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Bismuth redistribution induced by intermetallic compound growth in SnBi/Cu microelectronic interconnect

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Abstract It was found that Bi particles, with a diameter of 100 nm, precipitated along Cu_3Sn/Cu interface and Bi crystallites dispersed in Cu_3Sn layer in 42Sn58Bi/Cu microelectronic interconnect, when it was aged at 120 °C for 7 days. The mechanism for Bi redistribution like this was discussed. Cu_6Sn_5 turned into Cu_3Sn by Cu diffusion that is dominant in Sn/Cu inter-diffusion during the aging process. Bi precipitation occurred in Cu_3Sn due to lower Bi solubility in Cu_3Sn than that in Cu_6Sn_5. The Bi precipitates can traverse the formed Cu_3Sn quickly toward the Cu_3Sn/Cu interface, attributed to the Kirkendall effect. They stayed and nucleated there to form particles, owing to their unwettability on Cu. The formed Cu_3Sn got oversaturated with Bi, when the joint cooled from 120 °C to room temperature. Then Bi crystallites precipitated dispersedly in Cu_3Sn layer.

Introduction

Bismuth is an important alloy element in modern lead-free Sn-based solder alloys [1]. Bi-containing lead-free solders, such as eutectic 42Sn58Bi alloy, have been widely applied in industry because of their excellent wettability and mechanical properties. In order to better understand the interfacial structure evolution of solder joint during the performance, great efforts have been taken on the research on interfacial reaction between lead-free solder and Cu metallization. Many studies, such as literatures [2–4], have shown that intermetallic compound (IMC) Cu_6Sn_5 (η phase) forms, when Sn-based solder/Cu interconnect is reflowed. The Cu_6Sn_5 develops and a layer of Cu_3Sn (ε phase) forms between Cu_6Sn_5 and Cu, after the solder joint is aged, as shown in Fig. 1a. Vianco et al. [5] have found that Bi segregated along the interface between IMC and Cu in 42Sn58Bi/Cu joint aged at 100 °C for 400 days. It has been reported that Bi segregation at the Cu_3Sn/Cu interface induced a brittle fracture along this interface and a great drop of mechanical property of the interconnect [6–10]. This made SnBi/Cu solder joint questionable in industry application. Meanwhile, the problem of brittleness caused by the Bi segregation at grain boundary in Cu sample has attracted material scientists for a long time [11–13]. These facts led to suitability concern over the usage of Bi-containing solder alloys on Cu substrate. Therefore, it is very necessary to further investigate how the Bi segregated at the Cu_3Sn/Cu interface in the 42Sn58Bi/Cu joint. However, very fewer studies were reported on fundamental mechanism for Bi segregation along Cu_3Sn/Cu interface in 42Sn58Bi/Cu solder joint. In this work, the Cu_3Sn/Cu interfacial structure in the 42Sn58Bi/Cu solder joint aged at 120 °C for 7 days was examined by using scanning electron microscope (SEM) and transmission electron microscope (TEM). An electron microprobe analysis (EMPA) was employed to analyze the Bi contents in IMC Cu_6Sn_5 and Cu_3Sn. Thus the IMC formation process was identified in Sn/Cu inter-diffusion couple with the marker and Bi segregation process was quantitatively illustrated. The work will contribute to better understanding of structure evolution at interface in 42Sn58Bi/Cu interconnect in

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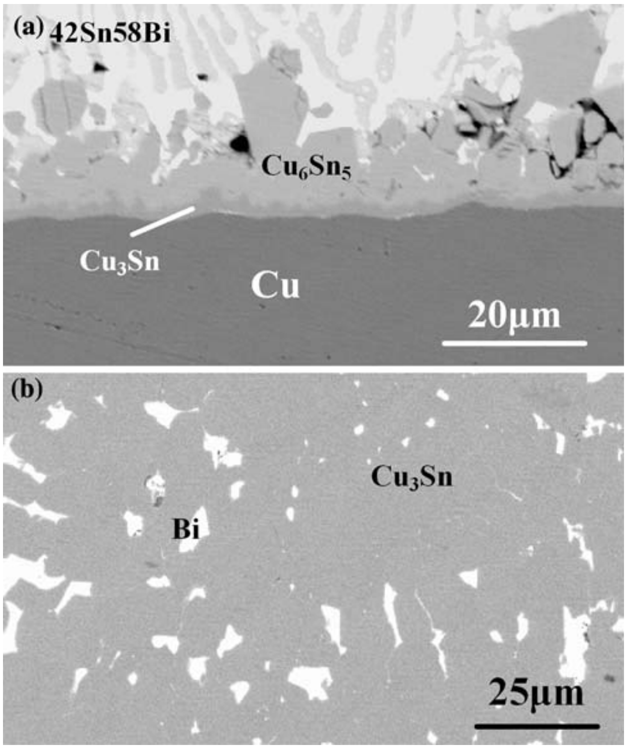

Fig. 1 SEM images of **a** IMC Cu_6Sn_5 and **b** Cu_3Sn on which the EMPA was carried out

service, and can also help to improve the reliability of SnBi/Cu microelectronic joint.

Experimental procedure

The 42Sn58Bi/Cu solder joint was prepared by reflowing commercial eutectic 42Sn58Bi solder paste between two sheets of Cu to form a sandwich structure. The Cu sheets were highly conductive and oxygen free. The reflow process was conducted at 110 °C for 15 min to evaporate rosin flux in paste and at 170 °C for 5 min to reflow eutectic 42Sn58Bi paste. Before soldering, the Cu sheets were polished with 0.5 μm diamond paste. The solder joint cooled in air after reflow process. In this stage, it was in as-reflowed condition. The solder joint in as-reflowed condition was aged at 120 °C for 7 days. The Cu_3Sn/Cu interfacial structure in the aged solder joint was investigated by using S360 Cambridge SEM and JEM-2010 TEM.

It is known that Bi cannot interact with Cu, according to the Bi–Cu phase diagram [14]. In our work, the IMCs could only form by means of inter-diffusion reaction between Sn and Cu in 42Sn58Bi/Cu solder joint during the aging process. Therefore, we can observe the IMC Cu_3Sn growth behavior in pure Sn/Cu interconnect instead of that in 42Sn58Bi/Cu joint. The pure Sn/Cu interconnect was obtained by electroplating a layer of pure Sn, with a thickness of about 40 μm, on a Cu sheet, which is oxygen free and highly conductive. Before electroplating, the Cu sheet was polished with 0.5 μm diamond paste. The pure Sn/Cu interconnect was aged at 160 °C for 1 day and then for 16 days again. The IMC Cu_3Sn growth behavior in the pure Sn/Cu can be confirmed by means of SEM, by comparing the interfacial structure in pure Sn/Cu interconnect aged for 1 day with that aged for 1 day and further 16 days.

The Cu_6Sn_5 sample was prepared by aging 42Sn58Bi/Cu joint in as-reflowed condition and then cooling down in air. The morphology of Cu_6Sn_5 can be found in Fig. 1a. The IMC Cu_3Sn with Bi phase dispersed in matrix was obtained by melting the Cu, 42Sn58Bi together and then cooling in high frequency induction vacuum furnace. The atomic ratio of Cu and Sn was 3:1. Its morphology was shown in Fig. 1b. The Bi contents in IMC Cu_6Sn_5 and Cu_3Sn matrix were analyzed by using CAMEBAX-MICRO EMPA and its activated area is about 2 μm^2. At least five points were tested for each sample. In order to verify that Bi can be soluble in IMCs, Bi contents were tested by using EMPA on these samples that were heated at 180 °C for 84 h and then quenched into water. The aging process was conducted in drying box with an accuracy of ±1 °C.

Results

The average thickness of IMC Cu_6Sn_5 in 42Sn58Bi/Cu joint in as-reflowed condition was determined to be approximately 2 μm by using SEM. IMC thickness increased to 10 μm, with IMC Cu_3Sn formed and developed to about 1 μm, when the solder joint aged at 120 °C for 7 days. Most of Bi particles, with a diameter of about 100 nm, were found to distribute along the Cu_3Sn/Cu interface in the joint, as shown in Fig. 2. The insets revealed that the highly dispersed Bi crystallites [see the indexed diffraction rings for Bi: monoclinic, $a = 6.05$ Å, $b = 4.2$ Å, $c = 4.65$ Å, $\alpha = 90°$, $\beta = 85.3°$, $\gamma = 90°$, PDF#70-2629] with a darker contrast existed within Cu_3Sn layer [orthorhombic, $a = 5.49$ Å, $b = 4.32$ Å, $c = 4.74$ Å, PDF#65-4653] in the joint. Those isolated diffraction spots came from polycrystalline Cu_3Sn besides the three diffraction rings. In short, we found that Bi was redistributed in Cu_3Sn phase, after the 42Sn58Bi/Cu joint aged and Cu_3Sn formed. Some Bi precipitated along the Cu_3Sn/Cu interface in form of nano-sized particles, while the others formed Bi crystallites dispersed in Cu_3Sn layer. But what was it that drove them to redistribute like this?

We set to solve this problem by investigating the IMC Cu_3Sn growth behavior. Previously, the migration of interfaces relative to the fixed marker in the 42Sn58Bi/Cu

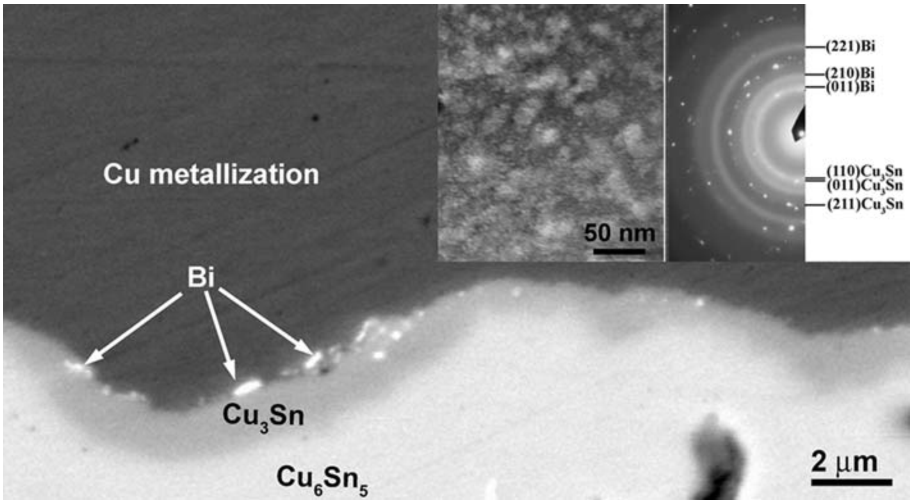

Fig. 2 SEM image for Bi particles distributed along the Cu_3Sn/Cu interface in 42Sn58Bi/Cu solder joint aged at 120 °C for 7 days. The insets are the bright-field TEM image of the Cu_3Sn and corresponding selected-area electron diffraction pattern in it

joint was monitored, during the aging process, as shown in Fig. 1 of literature [15]. The "reference line" in the figure was the marker indicating the initial position where eutectic 42Sn58Bi solder contacted Cu metallization. It was found that the interface between IMC and solder moved toward the solder, relative to the marker, after the joint was aged. But the interface between IMC and Cu kept nearly stable relative to the marker, during the aging process. It indicated that Cu diffused faster than Sn did in Sn–Cu inter-diffusion in solid state aging. As a consequence, defects such as twins and voids [15] can result from the loss of Cu in the Cu metallization.

However, the Fig. 1 in literature [15] did not clearly reveal the IMC Cu_3Sn growth behavior. The Cu_3Sn growth behavior in pure Sn/Cu was observed by using SEM, as shown in Fig. 3. About 3 μm-thick layer of Cu_6Sn_5 can be found in Sn/Cu joint, when it was aged at 160 °C for 1 day (see Fig. 3a). The Cu_6Sn_5 developed and a 7 μm-thick layer of Cu_3Sn formed between Cu_6Sn_5 and Cu, when the joint was aged further at 160 °C for 16 days, as shown in Fig. 3b. The interface between IMC and Cu can be regarded as a 'fixed' marker in pure Sn/Cu joint because of its stability in aging process as in 42Sn58Bi/Cu interconnect mentioned above. The Cu_6Sn_5 was confirmed to turn into Cu_3Sn by comparing Fig. 3b with Fig. 3a, while keeping the IMC/Cu interface fixed. The present results were in agreement with the previous work [16–18].

The Bi content in Cu_6Sn_5 formed in 42Sn58Bi/Cu joint was measured by using EMPA. The average Bi content in Cu_6Sn_5 was 1.80 ± 0.09 wt%, while that in Cu_3Sn matrix with Bi phase dispersed was 0.60 ± 0.06 wt%. The average Bi contents in Cu_6Sn_5 and Cu_3Sn at 180 °C were 2.36 ± 0.15 and 1.22 ± 0.09 wt%, respectively. The Bi contents in IMCs at high temperature were higher than those at room temperature. It can be proved that Bi contents obtained were its solubility in IMCs and those in Cu_3Sn were the maximum saturation solubility at room temperature and 180 °C. Therefore, Bi solubility in Cu_6Sn_5 formed in 42Sn58Bi/Cu joint is higher than Bi saturation solubility in Cu_3Sn.

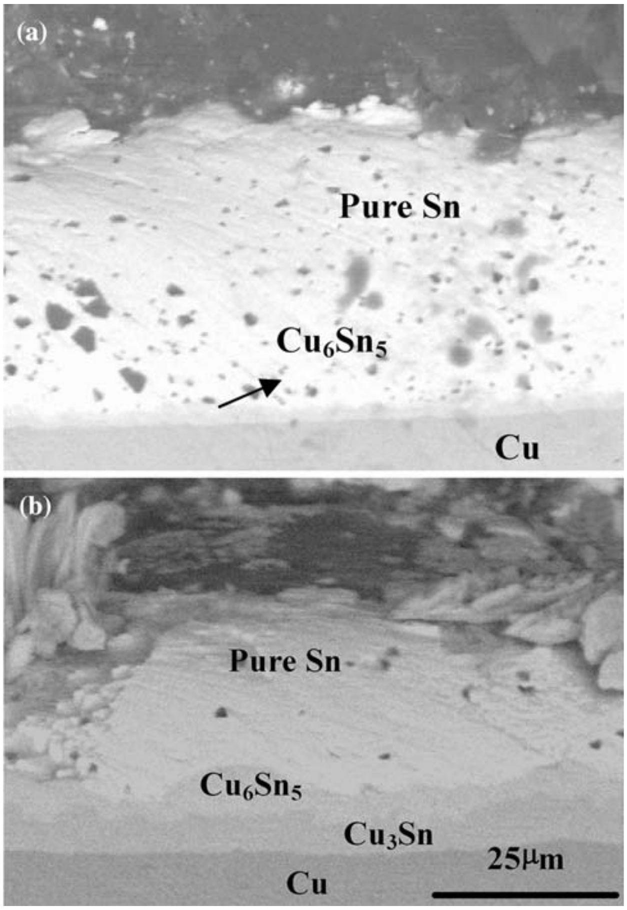

Fig. 3 SEM images of pure Sn/Cu interconnect aged **a** at 160 °C for 1 day **b** at 160 °C for 16 days after aging for 1 day. The IMC Cu_3Sn growth behavior can be found by examining Cu_3Sn/Cu_6Sn_5 interface migration relative to 'fixed' IMC/Cu interface

Discussion

The classical theoretical and experimental works [19, 20] have been reported, concerning the growth of IMCs Cu_6Sn_5 and Cu_3Sn in a Cu–Sn inter-diffusion couple. The IMCs' growth process and mechanism for Bi segregation are illustrated in the Fig. 4. A layer of Cu_6Sn_5 forms, when the solder wets on Cu metallization, as shown in Fig. 4a. The reaction can be expressed as

$$6\mathrm{Cu} + 5\mathrm{Sn(Solder)} \Leftrightarrow \mathrm{Cu_6Sn_5} \tag{1}$$

The 42Sn58Bi/Cu joint sample is in as-reflowed condition at this stage. The Cu_6Sn_5 develops, when it is aged, as shown in Fig. 4b. The formation rate of Cu_6Sn_5 is controlled by the Cu diffusion driven by its concentration gradient and Sn–Cu reaction rate at Cu concentration of about 55 at.%. v_1, which represents the average migration velocity of interface between Cu_6Sn_5 and solder, is dependent on Cu diffusion flux "staying" in dx_1. This part of flux is the difference between J_η and J_{Sn}, where J_η stands for Cu diffusion flux in η which enters into dx_1, and J_{Sn} is Cu diffusion flux which flows out of dx_1 to participate in diffusion process in solder. J_{Sn} is dependent on the solubility of Cu in solder. v_1 is expressed as following

$$v_1 = dx_1/dt = (J_\eta - J_{Sn})/(C_{\eta Sn} - C_{Sn\eta}) \tag{2}$$

where $C_{\eta Sn}$ and $C_{Sn\eta}$ are illustrated in Fig. 4c, which can be found in Sn–Cu phase diagram [21]. The Cu_3Sn begins to form and develop by the reaction between Cu_6Sn_5 and Cu at Cu concentration of about 75 at.%, when the sample is aged at a certain temperature for a sufficient time. The reaction is expressed as:

$$\mathrm{Cu_6Sn_5} + 9\mathrm{Cu} \Leftrightarrow 5\mathrm{Cu_3Sn} \tag{3}$$

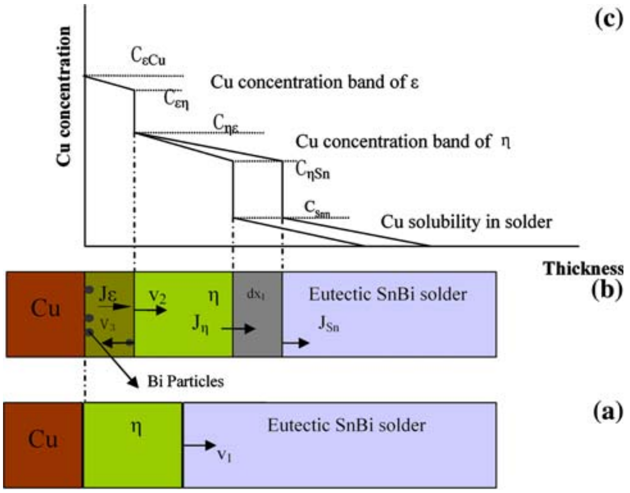

Fig. 4 Schematic illustrations for IMCs' growth and mechanism for Bi segregation at the Cu_3Sn/Cu interface in 42Sn58Bi/Cu solder joint during the aging process, the sample **a** in as-reflowed condition and **b** in aged condition. **c** Cu concentration profile along IMC thickness

v_2, the average migration velocity of the interface between Cu_6Sn_5 and Cu_3Sn, can be calculated as the way for v_1. v_2 relies on the difference between J_ε and J_η at the interface. It can be expressed as

$$v_2 = (J_\varepsilon - J_\eta)/(C_{\varepsilon\eta} - C_{\eta\varepsilon}) \tag{4}$$

where J_ε is Cu diffusion flux in ε phase; $C_{\varepsilon\eta}$ and $C_{\eta\varepsilon}$ are Cu concentrations at interface, as illustrated in Fig. 4c. The volume of Cu_6Sn_5 consumed in Cu_3Sn formation process can be calculated as:

$$V_\eta = V_\varepsilon * \rho_\varepsilon * m_\eta / 5m_\varepsilon * \rho_\eta \tag{5}$$

where V_η and V_ε stand for the volumes of η and ε phases participating in the reaction, respectively, ρ_η and ρ_ε represent mass densities of η and ε phases, and they are 8.3 g/cm^3 and 11.3 g/cm^3, respectively [22]. m_η and m_ε are the masses per mol for η and ε phases, they are 979 g/mol and 311 g/mol, respectively.

The thickness of Cu_3Sn developed up to 1 μm, when 42Sn58Bi/Cu joint was aged at 120 °C for 7 days. Based on Eq. 5, the volume of Cu_6Sn_5 consumed to form 1 μm^3 of Cu_3Sn was 0.86 μm^3.

The average solubility in Cu_6Sn_5 in 42Sn58Bi/Cu joint at 120 °C can be reasonably assumed to be 2.0 wt%, based on the above EMPA results. Then the quantity of Bi dissolved in 0.86 μm^3 of Cu_6Sn_5 was calculated to be 14.276E-14 g in 42Sn58Bi/Cu interconnect at 120 °C. The maximum content of Bi dissolved in 1 μm^3 Cu_3Sn would be 10.17E-14 g, when the average maximum solubility in Cu_3Sn also was reasonably assumed to be 0.9 wt% at 120 °C. Therefore, not all Bi dissolved in Cu_6Sn_5 can be accepted by Cu_3Sn phase, when the Cu_6Sn_5 turned into Cu_3Sn in aging process. As a result, 4.106E-14 g of Bi originally dissolved in Cu_6Sn_5 was left to precipitate, when 1 μm^3 of Cu_3Sn formed in the 42Sn58Bi/Cu interconnect aged at 120 °C for 7 days.

Bi precipitates appeared, when the reaction occurred at the interface between Cu_3Sn and Cu_6Sn_5 in the aging process. Meanwhile, the Bi precipitates from Cu3Sn phase migrated toward the Cu_3Sn/Cu interface in the presence of the Cu diffusion flux J_ε toward the direction of the solder, which was attributed to Kirkendall effect (see Fig. 4b). Their average velocity v_3 can be expressed as the following equation:

$$\begin{aligned} v_3 &= (D_{Cu} - D_{Sn})\partial N_{Cu}/\partial x \approx D_{Cu}(\partial N_{Cu}/\partial x) \\ &= -J_\varepsilon/(C_{\varepsilon Cu} - C_{\varepsilon\eta}) \end{aligned} \tag{6}$$

where D_{Cu} and D_{Sn} are the diffusion coefficients of Cu and Sn in ε phase, respectively. The latter is very small compared with the former. N_{Cu} is Cu atomic fraction in unit volume; $\partial N_{Cu}/\partial x$ is Cu atomic fraction gradient in unit volume of ε phase. $C_{\varepsilon \mathrm{Cu}}$ and $C_{\varepsilon\eta}$ are Cu concentrations as illustrated in Fig. 4c, which can be quantified from Sn–Cu phase diagram.

Therefore, the Bi precipitates from Cu_3Sn migrated along the direction opposite to that of Cu diffusion. And the quantity of its velocity was dependent on Cu diffusion flux in ε phase and Cu concentration band width of ε phase. According to the observation, the v_1/v_2 was estimated roughly to be 8, when the 42Sn58Bi/Cu interconnect was aged at 120 °C for 7 days. From Eqs. 2, 4, and 6, J_ε/J_η can be estimated to be 23/22, if J_{Sn} and $C_{\mathrm{Sn}\eta}$ were neglected. So the value of v_3/v_2 was calculated to be about 460. It is easily understood that most of Bi that precipitated from Cu_3Sn can continuously traverse ε phase quickly enough to reach the Cu_3Sn/Cu interface. They would stay and accumulate, then nucleate at the interface to form particles because of their unwettability on Cu substrate (see Fig. 4b).

The quantity of Bi precipitates from 1 μm^3 of Cu_3Sn has been obtained from the above calculation. The average diameter of Bi particles present at the interface was found to be about 100 nm. If the diameter of Bi particles is assumed to be 100 nm, their number can be calculated to be 8 (the mass density of Bi is 9.8 g/cm^3), when 1 μm^3 Cu_3Sn formed. This result is well consistent with our aforementioned observation.

The higher Bi solution in Cu_6Sn_5 in 42Sn58Bi/Cu joint in as-reflow condition could result from increased reflow temperature and cooling rate after reflow process. These factors can promote the Bi segregation in the solder joint, when it is in a long-term service.

On the other hand, Bi could also precipitate from formed Cu_3Sn layer, when 42Sn58Bi/Cu solder joint cooled from 120 °C to room temperature, since the Cu_3Sn was oversaturated with Bi at that time. The quantity of Bi, 3.99E-14 g, precipitated from 1 μm^3 Cu_3Sn during cooling would be obtained by the difference between the Bi solubility in ε phase at 120 °C and that at room temperature, if its solubility at 120 °C was assumed as mentioned above. Instead of being able to traverse Cu_3Sn to nucleate at the Cu_3Sn/Cu interface, Bi precipitates would disperse into Cu_3Sn layer to form crystallites in the absence of Cu diffusion flux as in aging process.

Conclusions

Bi redistribution process in the 42Sn58Bi/Cu solder joint aged at 120 °C for 7 days comprised 2 stages:

(1) During the aging process at 120 °C, the Bi precipitates resulted from phase transformation from Cu_6Sn_5 to Cu_3Sn, and most of Bi precipitates were driven to the Cu_3Sn/Cu interface by the Kirkendall effect. The quantity of Bi from 1 μm^3 of Cu_3Sn was reasonably estimated to be 4.106E-14 g. These Bi precipitates accumulated and nucleated to form particles, with the formation of more Cu_3Sn, when they reached Cu_3Sn/Cu interface, owing to the unwettability of Bi on Cu metallization. The number of Bi particles formed with a diameter of 100 nm was estimated to be about 8.

(2) When the joint cooled from 120 °C to room temperature in air, Bi also precipitated from formed Cu_3Sn layer to form highly dispersed crystallites. Its amount was also evaluated to be about 3.99E-14 g per μm^3 of Cu_3Sn.

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