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Bismuth segregation enhances intermetallic compound growth in SnBi/Cu microelectronic interconnect

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ABSTRACT

There was a sudden increase of intermetallic compound (IMC) Cu_6Sn_5 growth rate in the eutectic Sn58wt. %Bi/Cu joint during aging process. With aging time increasing, Bi accumulated at the Cu_3Sn/Cu interface and gradually induced the fracture mode of the joint to change from ductile to brittle one along this interface. Bi segregation enhanced IMC Cu_6Sn_5 growth by means of promoting the interfacial reaction at Cu_3Sn/Cu interface, which was concluded from IMCs (Cu_6Sn_5 and Cu_3Sn) growth behavior for pure Sn/Cu and Sn10wt. %Bi/Cu interconnects at the same temperature.

1. Introduction

Sn-based solder/Cu joint is important for reliability of electronic device. Eutectic Sn58wt. %Bi lead-free solder attracts much attention from the world due to its better mechanical properties and environmental concerns [1–4]. The interfacial reaction between solder and Cu is necessary to form IMC to make strong metallurgical bonding, when the components are reflowed. Many papers [5–10] have indicated that the IMC Cu_6Sn_5 (η phase) develops and Cu_3Sn (ε phase) forms between Cu_6Sn_5 and Cu substrate, when the interconnect is aged at a higher homologous temperature. But excessive growth of the IMC during the service of the electronic components may undermine the joint to make the components fail, because of the brittleness of IMCs. So the growth kinetics of IMC is essential in the solder joint reliability evaluation, and analytical techniques have been developed, which can be used to predict the long term IMC layer from short term isothermal experimental data. Many literatures [11–14] reported that the average thickness of IMC follows Arrhenius equation, described as following:

$$\overline{H} = \bar{h}_0 + A_0\sqrt{\exp\left(\frac{-Q_a}{RT}\right)}t^n \tag{1}$$

where $\bar{h}_0$ presents initial thickness of the joint; T, temperature; t, aging time. For most interconnects, the thickness values of total IMC layer was a linear function of the $\sqrt{t}$. So n value in equation is 1/2, Q_a value can be drawn from Eq. (1), as expressed by Eq. (2):

$$-\frac{Q_a}{2R} = \frac{d[\ln(d\overline{H}/dt)]}{d(1/T)} \tag{2}$$

Our previous works [8,12] have shown that besides the quick IMC Cu_6Sn_5 and Cu_3Sn growth and formation, nano-sized Bi particles segregated at Cu_3Sn/Cu interface in the solder joint, after it was aged at 120 °C for 7 days, as shown in the inset of Fig. 1. At this moment, the mechanical property dropped greatly and the fracture mode of solder joint changed from solder fracture to complete brittle one along Cu_3Sn/Cu interface, as shown in Fig. 2. And Bi particles at the interface were responsible for the brittle fracture. In this work, we reported an interesting phenomenon that the IMC growth was promoted after Bi segregation and the brittle fracture of the joint, occurring during aging process in eutectic SnBi/Cu interconnect. It is helpful to better understanding the interfacial reaction between Sn-based solder and Cu substrate.

2. Experimental procedures

The substrate used in this study was oxygen-free high conductivity copper sheet. Two copper sheets were soldered together with the commercial eutectic SnBi solder paste to form a copper–solder–copper sandwich structure. Before soldering, the copper surfaces were carefully polished by using 0.1 μm diamond paste, and then rinsed in water and methanol alcohol. After air drying, eutectic SnBi solder paste was dispersed on two copper sheets. Several thin metal shims were placed on one of the copper surfaces to control the solder thickness. Then two copper sheets were

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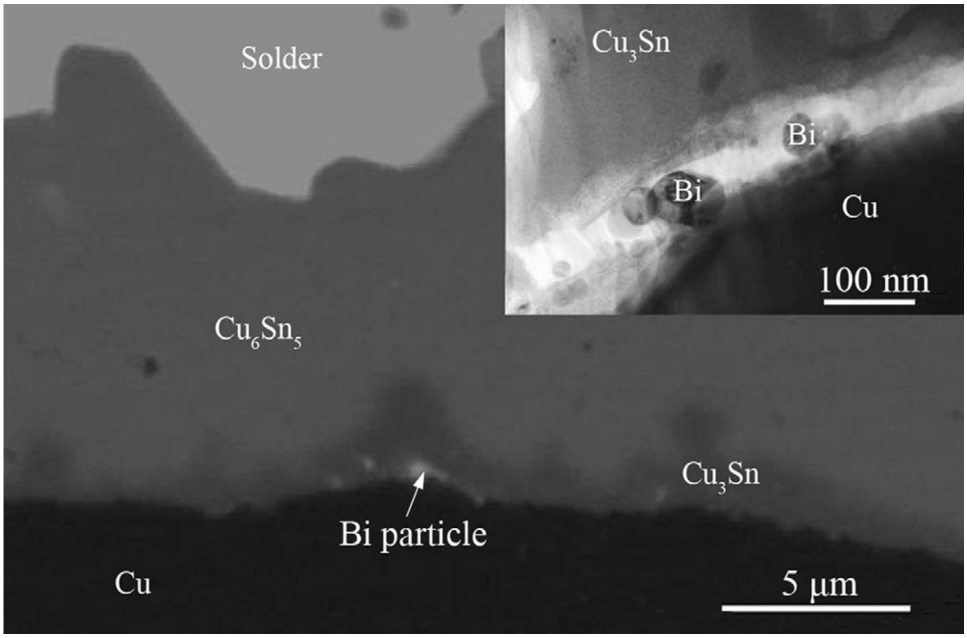

Fig. 1. The interfacial structure of eutectic SnBi/Cu joint aged at 120 °C for 7 days under SEM and nano-sized Bi particles can be found at Cu_3Sn/Cu interface under TEM as shown in the inset.

clamped together and heated in drying box, where the reflowed process was conducted at 170 °C for 5 min to reflow the solder joint. The specimen at this stage was in the as-reflowed condition. It was divided into several pieces. Thermal aging of the samples in as-reflowed condition was conducted at 110, 120, 130 °C, respectively, for different times in drying box with accuracy of temperature control ±1 °C. The melting point of eutectic SnBi alloy is 139 °C, and 110–130 °C are high homologous temperatures (with values of T/T_m 0.93–0.978). Then the samples were mechanically broken, and the fracture modes were marked in aging time *vs* temperature diagram.

In order to better understand the Bi effect on IMC growth, the IMC growth kinetics of pure Sn/Cu and Sn10wt. %Bi/Cu joints were studied. The pure Sn/Cu joint was prepared by placing a piece of pure Sn (with 99.999% purity) on a polished Cu sheet mentioned above with mildly activated rosin flux (type RAM). The reflow process was conducted at 250 °C for 5 min to flow pure Sn on Cu substrate. Then it was cut into pieces and they were aged at 180 °C for different times in drying box. The Sn10wt. %Bi solder alloy was prepared by melting pure Sn and Bi (with 99.999% purity) together in the vacuum induction-furnace, according to their weight percentage. Then the solder alloy was formed into sheet with thickness of 0.5 mm. The Sn10Bi/Cu joint was obtained in the same way as that of pure Sn/Cu joint mentioned above. The reflow process was conducted at 250 °C for 5 min to reflow the Sn10Bi solder. Then the as-reflowed Sn10Bi/Cu specimen was divided into pieces and they were aged at 180 °C for different times. The melting points of pure Sn and Sn10Bi alloy are 231.9 °C and about 220 °C, respectively. The ratios of 180 °C to melting points are 0.897 and 0.919, respectively. And it is also high homologous temperature. We selected 180 °C as the aging temperature to correspond to the aging temperatures 110–130 °C for eutectic SnBi/Cu joint. The interfacial structures of the samples in as reflowed and aged conditions were observed by using JEOL JSN-7001F scanning electron microscope (SEM) and transmission electron microscope (TEM).

3. Results and discussion

The average thickness of IMC Cu_6Sn_5 (there was no Cu_3Sn found under SEM) in the joint in as-reflowed condition was about 2 μm. It was found that two layers of IMC (Cu_6Sn_5 and Cu_3Sn respectively) formed between solder and Cu substrate, after the eutectic SnBi/Cu joint in as-reflowed condition was aged, as shown in Fig. 1. And nano-sized Bi particles were found to segregate at the Cu_3Sn/Cu interface under SEM and TEM. One of fracture surfaces of the joint changed from solder to completely reddish copper with the aging time increasing, as shown in Fig. 2. At temperature range of 110–130 °C, the average thickness of total IMC in the joints aged at different temperatures for different times was presented in Fig. 3. We can find that, at each temperature, there were 2 IMC growth stages. At each stage, the thickness of IMC exhibited linear dependence of the square root of aging time, $\sqrt{t}$. But at latter stage, the slope of the line, which represents the rate of IMC growth, became

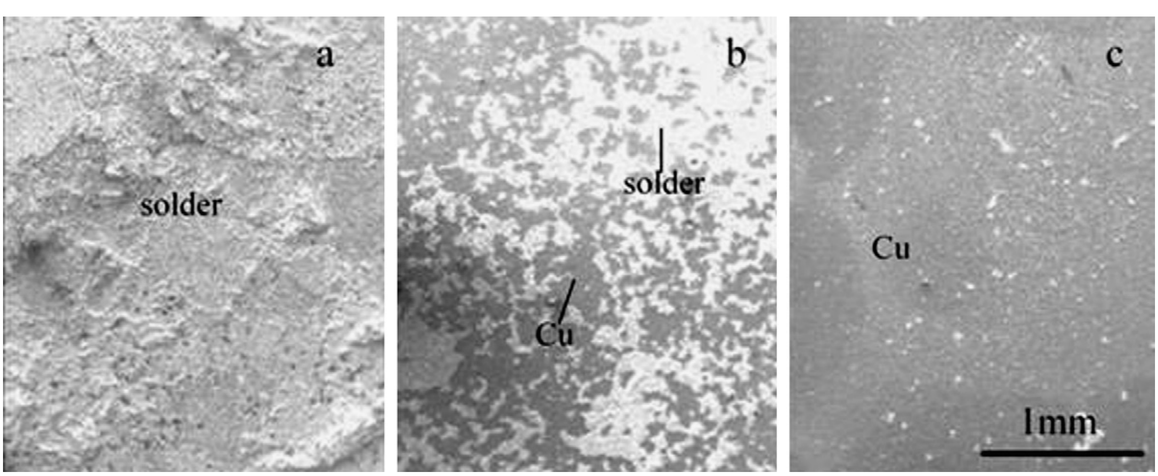

Fig. 2. The SEM images for the fracture surfaces of eutectic SnBi/Cu interconnects in as-reflowed condition (a), aged at 120 °C for 3 days (b), and aged at 120 °C for 7 days (c).

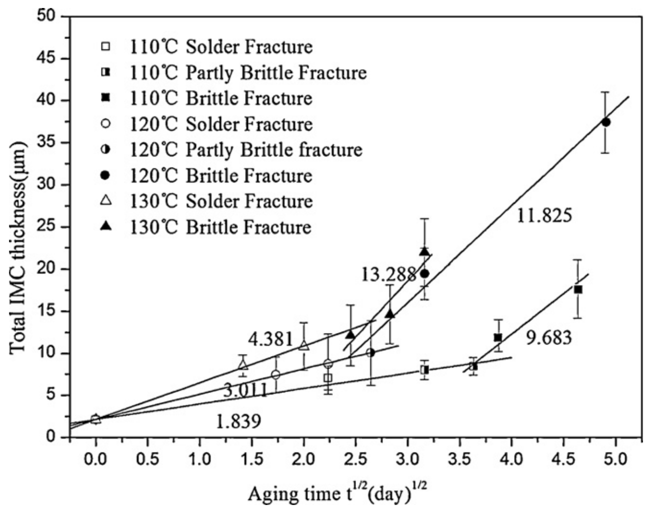

Fig. 3. The relation curves between IMC thickness and square root of aging time for eutectic SnBi/Cu solder joint aged at 110–130 °C. And fracture modes of the joints also were shown by symbols, as indicated in the legend.

greater than that at initial stage. The IMC growth was accelerated at the latter stage. The IMC includes Cu_6Sn_5 and Cu_3Sn. From the interfacial observations of the solder joints, the Cu_3Sn grew more slowly than Cu_6Sn_5 did. The Cu_6Sn_5 and Cu_3Sn growth kinetics can be found in Fig. 4 and the inset of the image, respectively. From Fig. 4, the average thickness of IMC Cu_3Sn developed linearly with the square root of aging time and there was no increase of IMC growth rate during the whole aging process. Because the IMC Cu_3Sn was very thin (only 1–2 μm at latter stage), compared with the IMC Cu_6Sn_5, the IMC Cu_6Sn_5 growth behavior was nearly the same as that of total IMC, as shown in Fig. 3. With the aging temperature increasing at the range of 110–130 °C, the growth rates of IMC Cu_6Sn_5, Cu_3Sn and total IMC all increased, respectively. And the fracture modes of the joints aged at these temperatures were also marked in Fig. 3. It can be found that at the latter stage, the fracture modes of the joints aged at 110–130 °C, all appeared to be completely brittle one, while those at initial stage were ductile or semi brittle fracture.

At initial stage, Q_a originated from data values in Fig. 3 according to Eq. (2) can be calculated to be 111.8 kJ/mol. At this stage

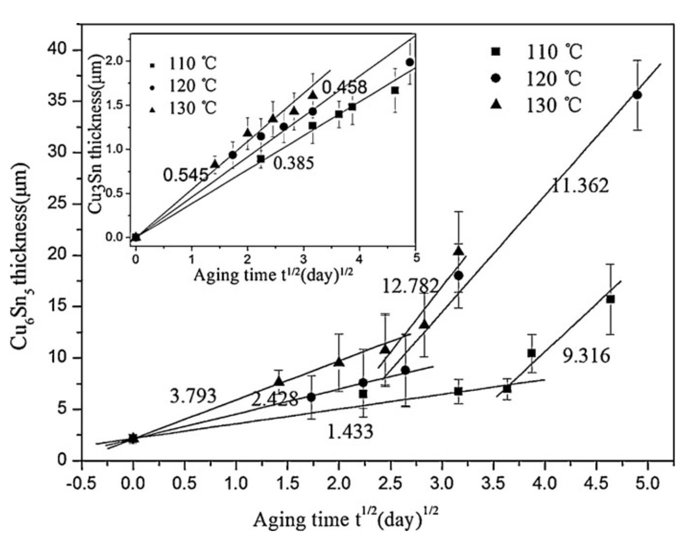

Fig. 4. The relation curves between IMC Cu_6Sn_5 thickness and square root of aging time for eutectic SnBi/Cu joint aged at 110–130 °C. And the IMC growth kinetics Curve for IMC Cu_3Sn can be found in the inset of the figure.

the results can be explained by classical diffusion control theory. Bi precipitated due to its lower Bi solubility in Cu_3Sn than that in IMC Cu_6Sn_5, when Cu_6Sn_5 turned into Cu_3Sn during IMC growth process [12]. With the aging time increasing, the more Cu_3Sn formed, the more Bi precipitated and migrated to the Cu_3Sn/Cu interface under Kirkendall effect, nucleated there to form nano-sized particles, because Bi cannot react with Cu. Then the connection between Cu_3Sn and Cu substrate was cut. Therefore, when a quantity of Bi segregated at the interface in the joint, the fracture mode of it changed to completely brittle one. On the other hand, the IMC growth rate was accelerated by the Bi segregation. At this stage, the Q_a, activation energy, was computed to be 40.8 kJ/mol, which was lower than that at initial stage.

In order to better explain the phenomenon, the IMC growth process should be understood. There are 2 processes for the IMC growth in the Sn-based solder/Cu inter-diffusion couple. One is inter-diffusion process, in which the Cu is dominant species in Sn–Cu inter-diffusion, reported by many previous works [14–18]. The other is interfacial reaction, in which the IMC formation occurs by the chemical reaction between Sn and Cu at the interfaces in solder/Cu interconnect. These 2 processes affect mutually. Diffusion process provides the atoms for the reaction, while chemical reaction makes it possible for atoms to enter IMCs.

From Sn–Cu and Bi–Cu phase diagrams [19], Sn can react with Cu to form intermetallic compound, while there is no interaction between Bi and Cu. There is Sn–Cu inter diffusion reaction in SnBi/Cu couple. Sn–Cu phase diagram shows that there is a Cu concentration band width in each phase of the IMC. There must be a Cu concentration gradient in each IMC layer in solder/Cu interconnect. And Cu is believed to be the dominant species in Sn/Cu inter diffusion couple. The Cu diffusion is driven by the higher chemical potential induced by increased Cu concentration gradient. The dominant Cu diffusion flow provides sufficient Cu atoms for the formation of IMC. Fig. 5 illustrates the growth process for IMC in Sn-based solder/Cu couple.

At Cu/Cu_3Sn interface, the interfacial reaction occurs and local chemical equilibrium is established at $C_{\varepsilon Cu}$, which is Cu concentration of ε near the Cu/Cu_3Sn interface, as shown in Fig. 5(c). Cu atoms from substrate enter into ε phase by chemical reaction expressed by Eq. (3). A part of them stay at the Cu/Cu_3Sn interface, and the others form the Cu diffusion flux (J_ε).

$$3Cu + Sn(Cu_3Sn) \leftrightarrow Cu_3Sn \quad (3)$$

At the Cu_3Sn/Cu_6Sn_5 interface, one part of J_ε reacts with Cu_6Sn_5 to form Cu_3Sn, and makes Cu_3Sn phase grow, which is expressed by Eq. (4). The other part of J_ε enters into η phase to form diffusion flux (J_η). The ratio of J_η to J_ε determines the migration rate of η/ε interface.

$$9Cu + Cu_6Sn_5 \leftrightarrow 5Cu_3Sn \quad (4)$$

At Cu_6Sn_5/solder interface, a part of J_η participates to form Cu_6Sn_5, and Cu_6Sn_5 develops, which is expressed by Eq. (5), while the other part of it dissolves in solder.

$$6Cu + 5Sn(solder) \leftrightarrow Cu_6Sn_5 \quad (5)$$

When Bi particles appeared at the Cu_3Sn/Cu interface, the chemical reaction, described by Eq. (3) changed from combination between pure Sn and Cu to reaction between Sn and Cu with the presence of Bi at the interface, and it can be described by following equation:

$$3Cu + Sn\,(Cu_3Sn) \xleftrightarrow{Bi} Cu_3Sn \quad (6)$$

In this circumstance, the Bi acted as a kind of catalyst in the process of chemical reaction between Sn and Cu, though it does not participate in the reaction directly. The chemical reaction includes

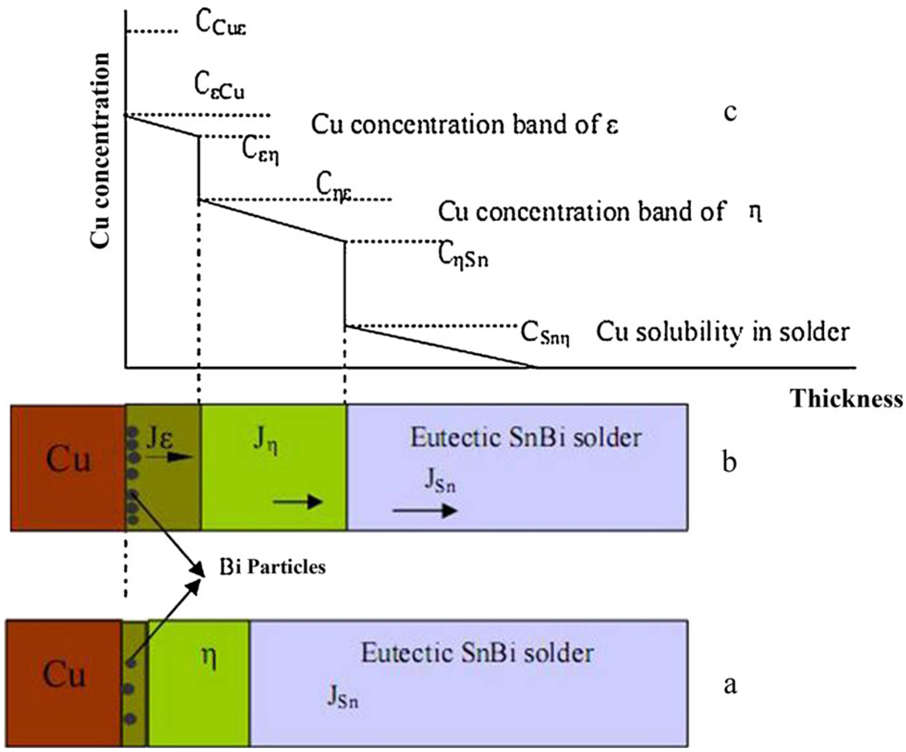

Fig. 5. Schematic diagram for IMC growth process: (a) interfacial structure evolution in solder/Cu interconnect during aging process. Little Bi segregation occurred because little Cu_3Sn formed. (b) With aging time increasing, the more Cu_3Sn formed, the more Bi segregated at the Cu_3Sn/Cu interface. (c) Cu concentration profile along thickness of IMC in the interconnect. Where, $C_{Cu\varepsilon}$, Cu concentration of Cu substrate near the Cu/ε interface; $C_{\varepsilon Cu}$, Cu concentration of ε near the Cu/Cu_3Sn interface; $C_{\varepsilon\eta}$, Cu concentration of ε near the ε/η interface; $C_{\eta\varepsilon}$, Cu concentration of η near the ε/η interface; $C_{\eta Sn}$, Cu concentration of η near the η/solder interface; $C_{Sn\eta}$, Cu concentration of solder near the η/solder interface.

many processes, such as atoms activation process, meta-stable mid-reaction, etc. The Bi can be helpful in breaking chemical bond between Cu atoms or that between Cu and Sn in Cu_3Sn molecules to make more of them activated. So the rate of interfacial reaction described by Eq. (6) would be faster than that of reaction described by Eq. (3).

The presence of Bi at Cu/Cu_3Sn would result in more atoms activated. So the interfacial reaction at the interface was accelerated, when enough Bi particles segregated there and resulted in brittle fracture of the joint. This would lead to the lower $C_{Cu\varepsilon}$, Cu concentration at Cu_3Sn/Cu interface near Cu substrate side as shown in Fig. 5(c), than that at the interface without Bi particles. The gradient of Cu concentration in the Cu substrate will be increased. As a consequence, more Cu atoms were driven to diffuse out of Cu substrate to participate in IMC formation. At the same time, the $C_{\varepsilon Cu}$, Cu concentration at IMC ε/Cu interface near Cu_3Sn side, was induced to increase due to the accelerated reaction here. The gradient of Cu concentration was increased in ε phase. This would promote more Cu migration to Cu_3Sn/Cu_6Sn_5 interface. And more Cu atoms entered into η phase to lead to higher Cu gradient in η phase. Then more atoms were provided to the chemical reaction at η/solder interface to form more IMC Cu_6Sn_5. The accelerated chemical reaction at ε/Cu interface led to the quick migration of the interface between IMC and solder towards solder in 42Sn58Bi/Cu interconnect during aging process and the total IMC developed at a higher rate. From Fig. 4, one can find that IMC Cu_3Sn did not experience the increased growth. It was because more Cu atoms were driven to η/solder interface to form Cu_6Sn_5. We all knew that IMC Cu_6Sn_5 would first form, when the solder/Cu interconnect was reflowed. And formation of IMC Cu_6Sn_5 was easier than that of Cu_3Sn. So more atoms were attracted to the η/solder interface to form more Cu_6Sn_5 and IMC Cu_3Sn formation was blockaded.

In order to better understand the effect of Bi on IMC formation, we conducted the experiments on IMC formation kinetics of pure Sn/Cu and Sn10wt. %Bi/Cu interconnects at the same temperature 180 °C. Our experimental results, as shown in Fig. 6, also indicated that Bi can accelerate the IMC growth. It can be found that the slope of the total IMC thickness *vs* square root of aging time curve was 2.284, higher than that of pure Sn/Cu at the same temperature 180 °C, which was 1.886. The IMC growth rate of Sn10wt. %Bi/Cu joint was higher than that of pure Sn/Cu joint. And the growth rate of Cu_6Sn_5 and Cu_3Sn in these joints can be found in the inset of

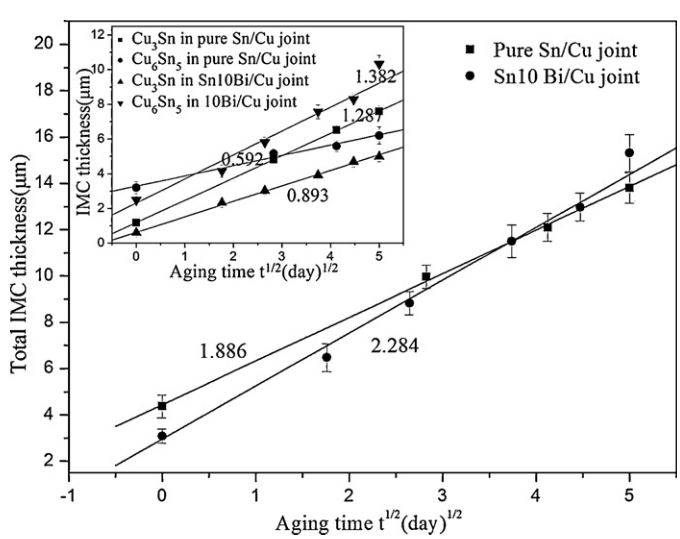

Fig. 6. The average IMC thickness *vs* $t^{1/2}$ curves for Sn10Bi/Cu and pure Sn/Cu interconnects aged at 180 °C.

Fig. 6, respectively. All IMCs in the solder joints developed linearly with the square root of aging time. The slope of curve for Cu_6Sn_5 in Sn10wt. %Bi/Cu joint was 1.382, higher than that for the Cu_6Sn_5 in pure Sn/Cu interconnect, which was 0.592. But the slope of curve for Cu_3Sn in pure Sn/Cu was 1.287, and that of Cu_3Sn in Sn10wt. %Bi/Cu joint was 0.893. When the pure Sn/Cu and Sn10wt. %Bi/Cu solder joints in as-reflowed condition were aged, the chemical reaction occurred at interfaces in the interconnects. But the reactions at Cu_6Sn_5/solder in the interconnects were different, because the chemical compositions at these interfaces were not the same. The chemical reaction rate at the Cu_6Sn_5/solder interface in Sn10wt. %Bi/Cu joint would be accelerated due to the presence of Bi in solder, compared with that of chemical reaction at the counter-interface in pure Sn/Cu joint. The IMC Cu_6Sn_5 growth in Sn10wt. %Bi/Cu interconnect was enhanced by consumption of more Cu atoms and resulted in the lower growth rate of Cu_3Sn, compared with that in pure Sn/Cu joint. At the mean time, we can find that IMCs in Sn10wt. %Bi/Cu and pure Sn/Cu interconnects, in which there was no Bi segregation during aging process, all developed linearly with square root of aging time. They have no sudden increase of IMC thickness during later time, as presented in Fig. 3. It showed that the Bi segregation at the Cu_3Sn/Cu interface in the eutectic SnBi/Cu interconnect heavily affected the growth of IMC during later aging time.

4. Summary

The kinetics of intermetallic compounds were studied for eutectic SnBi/Cu and pure Sn/Cu as well as Sn10wt. %Bi/Cu interconnects. In summary, several facts can be found:

1. There were 2 IMC growth stages for eutectic SnBi/Cu interconnect during aging process. At each stage, the IMC's thickness developed linearly with square root of aging time.
2. At initial IMC growth stage for eutectic SnBi/Cu joint, there was no enough Bi segregation at Cu_3Sn/Cu interface to make the joint fracture in completely brittle way. But after long aging time, and enough Bi segregation occurred, the eutectic SnBi/Cu joint appeared completely brittle fracture and at mean time there was a sudden increase of the IMC Cu_6Sn_5 growth rate.
3. Bi segregated at the Cu_3Sn/Cu interface accelerated IMC Cu_6Sn_5 growth rate in eutectic SnBi/Cu microelectronic interconnect. Bi can enhance interfacial reaction to form more IMC in Sn-based/Cu joint, which resulted from the kinetics of IMC growth in pure Sn/Cu joint with that of Sn10wt. %Bi/Cu interconnect.

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