging for 15 days.

According to formula (15), the competitive growth of Cu$_2$(In,Sn) and Cu(In,Sn)$_2$ is determined by the diffusion constants of Cu ($k_{1Cu2}$) and In ($k_{1In2}$) at interface 2. However, these data are absent for eutectic SnIn/Cu system in reported literatures. In order to calculate diffusion constants of $k_{1Cu2}$ and $k_{1In2}$ in In-48Sn/Cu solder joint at 60°C, the growth kinetics of Cu$_2$(In,Sn) and Cu(In,Sn)$_2$ were plotted in the square of the thickness as a function of aging time, as shown in Fig. 7. Though the growth of IMCs is due to the interdiffusion of end-member materials in heterogeneous system, according to partial chemical reactions (2) and (3), the growth of Cu$_2$(In,Sn) and Cu(In,Sn)$_2$ layers is mainly attributed to the diffusion of Cu and In atoms, respectively, when aged at 60°C. Moreover, the diffusion coefficient of Cu in Cu$_2$(In,Sn) layer is larger than that in Cu(In,Sn)$_2$ layer and the diffusion ability of In in Cu(In,Sn)$_2$ layer is stronger than that in Cu$_2$(In,Sn) layer, so the diffusion constants $k_{1Cu2}$ and $k_{1In2}$ can be reasonably derived from the plots in Fig. 7.

It is known that the growth of an IMC layer could generally be described by a power law

$$x^2 - x_0^2 = 2k_1t,$$  

(16)

where $x$ is the thickness of IMC aging for different time, $x_0$ is the thickness of IMC after soldering, $k_1$ is the diffusion constant of diffusing element, and $t$ is the aging time. According to the data presented in Fig. 7, on (100)Cu substrate $k_{1Cu2} = 1.59 \times 10^{-18}$ and $k_{1In2} = 1.46 \times 10^{-18}$ m$^2$/s, respectively, while on (111)Cu $k_{1Cu2} = 9.42 \times 10^{-19}$ and $k_{1In2} = 8.91 \times 10^{-19}$ m$^2$/s, respectively. Comparing the calculated results, the diffusion constant $k_{1Cu2}$ is slightly larger than $k_{1In2}$ on (100) and (111) single crystalline Cu at 60°C. Hence, the thickness of Cu$_2$(In,Sn) layer is slightly larger than that of Cu(In,Sn)$_2$ layer, and both two IMC layers can grow simultaneously. Moreover, the corresponding diffusion constants $k_{1Cu2}$ and $k_{1In2}$ on (100)Cu is larger than those on (111)Cu, which leads to a thicker Cu$_2$(In,Sn) and Cu(In,Sn)$_2$ layers on (100)Cu than those on (111)Cu when aged at 60°C. This agrees well with the reported works on the growth of Cu-Sn compounds on single crystalline Cu substrate, in which first principle calculations revealed that (111)Cu plane has a lower surface energy than (100)Cu and the release of Cu atoms on (111)Cu plane is more difficult for IMC growth.

2. Cu(In,Sn)$_2$ layer consumes and Cu$_2$(In,Sn) layer grows

Under the condition of Cu(In,Sn)$_2$ layer consumes and Cu$_2$(In,Sn) layer grows, namely $dx/dt > 0$ and $dy/dt < 0$, thus formulae (9) and (10) can be rewritten as

$$\frac{8k_{1In1} + k_{1Cu2}}{3k_{1In2}} > \frac{x}{y},$$  

(17)

$$\frac{2}{3k_{1In2} + k_{1Cu3}} > \frac{x}{y}.$$  

(18)

During solid-state aging, Cu(In,Sn)$_2$ consuming and Cu$_2$(In,Sn) growing will eventually lead to $x \gg y$. Putting $x \gg y$ into the inequality (18), it can be derived as

$$k_{1Cu2} \gg k_{1In2} + k_{1Cu3}.$$  

(19)

Owing to $k_{1Cu3} > 0$, it can be further described as

$$k_{1Cu2} \gg k_{1In2}.$$  

(20)

From the above calculations, it is known that under the condition of Cu(In,Sn)$_2$ consuming and Cu$_2$(In,Sn) growing, it is the strong diffusion ability of Cu atoms from (100) and (111) Cu substrates to diffuse through the IMCs that enables phase transformation from Cu(In,Sn)$_2$ into Cu$_2$(In,Sn) layer. The stronger diffusion ability of Cu atom than that of In atom ($k_{1Cu2} \gg k_{1In2}$) makes the partial chemical reaction 2 dominate over 3. Thus, Cu(In,Sn)$_2$ layer consumes and Cu$_2$(In,Sn) layer grows, until Cu(In,Sn)$_2$ transforms into Cu$_2$(In,Sn) IMC completely. As clearly shown in Fig. 4 and Table I, when the aging temperature was 80°C and 100°C,

![FIG. 7. Plots of the square of the thickness of Cu$_2$(In,Sn) layer and Cu(In,Sn)$_2$ layer on single crystalline (100)Cu (a) and (111)Cu (b) substrates as a function of aging time at 60°C.](image-url)
the Cu(In,Sn)₂ has transformed into Cu₂(In,Sn) completely only for 1 day on (100) and (111) Cu surfaces, after that only Cu₂(In,Sn) layer grows continuously. After the complete transformation from Cu(In,Sn)₂ to Cu₂(In,Sn), Cu₂(In,Sn) layer becomes the only growing interfacial IMC layer, and the whole reaction system changes from Fig. 5 to Fig. 8 with one IMC layer and two interfaces. Hence, the partial chemical reactions change from (1)–(4) to (21) and (22) at the interface during solid-state aging above 80 °C.

Layer Interface Partial chemical reactions

Cu₂In  1 In_{diffuse} + 2Cu_{surface} = Cu₂In, \quad (21)

2 2Cu_{diffuse} + In_{surface} = Cu₂In. \quad (22)

The change of reaction system from Fig. 5 to Fig. 8 can be verified by thickness measurement of formed IMC. According to the partial chemical reaction (2) during phase transformation, the following equations can be derived:

\[
\frac{m_{\text{CuIn}n_2}}{m_{\text{CuIn}}} = \frac{1}{2} \frac{M_{\text{CuIn}n_2}}{M_{\text{CuIn}}}, \quad (23)
\]

\[
\frac{\rho_{\text{CuIn}n_2} S_{\text{CuIn}n_2} \cdot x_{\text{CuIn}n_2}}{\rho_{\text{CuIn}} S_{\text{CuIn}} x_{\text{CuIn}}} = \frac{1}{2} \frac{M_{\text{CuIn}n_2}}{M_{\text{CuIn}}}, \quad (24)
\]

\[
\frac{\rho_{\text{CuIn}n_2} S_{\text{CuIn}n_2} \cdot x_{\text{CuIn}n_2}}{\rho_{\text{CuIn}} S_{\text{CuIn}} x_{\text{CuIn}}} = \frac{1}{2} \frac{M_{\text{CuIn}n_2}}{M_{\text{CuIn}}}, \quad (25)
\]

where \( m \) is the mass, \( M \) is relative molecular mass, \( \rho \) is the density of corresponding IMC, \( S \) is the wetting area and \( S_{\text{CuIn}n_2} = S_{\text{Cu2In}} \), \( x \) is the thickness of IMC. It can be calculated that \( \rho_{\text{CuIn}n_2} \) is about 7.86 g/cm³, \( \rho_{\text{Cu2In}} \) is about 8.41 g/cm³, \( M_{\text{CuIn}n_2} = 294 \text{ g/mol} \), and \( M_{\text{Cu2In}} = 243 \text{ g/mol} \). As In and Sn have very similar parameters, which makes no much difference. So, putting the above values into Eq. (25) yields the following equation:

\[
x_{\text{CuIn}n_2} = 1.54 x_{\text{CuIn}n_1}. \quad (26)
\]

It means when 1 \( \mu m \) of Cu(In,Sn)₂ consumes, 1.54 \( \mu m \) of Cu₂(In,Sn) IMC will grow. Based on the image analyses software, it is known that the thickness of continuous Cu(In,Sn)₂ and Cu₂(In,Sn) layers is about 1 \( \mu m \) and 1 \( \mu m \) after soldering at 160 °C for 5 s (see Fig. 1(a)), respectively. According to Eq. (26), when chemical reaction (2) takes place and the thickness of 1 \( \mu m \) Cu(In,Sn)₂ transforms into Cu₂(In,Sn) completely, the total thickness of Cu₂(In,Sn) layer should be 2.54 \( \mu m \), consisting 1 \( \mu m \) original reflowed layer and 1.54 \( \mu m \) transformed layer. However, after aging at 100 °C for 1 day the total thickness of Cu₂(In,Sn) layer is 5.41 \( \mu m \) and 4.95 \( \mu m \) on (100) and (111) Cu, respectively, which are much larger than theoretical thickness of 2.54 \( \mu m \).

It proves that after Cu(In,Sn)₂ IMC transforming into Cu₂(In,Sn) completely, the whole reaction system changes from Fig. 5 to Fig. 8, and Cu₂(In,Sn) grows continuously as the only existing interfacial IMC through chemical reactions (21) and (22), whose growth changes from monodiffusion of reacting species with two compound layers to interdiffusion with the only existing Cu₂(In,Sn) IMC layer.

Based on the thickness measurement of Cu₂(In,Sn), the interdiffusion coefficient can be calculated according to Eq. (16). When aged at 80 °C, it was obtained that \( D_{(100)} = 1.97 \times 10^{-17} \text{ m}^2/\text{s} \) and \( D_{(111)} = 1.51 \times 10^{-17} \text{ m}^2/\text{s} \), while when aged at 100 °C there are \( D_{(100)} = 1.03 \times 10^{-16} \) and \( D_{(111)} = 9.06 \times 10^{-17} \text{ m}^2/\text{s} \), where \( D \) represents interdiffusion coefficient. The above conditions of Cu₂(In,Sn) layer growing while Cu(In,Sn)₂ layer consuming can be summarized as \( k_{1\text{Cu2}} \gg k_{1\text{In2}} \).

3. Cu(In,Sn)₂ layer grows and Cu(In,Sn)₂ consumes

Fig. 9 shows the relationship of the thickness of IMCs on (100)Cu substrate as a function of aging time during solid-state aging at 40 °C, which represents the evolution process of chemical reactions at the interfaces. The upper black line, middle red line, and lower blue line represent the thickness of total IMCs, Cu(In,Sn)₂ IMC, and unreacted Cu(In,Sn), respectively. The total Cu(In,Sn)₂ IMC consists of two parts, one comes from soldering and the other is transformed from Cu(In,Sn) IMC. It can be clearly seen that the thickness of Cu₂(In,Sn) layer (the lower blue line) keeps almost stable during aging from 1 to 30 days with a slight decrease from 1.02 \( \mu m \) to about 0.92 \( \mu m \). Dramatic decrease

![FIG. 8. Schematic diagram illustrating the thickness change of Cu₂(In,Sn) layer growing between elementary substances Cu and SnIn solder at the expense of diffusion of both components.](Image)

![FIG. 9. Plots of the thickness of IMCs on (100)Cu as a function of aging time during solid-state aging at 40 °C for different time.](Image)
During solid-state aging at 40 °C, the condition of Cu2(In,Sn) consuming and Cu(In,Sn)2 growing leads to the thickness change of IMC layers y > x. Assuming y = x (at the beginning stage of aging), and put it into the inequality (27), it can be derived as

$$\frac{3}{8} \frac{k_{1In2}}{k_{1In1} + k_{1Cu2}} > \frac{y}{x}.$$  \hfill (27)

Owing to \(k_{1In1} > 0\), it can be safely concluded that

$$k_{1In2} > \frac{8}{3}k_{1Cu2}.$$  \hfill (29)

It means the diffusion ability of In atoms is at least several times stronger than that of Cu, and the partial chemical reaction (3) dominates over (2) when aged at 40 °C, making Cu2(In,Sn) transform into Cu(In,Sn)2. In this process, the consumption of Cu2(In,Sn) IMC (reaction 3) exceeds over its growth (reaction 2), which indicates Cu2(In,Sn) IMC is kinetically unstable not thermodynamically unstable in nature.

According to partial chemical reaction (3), the following equations can be derived:

$$\frac{m_{CuIn}}{m_{CuIn2}} = \frac{1}{2} \frac{M_{CuIn}}{M_{CuIn2}},$$  \hfill (31)

$$\rho_{CuIn} S_{CuIn} x_{CuIn} = \frac{1}{2} \frac{M_{CuIn}}{M_{CuIn2}}.$$  \hfill (32)

$$\rho_{CuIn} x_{CuIn} = \frac{1}{2} \frac{M_{CuIn}}{M_{CuIn2}}.$$  \hfill (33)

Inserting the above-mentioned values into Eq. (33) as described in Eq. (24), the relationship during phase transformation can be given as

$$x_{CuIn2} = 2.58x_{CuIn}.$$  \hfill (34)

It means when 1 μm of duplex structure Cu2(In,Sn) consumes, 2.58 μm of Cu(In,Sn)2 grows. As shown in Fig. 1(a), the initial thickness of both Cu2(In,Sn) and Cu(In,Sn)2 layer is about 1 μm after soldering. When Cu2(In,Sn) IMC transforms into Cu(In,Sn)2 layer completely, the total thickness of Cu(In,Sn)2 layer should be 3.58 μm, if no other chemical reactions take place besides the partial chemical reaction (3). However, the thickness of Cu(In,Sn)2 layer aging for 60 and 90 days reaches to 3.77 μm (Fig. 1(c)) and 4.69 μm (Fig. 1(d)), respectively. It indicates that besides the chemical reaction (3) other chemical reactions also contributed the growth of Cu(In,Sn)2 layer especially when Cu2(In,Sn) IMC was consumed completely.

Suffering long-term aging, Cu(In,Sn)2 becomes the only growing IMC at the interface, and the whole reaction system changes from Fig. 5 to Fig. 10. As a result, reactions (1)–(4) also change as follows:

\[\text{Layer Interface Partial chemical reactions}\]

- CuIn2 1 2In_{diffuse} + Cu_{surface} = CuIn2, \hfill (35)
- 2Cu_{diffuse} + 2In_{surface} = CuIn2. \hfill (36)

On the one hand, when In, Sn atoms with stronger diffusion ability reach Cu sides and react with Cu atom, the partial chemical reaction (35) takes place to form Cu(In,Sn)2 IMC. On the other hand, when Cu atoms with slower
diffusion ability diffuse through IMCs to eutectic SnIn solder, the partial chemical reaction (36) takes place to form Cu(In,Sn)₂ IMC. This was proved by experimental observations as shown in Fig. 1. The interface between Cu(In,Sn)₂ IMC layer and (100)Cu substrate becomes uneven and concaves into Cu sides, and the original Cu₂(In,Sn) IMC adjacent to Cu transforms into Cu(In,Sn)₂ during aging at 40°C for long time. The above conditions about the consuming of Cu₂(In,Sn) layer and the growth of Cu(In,Sn)₂ layer can be summarized as \( k_{1\text{In}2} > 8/3k_{1\text{Cu}2} \) at least.

According to physicochemical approach as discussed above, the different chemical reactions taking place at Cu/Cu₂(In,Sn)/Cu(In,Sn)₂/SnIn interfaces were mainly determined by the diffusion ability of Cu and In atoms through the IMC layer to the interface 2 for reaction, namely \( k_{1\text{Cu}2} \) and \( k_{1\text{In}2} \). Moreover, when the reaction system with two compound layers changes to the reaction system with only one compound layer, the monodiffusion of species changes to interdiffusion. Their values can be qualitatively compared or even quantitatively calculated through the analyses of growth kinetics of the IMC layer, which are summarized in Table II.

V. CONCLUSIONS

In the solder joint between eutectic SnIn and single crystalline Cu that can be regarded as the mutually insoluble substances system, three types of phase transformations between Cu(In,Sn)₂ and Cu₂(In,Sn) two IMC layers were observed during solid-state aging at different temperatures, which is rarely studied and reported before. Combining experimental observations on IMC growth and physicochemical analyses on interfacial reactions, the following conclusions can be drawn:

1. When solid-state aged at 40°C, Cu₂(In,Sn) compound transformed into Cu(In,Sn)₂ compound gradually, during which dramatic consumption of Cu₂(In,Sn) happened after 30 days. At this temperature, the diffusion rates of In and Sn atoms are at least several times stronger than that of Cu atoms, namely \( k_{1\text{In}2} > 8/3k_{1\text{Cu}2} \), which makes Cu(In,Sn)₂ layer grow and Cu₂(In,Sn) consume continuously.

2. Cu(In,Sn)₂ and Cu₂(In,Sn) layers would grow simultaneously at an aging temperature of 60°C. In this case, the diffusion ability of Cu and In/Sn atoms is close to each other (\( k_{1\text{Cu}2} \approx k_{1\text{In}2} \)), which can be calculated according to the growth kinetics of IMC layers as \( k_{1\text{Cu}2} = 1.59 \times 10^{-18} \text{ m}^2/\text{s}, k_{1\text{In}2} = 1.46 \times 10^{-18} \text{ m}^2/\text{s}, \) and \( k_{1\text{Cu}2} = 9.42 \times 10^{-19} \text{ m}^2/\text{s}, k_{1\text{In}2} = 8.91 \times 10^{-19} \text{ m}^2/\text{s}. \)

3. At an aging temperature of 80 or 100°C, Cu(In,Sn)₂ compound can transform into Cu₂(In,Sn) quickly within 1 day. Under this condition, the diffusion ability of Cu atom is much stronger than that of In atom, which is \( k_{1\text{Cu}2} \gg k_{1\text{In}2} \). The calculated interdiffusion coefficients are \( D_{(100)} = 1.97 \times 10^{-17} \text{ m}^2/\text{s} \) and \( D_{(111)} = 1.51 \times 10^{-17} \text{ m}^2/\text{s} \) at 80°C, and \( D_{(100)} = 1.03 \times 10^{-16} \text{ m}^2/\text{s} \) and \( D_{(111)} = 9.06 \times 10^{-17} \text{ m}^2/\text{s} \) at 100°C.

4. When one of Cu(In,Sn)₂ and Cu₂(In,Sn) compounds transformed into the other completely, the reaction system changes from double-IMC layers into single-IMC layer, and the reacting product between the two end-member substances is the only existing IMC; as a result, the monodiffusion of reacting species changes into interdiffusion.

5. Under the same reacting conditions, the thickness of the Cu₂(In,Sn), Cu(In,Sn)₂, and the total IMC layers on (100) single crystalline Cu substrate is larger than that on (111) single crystalline Cu substrate, which implies that (100)Cu surface is more active during interfacial reactions.

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