Effect of Zinc Addition on Void Formation in Solid-Liquid Interdiffusion Bonding of Copper

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Solid-liquid interdiffusion bonding of Cu was carried out at 573 K with deposited Sn and Cu films. The effect of Zn addition to the faying surfaces was investigated to reduce Kirkendall voids. At the beginning of the reaction, molten Sn reacted with Cu to form Cu₆Sn₅, and Cu₃Sn successively formed between the Cu₆Sn₅ and the Cu. Many voids formed in the Cu₃Sn phase, especially close to the Cu₃Sn/Cu interface. When Zn was added in the faying surfaces, Zn was segregated near the interface of Cu/Cu₃Sn and the grain boundaries of Cu₃Sn. The Zn segregation inhibited diffusion of Cu due to the effect of solute drag, which also delayed growth of the Cu₃Sn layer. As a result, the fluxes of Cu and Sn via the Cu₃Sn phase were balanced out, which reduced the Kirkendall void formation. [doi:10.2320/matertrans.MD201509]

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1. Introduction

Power devices are widely used as key technologies for power and railway systems. These power devices rely on bonds such as chip/Cu substrate (die bonding) and wire-lead/chip bonds, which have historically used Sn-based lead-free solders.

SiC and GaN are expected to be used as next-generation power semiconductors because they exhibit better efficiency and can operate at higher temperatures than Si chips. With junction temperatures approaching 473 K with SiC and GaN semiconductors, standard Sn-based lead-free solders cannot be applied for die bonding. To address the problems associated with the use of standard Sn-based lead-free solders at higher temperatures, solid-liquid interdiffusion bonding is a possible alternative for the die bonding process. In solid-liquid interdiffusion bonding, metals with low melting points such as Sn and In are sandwiched between copper bases and heated above the melting point of the inserted materials to realize die bonding by solid-liquid reaction diffusion.¹⁻⁶⁾ The liquid phase then reacts with the base copper to form a bond layer of intermetallic compounds (IMCs) that exhibits a higher melting point than the melting point of the inserted material.

In solid-liquid interdiffusion bonding in a Cu-Sn system, the final bond layer is composed of Cu₃Sn. However, voids are frequently observed near the Cu₃Sn/Cu interface and at the interface between the Sn-based solder and the Cu substrate. When the molten Sn-based solder alloy wets the copper, Cu₆Sn₅ and Cu₃Sn IMCs form at the solder/Cu interface. In most cases, voids also form at the Cu₃Sn/Cu interface and/or in Cu₃Sn.⁷⁻⁹⁾ Both the growth of IMCs and void formation affect the solder joint reliability, which can degrade the mechanical and electrical properties of the joints. It has been reported that the mechanism of void formation in the Cu/Sn system is basically caused by unbalanced diffusion fluxes ($Cu_{flux} > Sn_{flux}$) in the Cu₃Sn phase, that is to say, the Kirkendall effect.¹⁰⁾ Since Kirkendall voids are formed due to unbalanced diffusion fluxes, tiny amounts of additive elements will affect void formation and the growth of IMCs. Thus, the ef-

fects of various kinds of additive elements on the growth behavior of IMCs have been reported. For example, the addition of Ni was reported to reduce the growth of the Cu₃Sn layer.^{11,12)} Ma *et al.* reported that the addition of 0.05 mass% of La also reduced the growth of Cu₆Sn₅.¹³⁾ Above all, the addition of a small amount of Zn is significantly effective for suppressing the growth of Cu₆Sn₅ and Cu₃Sn and the formation of voids in the soldering process using Sn-based solders.^{14,15)} The growth of IMCs and the formation of voids were also suppressed between the Sn-Ag solder and the Cu-Zn alloy substrate due to the segregation of Zn at the Cu₆Sn₅/CuZn interface.¹⁶⁾

In the present study, a small amount of Zn was added to the faying surface in the solid-liquid interdiffusion bonding of Cu using a Sn thin-film filler metal to reduce void formation. Metallurgical examination was carried out to investigate the effect of Zn on the solid-liquid interdiffusion bonding.

2. Experimental procedures

The materials used were oxygen-free Cu rods 3 mm and 5 mm in diameter whose faying surfaces were polished with #4000-grit emery paper. They were then pickled in a 5% HCl solution and rinsed in ethanol. The designs of the faying interfaces and the bonding setup are shown in Table 1 and Fig. 1. The faying surface of Cu was coated with Sn, Cu, and/or Zn in order by vapor deposition in accordance with Table 1 by resistance heating under an atmosphere of 5×10^{-3} Pa. The faying surface of Design-A had only a 4-μm-thick Sn

Table 1 Designs of faying interfaces produced by vapor deposition coating.

	Thickness (μm)			
	Sn	Cu	Zn	Sn
Design-A	4	-	-	-
Design-B1	2	0.38	-	2
Design-B2	2	0.63	-	2
Design-C1	2	0.38	0.02	2
Design-C2	2	0.63	0.02	2

Fig. 1 (a1)–(a3) Designed faying surfaces prepared by vapor deposition coating and (b) set-up of solid–liquid diffusion bonding of copper. Details of the layered structures are shown in Table 1.

layer. A Cu thin film was deposited between the Sn films as an intermediate layer to fabricate a Sn/Cu/Sn faying surface, that is, Design-B. The thicknesses of the intermediate Cu layers in Design-B were 0.38 μm and 0.63 μm, denoted as Design-B1 and B2, respectively. Similarly, a 0.02-μm-thick Zn layer was deposited between the Sn and Cu layers on the Design-B1 and B2 faying surfaces, denoted as Design-C1 and

Fig. 2 Growth of IMC bond layers using deposited Sn coating (Design-A) at bonding times of (a) 300, (b) 600, and (c) 1800 s. Bonding temperature is 573 K.

C2 faying surfaces, respectively. The bonding between the φ3 mm and φ5 mm Cu specimens was performed at 573 K for bond times of 300, 600, and 1800 s under a bonding pressure of 10 MPa in nitrogen gas flow atmosphere (2 L/min), as shown in Fig. 1b. The microstructures of the bond layers were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with energy dispersive X-ray spectroscopy (EDX). The specimens for TEM observation were prepared by the focused ion beam (FIB) method.

3. Results and discussion

3.1 Bonding using mono-Sn film

The copper was bonded to itself using a mono-Sn film, that is, the Design-A faying surface, at 573 K. The cross sections

Fig. 3 Growth of IMC bond layers using deposited Sn/Cu/Sn coatings (Design-B faying surfaces) as a function of bond times of (a) 300, (b) 600, and (c) 1800 s for the Design-B1 faying surface and of (d) 300, (e) 600, and (f) 1800 s for the Design-B2 faying surface. Bonding temperature is 573 K.

of the bonded layers are shown in Fig. 2. When the temperature reaches 505 K, Sn melts, which improves the adhesion between the two materials. Once a liquid phase formed, Cu dissolved into the liquid Sn, resulting in the formation of Cu_6Sn_5 . Subsequently, Cu_3Sn formed at the interface between Cu_6Sn_5 and Cu due to reaction diffusion during the heating process up to 573 K (Fig. 2a). Because the amount of liquid Sn was quite small, it was consumed completely to form Cu–Sn IMCs immediately. The thickness of the Cu_3Sn layer increased with decreasing Cu_6Sn_5 thickness during the holding process at 573 K, until the whole bond layer was occupied by Cu_3Sn (Fig. 2c). It is worth noting that many voids appeared in the bond layer and at the interface of $\text{Cu}_3\text{Sn}/\text{Cu}$ as the thickness of the Cu_3Sn layer increased. In a Cu_3Sn phase, diffusion rate of Cu is faster than that of Sn as a result of the

so-called “ordered Cu_3Au rule.” In general, in compounds of the form A_mB_n , where m/n is greater than 2, the atoms of species A diffuse considerably faster than those of species B. d’Heurle *et al.* explained the phenomenon by the fact that, in general, the majority atoms constitute a continuous network in which a vacancy can easily migrate. On the other hand, the motion of minority atoms requires either the coexistence of two vacancies (minority and majority) or a local destruction of the crystalline lattice.^{17,18)} Therefore, the majority atoms of Cu are more mobile than the minority atoms of Sn in Cu_3Sn . In the present study, Cu_3Sn grew between Cu and Cu_6Sn_5 due to solid-phase reaction diffusion. Thus, most of these voids are believed to be Kirkendall voids.

Fig. 4 Effect of Zn addition on IMC growth as a function of bond times of (a) 300, (b) 600, and (c) 1800 s for the Design-C1 faying surface and of (d) 300, (e) 600, and (f) 1800 s for the Design-C2 faying surface. Bonding temperature is 573 K.

3.2 Bonding using Cu/Sn films

In the case of a mono-Sn film, Cu atoms were supplied from only Cu base metals to form Cu_3Sn . Then, a Cu thin film was supplied between the two Sn thin films of the faying surface (Fig. 1, Design-B) to shorten the apparent reaction time to form a Cu_3Sn layer. These Cu films are expected to work as another source of Cu to form Cu_3Sn . Figure 3 shows the cross sections of the bond interfaces of Cu bonded using Design-B1 and Design-B2 faying surfaces at 573 K with bond times of 300, 600, and 1800 s. Cu_6Sn_5 disappeared at the bond time of 600 s when using both Design-B1 and Design-B2 faying surfaces. Even at 300 s of bond time, most of the bond layer was composed of Cu_3Sn as a result of the increasing thickness of the intermediate Cu film (Fig. 3d). By locating a thin Cu film in the deposited layer as an intermediate supply source, the transformation from Cu_6Sn_5 to Cu_3Sn was completed in a

shorter time than in the case of bonding using only the mono-Sn film as the faying surface. However, the unbalanced diffusion flux between Sn and Cu in the Cu_3Sn phase has not been solved, and the addition of a Cu film into the Sn films increased the number of Cu/Sn interfaces. As a result, many more Kirkendall voids formed in the resulting bond layer than occurred using the mono-Sn film.

3.3 Effect of zinc

The addition of a deposited Cu film into the deposited Sn film shortened the apparent bond time; however, it increased the number of Kirkendall voids. Zn was therefore deposited between the deposited Cu/Sn films. Figure 4 shows the cross sections of the bond interfaces of Cu bonded using the Design-C1 and Design-C2 faying surfaces at 573 K with bond times of 300, 600, and 1800 s. The microstructure of the bond

Fig. 5 (a) SEM image and (b) Zn mapping of the distribution of Zn in the bond interface bonded for 1800 s using the Design-C1 faying surface. Bonding temperature is 573 K.

layer composed of Cu_3Sn and Cu_6Sn_5 was similar to that of the bond layer without Zn. However, the number of Kirkendall voids drastically decreased by the addition of Zn. On the other hand, it took longer for the whole bond layer to show only a Cu_3Sn phase than was the case with bonding without Zn. When Zn was added in the faying surface of Design-B1, Cu_6Sn_5 remained in the bond layer even at the bond time of 600 s (see Fig. 4b). In a similar fashion, Cu_6Sn_5 layers were obviously observed in the bond layer for the bond time of 300 s when Zn was added in the faying surface of Design-B2 (see Fig. 4d).

The distribution of Zn was investigated by SEM with EDX analysis. Figure 5 shows the Zn distribution in the bond layer using the faying surface with the addition of Zn. Zn was mainly segregated at the interface between the bond layer and the base metal, and some Zn remained around the voids located at the center of the bond layer. These voids were not Kirkendall voids since they were relatively-large compared with the voids that were formed at the Cu/bond layer interface. They were probably formed when the final liquid phase were solidified isothermally at the center of bond layer. The detailed microstructures of the bond layers with a bond time of 300 s were observed using TEM with EDX analyses (Fig. 6 and Fig. 7). Table 2 shows the results of quantitative EDX

Fig. 6 TEM observation of IMC layer bonded for 300 s with the Design-C1 faying surface. (a) Bright-field image of IMC layer, (b) highlighted area in (a), (c) SADP from point 1, and (d) SADP from point 2. Bonding temperature is 573 K.

analysis at each point shown in Fig. 7a. The beam diameter used for EDX analysis was ~ 2 nm. TEM observation revealed that the bond layer was composed of a $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ layered microstructure, and the grain size of Cu_3Sn was finer than that of Cu_6Sn_5 . Such obvious layered structure were not observed by SEM as shown in Fig. 4a. Because the layered structure is transition state, and the thickness of vapor deposition coating was not controlled perfectly. Therefore, some degree of variability on microstructures could occur even at the same bonding condition. Analysis points Nos. 1–5 in Fig. 7 correspond to Cu_3Sn and No. 6 corresponds to Cu_6Sn_5 . The EDX points and line analyses revealed that Zn was segregated at the interface between Cu_3Sn and the Cu base metal and at the grain boundary of Cu_3Sn .

Figure 8 shows the TEM bright-field images and selected area diffraction patterns (SADPs) of the IMC layer bonded for 1800 s. When the bond time reached 1800 s, most of the bond layer was composed of coarse grains, and there were fine grains near the interface between the bond layer and the Cu base metal. Cu_6Sn_5 completely disappeared in the bond layer. It is particularly worth noting that Cu_3Sn with fine grains formed next to the interface between the bond layer and the Cu base metal. As shown in Fig. 5, the fine grain area corresponds to where Zn was segregated. The grain boundary segregation of the solute inhibits the mobility of the grain boundary, that is to say, solute drag, which delays the grain growth of Cu_3Sn next to the Cu base metal. The interfacial and grain boundary segregation of Zn also inhibits diffusion of Cu in Cu_3Sn . The atoms of Sn are also affected by the seg-

Fig. 7 (a) TEM bright-field image and (b) EDX analysis of Zn near Cu/ Cu_3Sn bond interface. The bonding was carried out for 300 s using the Design-C1 faying surface. The compositions at each point in (a) are shown in Table 2. Bonding temperature is 573 K.

Table 2 Results of quantitative EDX analysis at each point shown in Fig. 7.

Point	Composition (at%)		
	Cu	Sn	Zn
1	92.9	5.2	1.9
2	75.7	24.0	0.3
3	72.2	23.4	4.4
4	74.5	35.4	0.1
5	69.5	30.1	0.4
6	54.7	45.1	0.2

regation of Zn. However, because Sn is the minor atom for diffusion, as mentioned above, the effect of Zn segregation on the mobility of Sn in the Cu_3Sn phase might be limited. As a result, the formation of Kirkendall voids is inhibited by the addition of Zn.

4. Conclusions

Copper was bonded to itself by using a deposited Sn film

Fig. 8 TEM observation of IMC layer bonded for 1800 s with the Design-C1 faying surface. (a) Bright-field image, (b) SADP from point 1, and (c) SADP from point 2. Bonding temperature is 573 K.

including Cu and/or Zn. The effect of Zn addition on the growth rate of the intermetallic compounds and the formation of Kirkendall voids was investigated. The following results were obtained:

(1) When Cu was bonded at 573 K using the faying surface of the deposited Sn film, liquid Sn immediately reacted with Cu to form Cu_6Sn_5 . Cu_3Sn formed successively between Cu_6Sn_5 and Cu, and the thickness of the Cu_3Sn layer increased with increasing bond time. Many voids formed near the interface between Cu_3Sn and the Cu base metal with increasing thickness of the Cu_3Sn phase. Finally, the bond layer consisted of only single-phase Cu_3Sn .

(2) The time needed to form single-phase Cu_3Sn in the bond layer was shortened by using Sn/Cu/Sn multilayered films. A thin Cu layer on the faying surface worked as an intermediate supply source to form Cu_3Sn . On the other hand, the number of Kirkendall voids increased at the Cu/ Cu_3Sn interface in the bond layer.

(3) The number of Kirkendall voids decreased by the addition of a small amount of Zn in the faying surface. The segregation of Zn at the Cu_3Sn /Cu interface and Cu_3Sn grain boundaries inhibited the mobility of Cu. On the other hand, the addition of Zn reduced the growth rate of the Cu_3Sn layer.

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