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Effect of Solder Joint Thickness on Intermetallic Compound Growth Rate of Cu/Sn/Cu Solder Joints During Thermal Aging

The sandwich structure Cu/Sn/Cu solder joints with different thicknesses of the solder layers (δ) are fabricated using a reflow solder method. The microstructure and composition of the solder joints are observed and analyzed by scanning electron microscopy (SEM). Results show that the thickness of intermetallic compound (IMC) and Cu concentration in the solder layers increase with the decrease of δ after reflow. During thermal aging, the thickness of IMC does not increase according to the parabolic rule with the increase of aging time; the solder joint thickness affects markedly the growth rate of IMC layer. At the beginning of thermal aging, the growth rate of IMC in the thinner solder joints ($\delta \le 25 \ \mu m$) is higher than that in the thicker ones ($\delta \ge 30 \ \mu m$). The growth rate of IMC ($\delta \le 25 \ \mu m$) and is nearly invariable when the δ equals to 30 $\ \mu m$ with aging time extending. The growth rate of IMC increases first and then decreases after reaching a peak value with the increase of δ in the later stage during aging. The main control element for IMC growth transfers from Cu to Sn with the reduction of size. [DOI: 10.1115/1.4034819]

Keywords: solder joint thickness, intermetallic compound, growth rate, main control element

1 Introduction

The solder joints used as interconnects in today's electronic packaging continue to get smaller and smaller in size to meet the demand on further miniaturization and multifunctionality of microelectronics [1,2]. From ball grid array packages (BGA) to wafer-level packages (WLP) and even in the three-dimensional (3D) die stacking package, the size of solder joints ranges from hundreds of micrometers to dozens of micrometers [3]. The miniaturization of solder joints leads to some changes in the microstructure of the solder joints and some new reliability problems. For example, the IMC layer proportion (the ratio of interfacial IMC layer thickness to the whole solder joint thickness) increases with decreasing size of solder joints [4]. Generally, IMCs are desirable to form a good bond between the solder and the pad. However, due to their brittle nature, the excessive IMC formation can potentially weaken the solder joint strength. It has been reported that the strength of solder joints decreases and thermal cycling fatigue life shortens with increasing thickness of the IMC layer at the interface [5–7]. The increase of the ratio of the IMC in smaller-sized solder joints can change the failure mode from ductile to a mixture of ductile and brittle [8,9]. As the solder joint size reduces, the component, thickness, and morphology of the IMC layer also experience great changes [10-12]. Such changes have an essential effect on joints' reliability. Therefore, it is necessary to investigate the size effect on the IMC evolution and growth, which can provide a theoretical basis and data for evaluating and improving the reliability of smaller-sized joints. Studies on IMC growth are especially important in emerging microelectronic applications such as compliant interconnects and microbumps for

3D stacked dies where the solder size is in the range of $10-20 \,\mu m$ [13,14]. The objective of this research is to study the IMC thickness, composition, and morphology in the sandwich structured solder joints with solder layers of dozens of microns after reflow and during thermal aging. Particularly, emphasis is placed on the effect of the solder joint size on the interfacial IMCs' growth rate during thermal aging.

2 Experimental Procedures

In electronic packaging industry, Sn-alloys (PbSn or SnAgCu) and NiPdAu or Electroless Nickel/Immersion Gold (ENIG) substrates are more widely used. The variety of solder and substrates makes the interfacial reaction and compounds more complicated [11,15–17]. In order to simplify the question, the pure Sn pieces and Cu substrate were chosen.

The solder joints used in this study are shown schematically in Fig. 1. The copper-clad laminate (CCL) is a fundamental material for the printed circuit board (PCB). The copper-clad laminates were cut into small slats 15 mm length and 4 mm width. Sn pieces of different thicknesses were selected as solder. Two copper-clad plates and one Sn piece are assembled into a sandwich structure. The gap between two copper-clad plates (δ) reflects the size of Cu/Sn/Cu solder joints after reflow. Therefore, the δ was varied from $10 \,\mu\text{m}$ to $50 \,\mu\text{m}$ to study the effect of the size of the solder joints on the interfacial structure. The Cu/Sn/Cu sandwich structures were reflowed with the peak temperature of 265 °C for 50 s. The working temperature of microjoint is about 100 °C in electronic packaging. To accelerate the interfacial reaction and shorten time, raising aging temperature is the common way. The temperature is usually chosen from 120 °C to 180 °C. Therefore, the samples were aged at 160 °C for 48, 96, 192, 384, and 600 h.

The microstructure of Cu/Sn/Cu solder joints was observed using the scanning electron microscopy (SEM). Image analysis software was used to measure the thickness of the IMC layers. In the present studies, the IMC thickness means the average

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Fig. 1 The schematic diagram of Cu/Sn/Cu solder joint

thickness of IMC at one side of the solder joint. In order to obtain the average results, at least ten specimens with the same δ were prepared as a group. The compositions of solder joints were analyzed by the energy-dispersive X-ray spectrometry (EDX).

3 Results and Analysis

3.1 The Microstructure and Compositions of the Solder Joint After Reflow. The microstructure of Cu/Sn/Cu solder joint consists of two IMC layers at both sides of the solder joint and a bulk solder layer after reflow, as shown in Fig. 2. As identified by EDX analysis, the IMC layer formed at interface is the Cu₆Sn₅ phase. At the beginning of reflow, the Cu substrate dissolves quickly, and the Cu atoms diffuse in the molten Sn solder. As the diffusivity of Cu in molten solder is very high [16], the Cu atoms can diffuse into the whole solder during reflow. Diffusion of Cu atoms results in the increase of Cu concentration. The Cu₆Sn₅ can form at the interface and in solder layer according to Cu–Sn phase diagram (Fig. 3).

The constituents' concentration in the solder is generally considered as a constant on hundreds of microns scale. However, it changes with the size of solder joint at dozens of microns scale. Figure 4 shows that the Cu concentration in the solder layer increases with the decrease of δ . For thinner solders, diffusion distance of Cu atoms is shorter, and the volume of solder is smaller than the thicker ones. Therefore, the Cu concentration rises faster. And it is higher than the thicker ones after the same reflow time.



Fig. 2 Cross section SEM images of Cu/Sn/Cu solder joint after reflow



Fig. 4 The thickness of Cu_6Sn_5 layer and Cu concentration with various δ

Figure 4 shows the average thickness of the IMC layer and Cu concentration in bulk solder joint with different δ ($\delta = 10-50 \mu m$). It is clearly shown that the Cu concentration in the solder layer increases with the decrease of δ . In the thinner solder joint, the Cu concentration rises faster because that diffusion distance of Cu atoms is shorter, and the volume of Sn solder is smaller than the thicker ones.

According to Fig. 4, the Cu concentration in the solder layer of all the solder joints exceeds Cu solubility in the liquid Sn (about 1.6 wt. %). This means that Cu is supersaturated in liquid Sn at reflow temperature. In this supersaturated state, the dissolved Cu exists in the form of solid solution and free Cu-rich particles in the liquid Sn [19,20]. The literature suggests that the higher the Cu concentration is, the more the Cu-rich particles are. Therefore, there are more Cu-rich particles in the solder layer of solder joints with the thinner δ than in thicker ones. Free Cu-rich particles will have more opportunities to attached Cu₆Sn₅ at the interface due to shorter moving path. This can increase the growth rate of Cu₆Sn₅ layer. With the increase of δ , the moving path increases, the Cu-rich particles have less effect on Cu₆Sn₅ layer thickening.

3.2 The Evolution of IMC Layer at Interface During Thermal Aging. The IMCs formed after soldering continue to grow at the service temperature by interdiffusion between the elements of the solder and the substrate. Thus, the interface takes on a more complicated microstructure. The cross-sectional morphology of the Cu/Sn/Cu solder joints with different δ after aging at

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160 °C for 600 h is shown in Fig. 5. The thickness of IMCs increases, and an extra IMC layer is observed between the Cu₆Sn₅ and both the Cu substrates. This extra layer is confirmed as Cu₃Sn by EDX. The proportion (the ratio of mean IMC thickness to the whole solder joint) is greater in the solder joint with the thinner δ than the thicker ones.

As shown in Fig. 6, the IMC layers in all the specimens thicken with the increase of aging time, and IMCs' thickness is affected by the δ during aging. Thickening of the IMC layer is one of the main failure modes of the solder joint. Therefore, it is an important part of solder joint reliability problem to study the growth of IMC layer. In the range of hundreds of microns, Cu concentration is very low and changes little in the solder during aging. Therefore, the thickness of IMC layer can be calculated using the diffusion equation ($x = x_0 + \sqrt{Dt}$). The diffusion equation shows a linear relationship between the IMC thickness and the square root of the aging time. However, the relationship between the IMC thickness and the square due to the δ reducing in the present experiments.



Fig. 5 Cross section SEM images of Cu/Sn/Cu solder joint after aging at 160 °C for 600 h: (a) $\delta = 10 \ \mu m$, (b) $\delta = 30 \ \mu m$, and (c) $\delta = 50 \ \mu m$



Fig. 6 The relationship between the average thickness of IMC layers and aging time at 160 $^\circ\text{C}$

At dozens of microns scale, the decrease of the δ results in changes of Cu concentration in the bulk solder and its gradient in front of Cu₆Sn₅/solder interface during aging. Figure 7 shows the changes of Cu concentration and its gradient at different stages of thermal aging. Cu concentration increases and its gradient decreases with the reduction of δ . On the one hand, Cu atoms through IMC layer are divided into two parts: some diffuse into solder layer, and the others participate in the interfacial reaction. The higher the Cu concentration in the solder layer is, the slower the diffusion of Cu atoms in the solder layer becomes, and there are more Cu atoms participating in the interfacial reaction. It is beneficial for the growth of the IMC. On the other hand, the increase of Cu concentration means the decrease of Sn concentration. The growth of IMC layer and Sn diffusion to Cu substrate may lead to the reduction of Sn solder. Because the amount of Sn diffusing into Cu substrate is relatively small, the relative consumption of Sn solder can be approximated to the ratio of the amount of Sn in the IMC layer to the initial amount of Sn solder. As shown in Fig. 8, the relative consumption of Sn solder increases with the aging time prolonging and is greater in solder joint with the thinner δ than the thicker ones. The decrease of Sn concentration leads to a decrease of the interfacial reaction rate and growth rate of IMC layer.

The diffusion of Cu atoms and the consumption of Sn solder are the main factors that change the IMC thickness. At the initial period of aging or in the solder joints with thicker δ , the IMC layer is thinner and the Cu concentration is smaller, and the rate of Cu atoms diffused into solder layer is faster and the relative consumption of Sn solder is lower. Therefore, the diffusion of Cu atoms has more significant impact on the IMC thickness. Otherwise, after a long time aging or in the solder joints with thinner δ , the consumption of Sn solder has more significant impact on the Cu concentration.

According to previously-mentioned analysis results, the decrease of the δ is the fundamental cause of the increase of Cu concentration and Sn relative consumption. Therefore, the size of the solder joint has a significant impact on the IMC growth.

3.3 The Growth Rate of IMC Layer and Transformation of Main Control Element. By fitting experiment data, the function of the IMC thickness and thermal aging time is obtained, as shown in Table 1. The growth rates of IMC layers can be calculated by taking the derivatives of functions in Table 1. The growth rates of IMC layer during thermal aging are shown in Fig. 9.

The chemical reaction between Cu and Sn atoms is a requirement for the growth of IMC, and the speed of chemical reaction depends on elements' composition at the interface. Therefore, the

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Fig. 7 The changes of Cu concentration in front of Cu_6Sn_5 /solder interface during aging at 160 °C: (*a*) aged for 0 h, (*b*) aged for 192 h, (*c*) aged for 384 h, and (*d*) aged for 600 h



Fig. 8 The changes of relative consumption of Sn solder during thermal aging at 160 $^\circ\text{C}$

Table 1 Fitting equations of IMC thickness and aging time

δ (μ m)	Fitting equation	Adj. R-square
10	$X(t) = 0.00491t + 0.10428t^{1/2} + 3.5783$	0.99051
20	$X(t) = 0.00445t + 0.16332t^{1/2} + 3.2510$	0.98665
25	$X(t) = 0.00844t + 0.07209t^{1/2} + 3.2041$	0.99072
30	$X(t) = 0.01141t + 0.00531t^{1/2} + 3.1466$	0.99006
40	$X(t) = 0.01166t - 0.02161t^{1/2} + 3.1463$	0.997
50	$X(t) = 0.01204t - 0.05984t^{1/2} + 3.1403$	0.99879

composition change in the front of the interface significantly influenced the growth rate of IMC with the reducing δ . Cu₆Sn₅ and Cu₃Sn are both Cu-rich phases relative to the Sn solder; therefore, higher Cu concentration in the front of the interface is beneficial for the growth of IMCs as long as there is a sufficient source of

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Fig. 9 Growth rate of IMC layer during thermal aging

Sn. This can explain that the growth rate of IMC in the thinner solder joints ($\delta < 30 \,\mu$ m) is higher than in the thicker ones ($\delta \ge 30 \,\mu$ m) at the beginning of thermal aging. In the thicker solder joints ($\delta \ge 30 \,\mu$ m), Sn source is relatively sufficient, and the growth of IMCs increases due to the increase of Cu concentration with the aging time extending. When the δ reduces to less than $30 \,\mu$ m, insufficient source of Sn makes the Sn concentration decrease in the front of the interface and limits IMC growth during thermal aging. Under this condition, the growth rate of IMC decreases with the aging time extending. The combination effects of higher Cu concentration and the decrease of Sn make the growth rate of IMC nearly invariable in the solder joint ($\delta = 30 \,\mu$ m) with aging time extending.

According to the previously-mentioned analysis, the growth rate of IMC depends on the concentration of Cu, Sn atoms in the

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Fig. 10 Growth rate of IMC layer versus the δ

front of the interface at dozens of microns scale. Cu and Sn atoms come from Cu substrate and Sn solder, respectively. In the solder joints with the thicker δ ($\delta > 30 \,\mu$ m), the Sn concentration is higher and changes little during thermal aging. The composition at interface is controlled by the diffusion of Cu atoms. Therefore, Cu is the main control element of IMC growth. Both Cu and Sn concentrations change greatly during aging in the solder joints with the thinner δ ($\delta < 30 \,\mu$ m). This must affect interfacial reaction rate. The reduction of Sn solder is the main influencing factor of this change. Therefore, Sn becomes the main control element of IMC growth. This transformation becomes obvious in the later stage of aging. In the solder joints with the thinner δ ($\delta < 30 \,\mu$ m), Sn is the main control element, the growth rate of IMC decreases with the reduction of the δ , while the growth rate of IMC decreases with the increase of the δ in the solder joints with the thicker δ (δ > 30 μ m), because that Cu is the main control element in thicker solder joint, as shown in Fig. 10.

4 Conclusions

After reflow, with the reduction of the δ from 50, 40, 30, and 20 to 10 μ m, the IMC thickness in the Cu/Sn/Cu solder joints and the average Cu concentration in the solder layer increase markedly. During thermal aging, Cu and Sn concentrations in the front of Cu₆Sn₅/Sn interface experience significant change. The thinner the δ is, the greater the Cu and Sn concentrations become. The relation between the IMC thickness and the aging time does not comply with traditional parabolic law for the changes of Cu and Sn concentrations.

The solder joint size is an important factor affecting the growth rate of IMC. At the beginning of thermal aging, the growth rate of IMC in the thinner solder joints ($\delta \le 30 \,\mu$ m) is higher than in the thicker ones ($\delta > 30 \,\mu$ m). For the thinner solder joints, the growth rate of IMC decreases over aging time, and the growth rate of IMC decreases with the reduction of the δ in the later stage during aging. For the thicker solder joints, the growth rate of IMC increases over aging time, and the growth rate of IMC increases over aging time, and the growth rate of IMC increases with the reduction of the δ in the later stage during aging. The growth rate of IMC in all the specimens reaches relatively stable value with aging time increasing. The main control element of IMC growth shifts from Cu to Sn with solder joint thickness reducing and aging time prolonging at dozens of microns scale. A solder layer with the thickness over $30 \,\mu\text{m}$ can keep initial IMC layer thin, and IMC growth rate decreases with the thickening of the solder layer, which implies good reliability for thicker solder joints.

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References

- [1] Lu, H., Takagi, Y., Suzuki, Y., Sawyer, B., Taylor, R., Sundaram, V., and Tummala, R., 2014, "Demonstration of 3-5μm RDL Line Lithography on Panel-Based Glass Interposers," 2014 IEEE 64th Electronic Components and Technology Conference (ECTC), Orlando, FL, May 27–30, pp. 1416–1420.
- [2] Ouyang, F. Y., and Jhu, W. C., 2013, "Comparison of Thermomigration Behaviors Between Pb-Free Flip Chip Solder Joints and Microbumps in Three Dimensional Integrated Circuits: Bump Height Effect," J. Appl. Phys., 113, p. 043711.
- [3] Wu, F., Wang, B., Du, B., An, B., and Wu, Y., 2009, "Effect of Stand-Off Height on Microstructure and Tensile Strength of the Cu/Sn9Zn/Cu Solder Joint," J. Electron. Mater., 38(6), pp. 860–865.
- [4] Wang, B., Wu, F., Wu, Y., Liu, H., Zhou, L., and Fang, Y., 2010, "Effect of Stand-Off Height on the Microstructure and Mechanical Behaviour of Solder Joints," Soldering Surf. Mount Technol., 22(1), pp. 11–18.
- [5] Tian, Y., Hang, C., Wang, C., Yang, S., and Lin, P., 2011, "Effects of Bump Size on Deformation and Fracture Behavior of Sn3.0Ag0.5Cu/Cu Solder Joints During Shear Testing," Mater. Sci. Eng. A, 529, pp. 468–478.
 [6] Yang, M., Li, M., Wang, L., Fu, Y., Kim, J., and Weng, L., 2011, "Cu₆Sn₅ Mor-
- [6] Yang, M., Li, M., Wang, L., Fu, Y., Kim, J., and Weng, L., 2011, "Cu₆Sn₅ Morphology Transition and Its Effect on Mechanical Properties of Eutectic Sn-Ag Solder Joints," J. Electron. Mater., 40(2), pp. 176–188.
- [7] Che, F., and Pang, J. H., 2012, "Characterization of IMC Layer and Its Effect on Thermomechanical Fatigue Life of Sn-3.8Ag-0.7Cu Solder Joints," J. Alloys Compd., 541, pp. 6–13.
- [8] Li, X., Xia, J., Zhou, M., Ma, X., and Zhang, X. P., 2011, "Solder Volume Effects on the Microstructure Evolution and Shear Fracture Behavior of Ball Grid Array Structure Sn-3.0Ag-0.5Cu Solder Interconnects," J. Electron. Mater., 40(12), pp. 2425–2435.
- [9] Yang, L., Zhang, Q., and Zhang, Z. F., 2012, "Effects of Solder Dimension on the Interfacial Shear Strength and Fracture Behaviors of Cu/Sn-3Cu/Cu Joints," Scr. Mater., 67(7–8), pp. 637–640.
- [10] Anderson, I. E., Boesenberg, A., Harringa, J., Riegner, D., Steinmetz, A., and Hillman, D., 2012, "Comparison of Extensive Thermal Cycling Effects on Microstructure Development in Micro-Alloyed Sn-Ag-Cu Solder Joints," J. Electron. Mater., 41(2), pp. 390–397.
- [11] Tian, Y., Chow, J., Liu, X., and Sitaraman, S. K., 2015, "The Size Effect on Intermetallic Microstructure Evolution of Critical Solder Joints for Flip Chip Assemblies," Soldering Surf. Mount Technol., 27(4), pp. 178–184.
- [12] Li, X., Sun, F., Liu, Y., Zhang, H., and Xin, T., 2014, "Geometrical Size Effect on the Interface Diffusion of Micro Solder Joint in Electro-Thermal Coupling Aging," J. Mater. Sci.: Mater. Electron., 25(9), pp. 3742–3746.
- [13] Ostrowicki, G. T., Fritz, N. T., and Sitaraman, S. K., 2012, "Domed and Released Thin-Film Construct—An Approach for Material Characterization and Compliant Interconnects," IEEE Trans. Device Mater. Reliab., 12(1), pp. 15–23.
- [14] Liu, X., Chen, Q., Sundaram, V., Wachtler, K. P., Tummala, R. R., and Sitaraman, S. K., 2012, "Reliability Assessment of Through-Silicon Vias in Multi-Die Stack Packages," IEEE Trans. Device Mater. Reliab., 12(1), pp. 263–271.
- [15] Ho, C. E., Lin, Y. W., Yang, S. C., Kao, C. R., and Jiang, D. S., 2006, "Effects of Limited Cu Supply on Soldering Reactions Between SnAgCu and Ni," J. Electron. Mater., 35(5), pp. 1017–1024.
- [16] Chada, S., Fournelle, R. A., Laub, W., and Shangguan, D., 2000, "Copper Substrate Dissolution in Eutectic Sn-Ag Solder and Its Effect on Microstructure," J. Electron. Mater., 29(10), pp. 1214–1221.
- [17] Islam, M. N., Sharif, A., and Chan, Y. C., 2005, "Effect of Volume in Interfacial Reaction Between Eutectic Sn-3.5% Ag-0.5% Cu Solder and Cu Metallization in Microelectronic Packaging," J. Electron. Mater. 34(2), pp. 143–149.
- tion in Microelectronic Packaging," J. Electron. Mater., 34(2), pp. 143–149.
 [18] Massalski, T., 1996, *Binary Alloy Phase Diagrams*, Vol. 3, ASM International, Metals Park, OH.
- [19] Rhee, H., Guo, F., and Lee, J. G., 2003, "Effects of Intermetallic Morphology at the Metallic Particle/Solder Interface on Mechanical Properties of Sn-Ag-Based Solder Joints," J. Electron. Mater., 32(11), pp. 1257–1264.
- [20] Sharif, A., Chan, Y. C., and Islam, R. A., 2004, "Effect of Volume in Interfacial Reaction Between Eutectic Sn-Pb Solder and Cu Metallization in Microelectronic Packaging," Mater. Sci. Eng. B, 106(2), pp. 120–125.

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