Effects of anisotropic β-Sn alloys on Cu diffusion under a temperature gradient

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Abstract

The diffusion mechanism of Cu in a thin layer of Sn–3.5Ag sandwiched between two Cu foils was systematically investigated under a temperature gradient of 2200 °C m⁻¹. Experimental observation and theoretical derivation reveal that the microstructural evolutions induced by thermomigration are significantly affected by the tetragonal anisotropy of Sn. The thermomigration flux of Cu increased with the squared value of cos α, the angle between the c-axis of the Sn grain and the temperature gradient. When the c-axis of the Sn grain was parallel to the temperature gradient, a larger thermomigration flux of Cu was induced and the Cu atoms migrated from the hot end toward the cold end. This tended to form a prominent asymmetrical microstructure and cause failure: serious dissolution of intermetallic compounds (IMCs) and excessive consumption of Cu foil occurred at the hot end whereas abnormal accumulation of IMCs was observed at the cold end. Instead, when they are perpendicular, thermomigration would be mitigated due to the lower induced flux. No failure or symmetrical growth of IMCs was found at either interface.

Keywords: Thermomigration; Lead-free solder; Under bump metallization; Sn grain orientation; Intermetallic compound

1. Introduction

Thermomigration (TM), one kind of mass transport induced by a temperature gradient, has been regarded as one of the critical reliability issues for electronic packaging technology. In flip-chip technology, thermomigration of solder joints has been observed to occur because of electromigration [1–4]. When the solder joints are current-stressed, the resultant Joule heating from the chip side is higher than that from the substrate side due to the geometrical configurations of the electronic package [4,5], causing a non-uniform temperature distribution in solder joints. In addition, the effect of current crowding leads to the chip side of solder joints being hotter than the substrate side.

Consequently, a temperature gradient is established across solder joints. Many investigations have reported that a temperature gradient of 1000 °C cm⁻¹ is sufficient to trigger thermomigration and thermomigration can cause element redistribution in solder alloys [2–4,6,7]: Sn atoms move to the hot end while Pb and Bi atoms move toward the cold end. The under-bump-metallization (UBM) element, such as Cu and Ni, tends to migrate under a temperature gradient as well. Chen et al. [8,9] observed the temperature-gradient-induced dissolution of the Cu UBM layer at the hot end and the direction of Cu migration toward the cold end. They also found that the critical temperature gradient to trigger thermomigration of Cu atoms in Pb-free solders was ∼400 °C cm⁻¹ [8]. Moreover, in Ouyang’s study [10,11], Ni atoms were observed to be driven from the hot end toward the cold end in micro-solder joints when a temperature gradient existed.
Recently, a three-dimensional integrated circuit (3-D IC), a vertically integrated system, has been regarded as one good solution to fulfill the demand for both the trend of miniaturization for electronic devices and for the better performance in the electronic packing technology. Accompanied with the development and implementation of the 3-D IC, packaging technology is now facing new problems and challenges. One problem is the amount of Joule heating generated in 3-D IC packaging; lots of heat will be produced when many transistors work simultaneously inside a compact vertically stacked module. If the heat is dissipated from the surfaces of the module, a temperature difference between the surface and the inner parts of the module could create a temperature gradient across the module. In addition, the peak temperature of a working 3-D IC module has been reported to be much higher than that of flip-chip technology [12], leading to faster atomic diffusion. Moreover, the height of solder joints will drop drastically from a few hundreds of micrometers to only a few micrometers in 3-D IC packaging technology. The reduction in height and the higher peak temperature may facilitate the occurrence of thermomigration in 3-D IC. Hence, thermomigration is believed to be a potentially serious reliability problem in the development of 3-D IC packaging technology.

Another emerging concern in the development of the 3-D IC packaging technology is the anisotropic nature of Sn with a body-centered tetragonal (bct) crystal structure [13]. Sn is a major component of Pb-free solders. When a solder joint is significantly downsized into a few micrometers, it may be composed of only a few Sn grains. It now becomes important to understand how anisotropic Sn affects the performance and the reliability of solder joints once only one or two grains exist in the joint. The influences of the anisotropy of Sn on failure mechanism of Pb-free solders during electromigration have been extensively investigated [14–21]. When electrons flow along the c-axis of the Sn grain in the solder joints [17,20], fast dissolution of the UBM layer occurs. Pancake-type voids of solder have been observed when electrons flow perpendicular to the c-axis of the Sn grain. The growth of IMCs during current stressing was also found to be related to the direction of the c-axis of the Sn grain [18,19,21]. However, no study has yet reported on how the anisotropic β-Sn affects the diffusion behavior and interfacial reaction in the Pb-free solders under a temperature gradient.

In the present work, we systematically studied the relation between the anisotropy of Sn and the thermomigration behavior of Cu in Pb-free solders when Sn–3.5Ag solders reacted with Cu UBM layers. Through microstructural examination using scanning electron microscopy (SEM) and the aid of electron backscatter diffraction (EBSD) analysis, the effect of anisotropic Sn on Cu atomic diffusion as well as on the Cu–Sn interfacial reaction in Pb-free solders under a temperature gradient was elucidated. The corresponding theoretical model was also developed to quantitatively explain the fundamentals of thermomigration of Cu regarding grain orientation. The findings provide not only further insight into the kinetic analysis of diffusion anisotropy under a temperature gradient, but also guidance to the preferred grain orientation for Pb-free soldering technology in next-generation electronic products.

2. Experimental

The samples were fabricated as a sandwich structure: Cu/Sn–3.5Ag solder/Cu. To achieve better wettability, Cu plates (5 × 5 × 1 mm) were first ground, polished and cleaned in advance to remove surface oxides. The Sn–3.5Ag solder pastes were then uniformly applied onto the flat Cu surfaces. The use of solder paste also helps to obtain better wettability and stronger connection due to the incorporation of a certain amount of flux in the paste, making it less easy to form voids at the interface between the solder layer and the substrate during the soldering process. Next, two Cu plates with a thin layer of solder paste on each side were assembled and reflowed on a hot plate. The peak temperature of the reflow process was 260°C and the duration was 60 s. The thickness of the solder layer varies from 282 to 285 μm. After assembly, to facilitate an observation of the effect of grain orientation on the thermomigration test, samples were post-annealed at 150°C for 48 h to coarsen Sn grains.

Table 1 lists the test conditions. As depicted in Fig. 1, a thermomigration test was conducted by placing samples in between a heat source and a heat sink device, following the method developed by Ouyang et al. [10,11]. Thermocouples were respectively attached to both devices to continuously monitor temperature variations during the tests, and a feedback system was utilized to maintain the temperature of each device. The heat source was fixed at 200°C and the heat sink maintained at 100°C. The temperature gradient of the samples was established from the upper Cu plate toward the bottom Cu plate. To understand the temperature gradient across the solder layer, the finite element method was employed. The thermal boundary conditions were set based on the recorded temperature of the thermocouple of each device. The top surface of the upper Cu plate was set to be 473 K (200°C) and the surface of bottom Cu plate attached to the heat sink was set to be 373 K (100°C). The thermal conductivity of Cu and Sn–3.5Ag used in the simulation is 389 W m⁻¹ K⁻¹ and 33 W m⁻¹ K⁻¹, respectively [22,23]. For the sake of comparison, some samples were subject to isothermal treatment at 150°C for different durations.

After tests, scanning electron microscopy (FE-SEM, JSM-6500F, JEOL) and energy dispersive X-ray
spectroscopy (EDS) were utilized to reveal the microstructure evolution and characterize the phase composition. The grain orientation of Sn–3.5Ag solder was determined by an EDAX electron backscatter diffraction (EBSD) system.

3. Results and discussion

3.1. Simulation of temperature gradients

Fig. 2a illustrates the distribution of temperature in the solder layer during the thermomigration test, analyzed by finite element ANSYS simulation. The highest temperature within a solder layer was 456.3 K (183.3 °C) at the upper Cu/solder interface, i.e. the hot end. The temperature at the lower solder/Cu interface, considered to be the cold end, was 392.5 K (119.5 °C). As shown in Fig. 2b, the thickness of the solder layers varied from 282 to 285 μm. Accordingly, the temperature gradients across the solder layer were calculated to be in the range 2213.3–2235.2 °C cm⁻¹. Because this temperature gradient was higher than 400 °C cm⁻¹, thermomigration of Cu in Pb-free solders was expected to occur.

3.2. Microstructural evolutions during thermomigration

The microstructural evolution of the solder layer after 644 h of the thermomigration test is shown in Fig. 2b.
scallopl-type Cu$_6$Sn$_5$ layer was decomposed entirely after 192 h. A gray band was then found above the upper Cu/solder interface after 477 h. The gray area was broadened with test time. This peculiar phenomenon could possibly be attributed to the movement of the interface and the hot-end interface seemed to move backward during the test. In contrast, Fig. 3b shows a gradual transformation of IMC morphology from a scallop type to a layer type at the colder interface and the thickness of IMC increased. Fig. 3c shows an enlarged slightly polished microstructure of the two interfaces at region A after 644 h of the test. At the hot end, due to the serious dissolution observed in Fig. 3b, a thin layer of IMC remained. The IMC layer at the hot end was composed of Cu$_6$Sn$_5$ and Cu$_3$Sn (based on EDX analysis). The majority was Cu$_6$Sn$_5$ and only a very thin layer of Cu$_3$Sn was found in between Cu$_6$Sn$_5$ and Cu, as indicated in Fig. 3c. The dashed line indicates the initial position of the upper Cu/solder interface before the test. It is evident that the hot end interface moved backward and non-uniform dissolution at the hot end was observed; in particular, the Cu near the upper-left-hand corner at upper interface was remarkably consumed. On the other hand, the growth of layered-type Cu$_6$Sn$_5$ and Cu$_3$Sn was found at the cold end and the interface still stayed at the same position, suggesting that the Cu substrate at the cold end remained intact.

To our surprise, the microstructural evolution in region B did not exhibit asymmetrical features. Fig. 4a shows a series of microstructural evolutions at region B with different periods of time. No significant dissolution of the IMC layer at the hot end was observed with test time. Some precipitations of Cu$_6$Sn$_5$ were also found at grain boundaries based on SEM images in Figs. 2b and 4a. Fig. 4b shows an enlarged slightly polished microstructure of the two interfaces at region B after 644 h of the test. Different from Fig. 3c, both Cu$_6$Sn$_5$ and Cu$_3$Sn were observed at the hot end in Fig. 4b and both IMCs became relatively thick. The morphology and the composition of the hot-end IMCs were similar to that of the cold-end IMCs. Hence the microstructure in region B was regarded as a symmetrical feature.

3.3. Comparison of isothermal aging test and thermomigration test

To clarify the two different thermomigration behaviors in Pb-free solders, an isothermal aging test was conducted as a comparison. The aging test was conducted at 150 °C based on the average temperature within the solder layer calculated from the result of simulation. Fig. 5a and b displays the microstructures at an upper and lower interface, respectively, subject to isothermal aging for 783 h. Both upper- and lower-interface IMCs were composed of Cu$_6$Sn$_5$ and Cu$_3$Sn. Some Ag$_2$Sn particles were found to be embedded in Cu$_6$Sn$_5$ layers. The existence of Ag$_2$Sn particles within the Cu$_6$Sn$_5$ layer is related to the depletion of Sn close to the intermetallic layer according to previous studies [24,25]. The Cu$_6$Sn$_5$ IMCs maintained a scallop shape and this phenomenon was attributed to the effect of initial morphology of IMCs after the soldering reaction [26]. No dissolution of Cu$_6$Sn$_5$ IMCs or apparent consumption of the Cu substrate was observed at the interfaces and the interfacial IMCs grew in a symmetrical fashion – namely, both upper- and lower-interface IMCs thickened during isothermal aging. Evidently, the resulting microstructure exhibited a symmetrical feature in the microstructure after the isothermal aging test.

Fig. 6 depicts the change in average thickness of the IMC at two interfaces of samples under thermomigration and the isothermal aging test. The average thickness of the IMC layer at each interface was measured and calculated using image processing software. For isothermal aging samples, the average thickness of the IMC at both interfaces was 9.5 μm after 783 h aging at 150 °C. As for the TM sample in region A, the hot-end IMC layer was measured to be 3.8 μm. Because the temperature at the hot end (183.3 °C) in the TM sample was higher than 150 °C, the growth of IMCs at higher temperature was expected to be more prominent; however, the average thickness of hot-end IMCs decreased. For the cold interface (119.5 °C) in region A, the thickness of IMC layers was found to be 9.5 μm, i.e. as thick as the IMC layer in isothermal aging samples, suggesting that abnormal growth of IMCs occurs at the cold end in TM samples. The above findings suggest that the temperature gradient induces Cu atoms to migrate from the hot end to the cold end, leading to dissolution of the IMC near the hot end.

Fig. 4. The microstructural evolutions (a) at the hot end and (b) the cold end in region B. (c) Enlarged SEM image of both interfaces after thermomigration test for 644 h showing the symmetrical growth of IMCs in region B.
When Cu atoms arrived at the colder interface by interstitial diffusion through the Sn lattice [27,28], the Cu atoms then accumulated and precipitated at the interface between the initial IMC layer and solder matrix. Accordingly, the thickness of cold-end IMCs increased and the morphology of cold-end IMCs changed from the scallop type to layer type. As a result, the asymmetrical growth of IMCs at two interfaces induced by thermomigration of Cu was observed in region A. Similar observations have been reported by Chen et al. [8,9], showing the dissolution of \( \text{Cu}_6\text{Sn}_5 \) IMCs near the hot end in the solder bumps induced by thermomigration. Guo et al. [29] also observed an asymmetrical growth of IMC in molten SnAg solder due to the thermomigration of Cu during the reflow process.

On the other hand, the average thickness of both hot-end and cold-end IMCs for the TM sample in region B was found to be \( \sim 9.4 \) \( \mu \)m, indicating that no significant dissolution of IMC occurred at the hot end in region B. In addition, the symmetrical feature of interfacial IMCs in region B is quite similar to the result from isothermal aging samples where the thickness of both upper and bottom IMC layers increased. The above findings suggest that thermomigration is less prominent in region B although the temperature gradient existing in region B is the same as that in region A according to the simulation results in Fig. 2a. Thus, we proposed that the different thermomigration behaviors between region A and region B could be attributed to the effect of Sn grain orientation.

### 3.4. Effect of Sn grain orientation on Cu thermomigration

Fig. 7a reveals the 3-D crystallographic orientation of each Sn grain in region A and B by EBSD analysis. The grains in the same region exhibit similar 3-D crystal orientations, whereas a distinct 3-D crystal orientation between regions A and B was found. Fig. 7b and c illustrates the 001 pole figures of Sn grains in region B and region A, respectively. The temperature gradient across the solder layer was along the transverse direction (TD) in EBSD analysis. The pole figure in Fig. 7b implies a strong preferred orientation with the c-axis almost perpendicular to the TD, the temperature gradient, in region B. As for region A in Fig. 7c, the c-axes of Sn grains tend to be parallel to the temperature gradient. The orientation map in Fig. 8 presents angles between the [001] direction and the TD by colors, i.e. the angle of the c-axis of Sn grain and the temperature gradient. The red and blue represent 90° and 0°, respectively. In region B, highly occupied red and orange grains, angled from 77° to 89°, show that [001] were almost perpendicular to the TD. However, the solder layer in region A was mainly composed of green and yellow grains, angled from 35° to 45° with the TD.

The relation between the Sn orientation and thermomigration behavior of Cu can be clarified through the comparison between SEM images and EBSD analysis. The orientation map in Fig. 9a shows the area near the hot end where a red grain located next to a green grain. As shown in Fig. 9b, the SEM image reveals a distinctive microstructure between two grains. The IMC layer, comprising \( \text{Cu}_6\text{Sn}_5 \) and \( \text{Cu}_3\text{Sn} \), in the red grain remained relatively thick after 644 h of the TM test. On the other hand, the IMC layer in the green grain dissolved. Only a thin layer of \( \text{Cu}_6\text{Sn}_5 \) left at the interface and the \( \text{Cu}_3\text{Sn} \) layer is difficult to distinguish at the interface from the
micrograph. Moreover, it is apparent that the solder/Cu interface (hot end) moved backward. Not only the dissolution of IMCs, but also a severe consumption of Cu substrate, occurred in the green grain. Therefore, the different thermomigration behaviors observed in region A (Fig. 3) and region B (Fig. 4) were apparently caused by different orientations of Sn grains.

Because β-Sn is a bct structure with the c-axis (0.318 nm) being shorter than a-axis and b-axis (0.583 nm), the bct crystal structure provides a more open structure for atomic diffusion along the c-axis than the a- or b-axis. According to the simulated result in Fig. 2, the average temperature of the solder layer is at ~150 °C and the diffusivity of Cu along the a-axis of the Sn grain, $D_{\text{Cu in Sn, a-axis}}$, is $1.99 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 150 °C [28]. The diffusivity of Cu along the c-axis of the Sn grain, $D_{\text{Cu in Sn, c-axis}}$, is $8.57 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, about 43 times larger than $D_{\text{Cu in Sn, a-axis}}$ at 150 °C [28]. Accordingly, in the red Sn-grain region, diffusion of Cu was retarded and hence no prominent dissolution of hot-end IMCs was observed; however, for yellow and green grains in region

![Fig. 7. (a) Orientation of Sn grain by EBSD analysis. The 001 pole figure of grains in (b) region B and (c) region A.](image)

![Fig. 8. The angle between the c-axis of the Sn grain and temperature gradient defined by colors. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

![Fig. 9. (a) The orientation map and the 3-D crystal orientation of Sn near a hot-end interface. (b) The enlarged SEM image of the circled area.](image)
A, the lower angles facilitated the diffusion of Cu and resulted in the decomposition of hot-end IMCs. A similar phenomenon was reported for Pb-free solders under electromigration tests by both Kinney and Linares [14,15].

3.5. Theoretical derivation of thermomigration flux

Chen et al. reported a kinetic study of the effect of grain orientation on electromigration [16]. In this study, we adopted a similar coordinate system to theoretically examine the thermomigration of Cu in terms of the anisotropy of Sn. When a temperature gradient is present, the net Cu atomic flux of thermomigration, \( J_{\text{Cu,TM}} \), can be expressed as:

\[
J_{\text{Cu,TM}} = \frac{CD'}{kT} \left( -\frac{\partial T}{\partial x} \right) \tag{1}
\]

where \( C \) is the concentration of atoms per unit volume, \( D \) is the diffusivity, \( Q' \) is the heat of transport and \( \frac{\partial T}{\partial x} \) is the temperature gradient. Based on our findings, the orientation of Sn plays an important role in the diffusion of Cu induced by a temperature gradient. To investigate the effect of Sn orientation on the thermomigration of Cu, the anisotropy of diffusivity of Cu should be considered. The diffusivity \( D \) of Cu can be expressed as a tensor \( \bar{D} \) as follows:

\[
\bar{D} = \begin{pmatrix} D_{11} & D_{12} & D_{13} \\ D_{21} & D_{22} & D_{23} \\ D_{31} & D_{32} & D_{33} \end{pmatrix} \tag{2}
\]

Accordingly, the net flux of Cu in Eq. (1) can be rewritten as

\[
\bar{J} = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) \bar{D} \times \nabla \bar{T} \tag{3}
\]

where

\[
\nabla \bar{T} = \frac{\partial T}{\partial x} \hat{i} + \frac{\partial T}{\partial y} \hat{j} + \frac{\partial T}{\partial z} \hat{k} = TG_1 \hat{i} + TG_2 \hat{j} + TG_3 \hat{k} \tag{4}
\]

Eq. (3) can be simplified if \( D_{ij} \) is supposed to be 0 when \( i \neq j \).

\[
\bar{J} = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) \begin{pmatrix} D_{11} & 0 & 0 \\ 0 & D_{22} & 0 \\ 0 & 0 & D_{33} \end{pmatrix} \begin{pmatrix} TG_1 \\ TG_2 \\ TG_3 \end{pmatrix} \tag{5}
\]

After rearrangement,

\[
\bar{J} = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) \begin{pmatrix} D_{11}TG_1 + D_{22}TG_2 + D_{33}TG_3 \end{pmatrix} \tag{6}
\]

where \( D_{11} = D_a = D_{22} = D_b \) and \( D_{33} = D_c \).

The corresponding magnitude of \( J \) can be expressed as

\[
|\bar{J}| = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) \sqrt{(D_c^2TG_1^2 + D_b^2TG_2^2 + D_a^2TG_3^2)} \tag{7}
\]

Fig. 10 illustrates the coordinate system composed of the \( a-, b- \) and \( c- \) axes of the Sn unit cell. \( \alpha \) is the angle between the \( c- \) axis and the temperature gradient and \( \beta \) is the angle between the projection of the temperature gradient on the (001) plane and \( a- \) axis. Accordingly, the temperature gradient resolved in the \( a-, b- \) and \( c- \) axes is given by

\[
TG_1 = |\nabla \bar{T}| \sin \alpha \cos \beta \tag{8}
\]

\[
TG_2 = |\nabla \bar{T}| \sin \alpha \sin \beta \tag{9}
\]

\[
TG_3 = |\nabla \bar{T}| \cos \alpha \tag{10}
\]

By combining Eqs. (7–10), the magnitude of Cu atomic flux \( J \) is

\[
|\bar{J}| = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) |\nabla \bar{T}| \sqrt{(D_c^2 \sin^2 \alpha + D_b^2 \cos^2 \alpha)} \tag{11}
\]

Furthermore, the atomic flux along the temperature gradient can be expressed as

\[
J_{\text{TG}} = |\bar{J}| \cos \phi \tag{12}
\]

where \( \phi \) is the angle between \( \bar{J} \) and \( \nabla \bar{T} \).

Applying \( \cos \phi = \frac{\bar{J} \cdot \nabla \bar{T}}{|\bar{J}| |\nabla \bar{T}|} \) into Eq. (12),

\[
J_{\text{TG}} = |\bar{J}| \cos \phi = |\bar{J}| \sqrt{\frac{D_c \sin^2 \alpha + D_b \cos^2 \alpha}{D_c^2 \sin^2 \alpha + D_b^2 \cos^2 \alpha}} \tag{13}
\]

Substituting Eq. (11) into Eq. (13), the atomic flux of Cu along the temperature gradient, \( J_{\text{TG}} \), can be expressed as

\[
J_{\text{TG}} = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) |\nabla \bar{T}| \sqrt{(D_c \sin^2 \alpha + D_b \cos^2 \alpha)} \tag{14}
\]

Rearranging Eq. (14) into the form of

\[
J_{\text{TG}} = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) \sqrt{(D_c - D_a) \cos^2 \alpha + D_a} \tag{15}
\]

Recall that the ratio of \( D_c/D_a \) is \( \sim 43 \) at 150 °C and substitution of this result into Eq. (15) gives

\[
J_{\text{TG}} = \left( \frac{c}{kT} \right) \left( \frac{Q'}{T} \right) \sqrt{(D_a) (1 + 42 \cos^2 \alpha)} \tag{16}
\]

Note that the angle \( \alpha \) dominates the atomic flux of thermomigration. The flux induced by the temperature gradient increases inversely with angle \( \alpha \). Therefore, the
distinct microstructure observed between region A and region B under a temperature gradient can be theoretically explained on the basis of $J_{TG}$ in Eq. (16). For yellow and green grains with smaller $\alpha$ angles in region A (Fig. 3), the flux of Cu from the hot end toward the cold end is predicted to be large, leading to the serious dissolution of IMCs and Cu at the hot end. Once the huge flux has arrived at the cold end, the Cu atoms then accumulate and precipitate, resulting in abnormal growth of IMCs at the cold end. Conversely, a smaller amount of flux is expected to be induced for red grains in region B due to large $\alpha$ angles, and thus no asymmetrical growth was observed in region B.

Table 2 lists the thickness of hot-end IMC at different regions in terms of different $\alpha$ angles. Note that the thickness decreases as the $\alpha$ angle decreases. The IMC layer was around 9 $\mu$m with large $\alpha$ angles but that with small angles dropped down to 3–5 $\mu$m. The IMC dissolution was determined by the difference between the thickness of the hot-end IMC and the average thickness of the IMC layer in isothermal aging samples (9.5 $\mu$m). Obviously, the dissolution of the hot-end IMC was strongly related to angle $\alpha$. The dissolution of IMC was very small in the region with large $\alpha$ angles. The negative value in the table means that the thickness of IMC increased; however, the increment was very small. On the other hand, IMC dissolution was apparently serious in the regions with smaller $\alpha$ angles.

In addition, the consumption of Cu substrate at the hot end was also measured based on SEM images and is listed in Table 2. No consumption of Cu substrate was found at the large-$\alpha$ region, yet severe consumption occurred in the small-$\alpha$ region where serious dissolution of IMC also occurred. To make a comparison, the dissolution amount of Cu$_6$Sn$_5$ IMC can be transformed into the equivalent consumption amount of Cu. The value in the parentheses represents the equivalent consumption in Cu. The total dissolution at the hot end was determined by the sum of consumption of equivalent-Cu and the Cu substrate. According to Eq. (16), the total dissolution at the hot end was related to $\cos^2 \alpha$ and was plotted against the value of $\cos^2 \alpha$ in Fig. 11. The resulting plot was in quite good agreement with the theoretical derivation discussed above. At small $\cos^2 \alpha$ (large $\alpha$ angle), the dissolution was very little, implying that a very small amount of thermomigration flux existed. As the $\cos^2 \alpha$ increases, the total Cu dissolution becomes more prominent and this phenomenon results from the greater thermomigration flux. Fig. 12 illustrates how the grain orientation of Sn affects the thermomigration behavior of Cu. When the $c$-axis of the Sn grain is perpendicular to the temperature gradient (Fig. 12a), the thermomigration flux is very small due to the low value of $\cos^2 \alpha$. Hence the dissolution of hot-end IMC was not obvious and resulted in a symmetrical feature of IMCs. However, as the $c$-axis of the Sn grain and temperature gradient was parallel (Fig. 12b), a large thermomigration flux induced serious dissolution of hot-end IMC as well as the consumption of Cu substrate. Once a large amount of Cu atoms dissolved into solder and then were driven by temperature gradient to interstitially migrate to the cold end, an abnormal growth of IMC occurred, resulting in an asymmetrical feature. This asymmetrical feature of the microstructure adversely affects the reliability. The accumulation of IMCs at the cold end may affect the mechanical properties of the solder joint and lead to brittle failure. Serious dissolution of
IMCs and excessive consumption of Cu UBM at the hot end may result in circuit failure.

It is worth noting that, unlike electromigration in which the void formation in solders is easily observed, voids were hardly found after the thermomigration test. The formation of voids during electromigration is mainly because the substitutional diffusion of Sn atoms dominates the whole diffusion process. However, the heat of transport ($Q^*$) of Cu (+20 kJ mol$^{-1}$ [29]) is much greater than that of Sn (−3.38 kJ mol$^{-1}$ [4]) and the diffusivity of Cu is also approximately four orders of magnitude faster than that of Sn [30,31]. Thus, the thermomigration flux of Cu is larger than that of Sn, suggesting that the migration of Cu rather than Sn is dominant during thermomigration in this study. Cu atoms diffuse interstitially in Sn matrix from the hot end toward the cold end and cause the dissolution of hot-end Cu$_6$Sn$_5$ IMCs and the Cu substrate. The Cu-dissolved IMCs would transform to highly vacant Sn grains and results in a large Sn concentration gradient between highly vacant Sn grains and Sn matrix [32]. Once Sn atoms migrate from the cold side to the hot side under a temperature gradient, the large Sn concentration gradient would drive Sn atoms to fill in the region of dissolved IMC. Consequently, no voids were found at the hot end of samples during thermomigration.

4. Conclusions

This study investigates the effect of anisotropy of Sn on the behavior of thermomigration of Cu by inserting sandwich (Cu/Sn3.5Ag/Cu) samples between a heat source and a heat sink device. A theoretical derivation of thermomigration flux of Cu shows that the flux is controlled by and inversely changes with an angle, $\alpha$, between the $c$-axis of the Sn grain and temperature gradient. The experimental results show that an asymmetrical feature in the microstructure with a thin layer of IMC at the hot end and a thick layer of IMC at the cold end was observed in the regions with small $\alpha$ angles. With small angle $\alpha$, a large thermomigration flux was induced and further led to serious dissolution of IMC at the hot end. Severe consumption of Cu substrate at the hot end also occurred accompanied with dissolution of IMCs. The dissolved Cu atoms were driven by the temperature gradient to migrate toward the cold end and also resulted in an abnormal growth of IMC at the cold end. However, in the region where the $c$-axes of Sn grains were perpendicular to the temperature gradient (large $\alpha$ angles), a very small thermomigration flux was induced, and hence no dissolution of hot-end IMC was observed and a symmetrical microstructure was found at both hot and cold interfaces. Failure induced by thermomigration was hardly found in this region. The above findings also indicate that the optimum grain orientation of Sn to inhibit thermomigration-induced failure of Cu is with the $c$-axis of Sn grains perpendicular to the temperature gradient.

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References
