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Effect of high intensity magnetic field on intermetallic compounds growth in SnBi/Cu microelectronic interconnect

C.Z. Liu^{a,*}, T.Y. Kang^b, W. Wei^a, K. Zheng^a, L. Fu^{a,c}, L. Hui^a, J.J. Wang^a, W.P. Tong^{b,**}

- ^a Shenyang Aerospace University, Shenyang, 110136, China
- b Key Laboratory of Electromagnetic Processing of Materials, Ministry of Education, Northeastern University, Shenyang, 110819, China
- ^c State Key Laboratory for Manufacturing Systems Engineering Xi'an Jiaotong University, Xi'an, China

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ABSTRACT

The growth kinetics of intermetallic compounds (IMCs) (Cu_6Sn_5 and Cu_3Sn) in eutectic Sn58 wt.%Bi/Cu joints were studied, after they were aged at 85, 100 and $120\,^{\circ}C$ for different times in 0, 12 Tesla (T) magnetic fields, respectively. The Cu is believed to be dominant species, when Cu and Sn inter-diffuse to form IMCs in the interconnect. When the solder joints were aged in the magnetic field, magnetic field direction (denoted by magnetic flux density \overrightarrow{B}) was arranged to be parallel and anti-parallel as well as perpendicular to that of Cu diffusion. The results indicated that chemical compositions of the IMCs formed in magnetic fields were the same as those formed without magnetic field. The IMC growth rate in magnetic field was higher than that without magnetic field. And the activation energy for IMC growth in 12 T magnetic field was 43.29 kJ/mol, lower than 84.45 kJ/mol for IMC growth without magnetic field. The accelerated IMC growth was independent of magnetic field direction. The phenomenon resulted from promoted interfacial reaction by magnetic field.

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1. Introduction

Lead-free solder eutectic SnBi alloy is of interest in electronic industry because of its advantages including low melting point (139 °C), excellent wetting performance and superior mechanical properties. Previous studies, such as literatures [1–5], have indicated that the IMC Cu_6Sn_5 always forms (IMC Cu_3Sn also forms, however it is too thin to be found), after Sn-based solder/Cu joint is reflowed. The Cu_6Sn_5 develops and Cu_3Sn can be found between Cu_6Sn_5 and Cu substrate, when it is aged for long time. The mechanical properties always drop greatly due to the excessive growth of IMC layer [6,7]. So the interfacial reaction kinetics between solder and Cu substrate is an important issue in reliability evaluation of electronic device. Many studies indicated that the average IMC thickness increased with the aging time, as described by Eq. (1).

$$\overline{H} = \overline{h_0} + A_0 \sqrt{\exp\left(\frac{-Q_a}{RT}\right)} t^n \tag{1}$$

where $\overline{h_0}$ presents initial thickness of IMC in the joint, after the joint is reflowed; T, temperature; t, time; T, constant; T is the average IMC thickness, after the interconnect is aged at T temperature for

E-mail addresses: chunzliu@yahoo.com (C.Z. Liu), wptong@mail.neu.edu.cn (W.P. Tong).

time t. For most interconnects, the total IMC thickness values is a linear function of the \sqrt{t} . So n value in equation is 1/2, Q_a value (activation energy) can be drawn from following Eq. (2):

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

With the development of new technology, many electronic devices have to work in the more complicated electromagnetic environment. Many papers [8–12] have showed that the high magnetic field can influence the metallurgical processes and significantly change the thermodynamic conditions of materials. Very few researches have been reported about the effect of magnetic field on the IMC growth in eutectic SnBi/Cu joint applied in electronic packaging. In this paper, a phenomenon of the IMC growth behavior in eutectic SnBi/Cu interconnect aged in high magnetic field is reported. This will be helpful to the design and choices of lead-free solder alloys for electronic devices in complicated electromagnetic condition.

2. Experimental procedures

The Cu sheets used in the study were pure, highly conductive and oxygen free. They were ground and polished with $0.5\,\mu m$ diamond paste. The sandwich structured Cu/Solder/Cu joint was prepared by placing commercial eutectic SnBi solder paste on one of two Cu sheets. Several shims were placed on the Cu sheet to control the thickness of solder paste. Then two Cu sheets were aligned and clamped together. The reflow process was conducted at $170\,^{\circ}\text{C}$ for $5\,\text{min}$ to reflow the solder paste. The sample in this stage was in as-reflowed condition. Then it was cut into small pieces and aged in a special furnace. This furnace consists of a supercon-

^{*} Corresponding author. Tel.: +86 24 89724198.

^{**} Corresponding author. Tel.: +86 24 83682376.

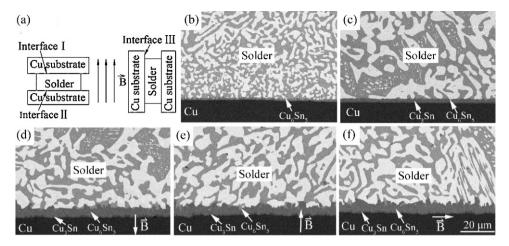


Fig. 1. The schematic diagram of sandwich structured samples in the magnetic field (a); and the interfacial structures of eutectic SnBi/Cu interconnects in various conditions: as reflowed (b); aged at 120 °C for 70 h, at interface II (e); aged at 120 °C for 70 h, at interface II (e); aged at 120 °C for 70 h, at interface III (f).

ducting magnetic device (JMTD-12T 100, JASTEC, Japan) which can generates a high magnetic field with maximum \overrightarrow{B} of 12 T, and a vacuum resistance furnace. The specimens were aged at 85, 100 and 120 °C for 7, 38 and 70 h in 0 T and 12 T magnetic fields, respectively. The specimens were also aged at 120 °C in 6 T magnetic field for comparative purpose. When the specimens were aged in magnetic fields, they were arranged with their solder/Cu interfaces (I, II, III) perpendicular and parallel to the \overrightarrow{B} direction, as shown in Fig. 1(a). The interfacial structures of these specimens were observed under JEOL JSN-7001F Scanning Electron Microscope (SEM). The chemical compositions of IMCs were analyzed by energy dispersive X-ray spectroscopy (EDS). The average thickness of the IMC layer was measured by using image analysis software Image pro plus 6.0.

3. Results and discussion

The interfacial structures of the eutectic SnBi/Cu joints in different conditions can be found in Fig. 1(b)-(f). The IMC layer in as-reflowed condition, as shown in Fig. 1(b), was identified to be Cu₆Sn₅ by EDS and previous studies [3,6]. And its thickness was about 1.31 µm. The solder alloy in the joint appeared to be eutectic lamella structure. Fig. 1(c) indicated the interfacial structure of the joint aged at 120 °C for 70 h without magnetic field. The grain size of the eutectic solder alloy developed after it was aged, compared with that of the solder in as-reflowed condition, as shown in Fig. 1(b). The average thickness of Cu₆Sn₅ grew from 1.31 to 2.76 µm, and a new layer of Cu₃Sn identified by EDS and previous studies appeared between Cu₆Sn₅ and Cu substrate. The interfacial structures of the interconnects aged at 120 °C for 70 h in 12 T magnetic field can be found in Fig. 1(d)–(f). The solder alloys aged in 12 T magnetic field appeared the same structure as that aged without magnetic field, as shown in Fig. 1(c). The IMC layer was composed of two sub-layers, Cu₆Sn₅ and Cu₃Sn. The results demonstrated that chemical compositions of IMCs formed in interconnects aged in high magnetic field were the same as those aged without magnetic field. The average thickness of IMC layer at interface I was 5.51 µm, while it was 5.53 µm at interface II and 5.83 µm at interface III, respectively, when they were aged at 120 °C for 70 h in 12 T high magnetic field. The magnetic field directions do not significantly influence the IMC thickness. The same situation occurred for all samples aged at 85 and 100 °C in 6T and 12T magnetic fields. The relation curves between average thickness of the total IMC at three interfaces aged at 85, 100 and 120 °C in 0T and 12T magnetic fields and square root of aging time were presented in Fig. 2. We can find that the average thickness of IMC in eutectic SnBi/Cu joints aged at 85, 100 and 120 °C in 0T and 12T magnetic fields increased linearly with the square root of aging time. The slopes of curves stand for the IMC growth rates. For the interconnects aged at 85,

100 and 120 °C in 12T magnetic field, the IMC growth rates were 0.275, 0.361 and $0.524 \,\mu m/h^{1/2}$, respectively. They were greater than that of IMC formed at 85, 100 and 120 °C in 0T magnetic field, which were 0.048, 0.083 and 0.164 μ m/h^{1/2}, respectively. The growth rate for IMC aged at 85 °C in 12 T was 0.275 µm/h^{1/2}, greater than $0.164 \,\mu\text{m/h}^{1/2}$, which was growth rate for IMC aged at $120\,^{\circ}\text{C}$ in 0T. The activation energies for them can be derived from these data by Eq. (2). They are 43.29 kJ/mol and 84.45 kJ/mol, respectively. These results demonstrated that the IMC growth in joints aged in 12 T high magnetic field was accelerated. A part of the Cu₆Sn₅ will turn into Cu₃Sn with Cu diffusion into Cu₆Sn₅, therefore the total IMC growth kinetics is the same as that of Cu_6Sn_5 in the solder joint. The IMC growth kinetics for the joints aged at 120 °C in 0, 6 and 12 T magnetic fields was presented in Fig. 3. We can find that the IMC growth rate increased with the magnetic intensity increasing. They were 0.164, 0.255 and 0.524 μ m/h^{1/2}, for total IMC aged at 120 °C in 0, 6 and 12T magnetic fields, while they were 0.071, 0.084 and $0.114 \,\mu\text{m/h}^{1/2}$ for IMC Cu₃Sn, which can be found in the inset of Fig. 3. However, the IMC growth rate was not linear dependence of the intensity of the magnetic field (see Fig. 4).

Many studies [13–16] have revealed that Cu diffusion is dominant in the Sn/Cu inter-diffusion couple during the aging process. At interface I, the $\stackrel{\rightarrow}{B}$ direction was reverse to that of Cu diffusion.

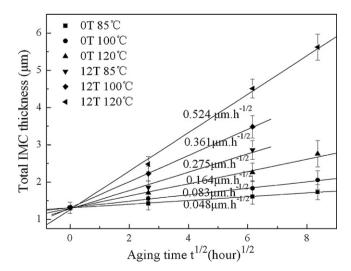


Fig. 2. The relation curves between average thickness of total IMC and square root of aging time $t^{1/2}$ for joints aged at different temperatures in 12 T and 0 T magnetic fields.

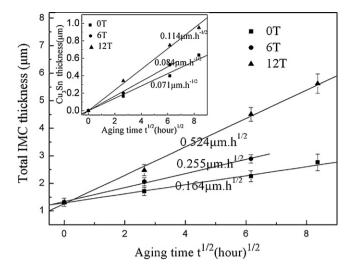


Fig. 3. The relation curves between average thickness of total IMC and square root of aging time $t^{1/2}$ for joints aged at $120\,^{\circ}$ C in 0, 6 and $12\,\text{T}$ magnetic fields. The inset is the kinetics for IMC Cu₃Sn in the joints aged at $120\,^{\circ}$ C in 0, 6 and $12\,\text{T}$ magnetic fields.

At interface II, it was the same as Cu diffusion direction, while it was perpendicular to the Cu diffusion direction at interface III. The IMC thickness at three interfaces was nearly the same, when they were aged at the same temperature for the same time in the magnetic field. This indicated that the \overrightarrow{B} direction has no obvious influence on the Cu diffusion. Diffusion and interfacial chemical reaction are two processes for IMC formation and growth in the solder/Cu joint. And these two processes will mutually affect each other. We have known that \overrightarrow{B} direction has no influence on Cu diffusion. Then, we can confirm that the interfacial reactions occurred at the interfaces in solder joints were enhanced by magnetic field. During aging process, at interface Cu₃Sn/Cu, Cu₃Sn/Cu₆Sn₅ and Cu₆Sn₅/Solder, chemical reactions occur, respectively. The IMC formation process was discussed in detail in literature [13]. Chemical reaction includes many processes, such as atoms activation process, meta-stable mid-reaction, etc. The rates of reactions do not entirely depend on the dynamic energy factors. They are also affected by the order of reaction system-entropy of the system [17]. According to Lewis collision theory, the chemical reaction can occur, only when the atoms (or molecules) involving in reaction collide with each other in a proper direction. This kind of collision is effective. And the reaction rates are dependent on the number of effective col-

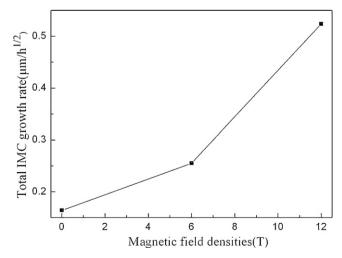


Fig. 4. The relation curve between total IMC growth rate in SnBi/Cu joint aged at 120 °C and intensity of the magnetic field.

lision between them. The high magnetic field can affect unpaired electron spin of all the atoms (or molecule) involving in the reaction. We knew that Sn and Cu, which are main elements in the reaction under investigation, are paramagnetic and diamagnetic, respectively. When the joint was aged in high intensity magnetic field, the Cu and Sn atoms were forced to rotate to a direction and in which more Cu and Sn atoms can collide in a proper relative position to make the collision effective. So a part or all of chemical reaction rates at the interfaces were accelerated in the solder joint by the magnetic field. And it was external high magnetic field that forced the Sn and Cu atoms involving in the reaction to rotate and collide effectively. When magnetic field direction changed, Cu and Sn atoms may rotate to other direction. But their proper relative position in which they collide effectively was not changed. In other direction, they also can collide effectively. That is why we can find IMC growth rates at three interfaces were the same and all enhanced. The magnetic field affected the atom activation process for chemical reaction. The accelerated reactions would consume more Cu atoms and decrease the Cu concentrations at interfaces, especially that at Cu₆Sn₅/solder interface. Then the Cu concentration gradient increases in IMC phases. The increased Cu concentration gradient would accelerate the Cu atoms diffusion to compensate the loss of Cu atoms due to more IMC formation. Consequently, the total IMC in high magnetic field grew faster than that did without magnetic field.

4. Conclusions

In summary, the IMC growth behavior in Sn58 wt.%Bi/solder joint was examined, after it was aged at 85, 100 and 120 °C in 0 T and 12 T high magnetic fields. From the present study high magnetic fields can accelerate the growth rate of IMC $\rm Cu_6Sn_5$ and $\rm Cu_3Sn$ by promoting the interfacial reaction rates in the solder joint without influencing the chemical compositions of these IMCs. The activation energy for IMC growth in eutectic SnBi/Cu interconnect aged in 12 T magnetic field was 43.29 kJ/mol, while it was 84.45 kJ/mol for the joints aged without magnetic field. The accelerated IMC growth was independent of the magnetic field direction.

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