Journal of ELECTRONIC MATERIALS, Vol. 49, No. 2, 2020
https://doi.org/10.1007/s11664-019-07838-8

Effect of Zinc Addition on the Evolution of Interfacial Intermetallic Phases at Near-Eutectic 50In-50Sn/Cu Interfaces

JINGZE WANG,[1,2] DONGXIN MAO,[1] HONGTAO CHEN,[1]
XIAOHUA ZHANG,[1] LEI SHI,[1] and JIANBING WANG[1]

1.—School of Materials Science and Engineering, Harbin University of Science and Technology, Harbin 150040, China. 2.—e-mail: wangjingze310@163.com

The effect of Zn addition on the evolution of IMC at near-eutectic 50In-50Sn/Cu interfaces was investigated at 210°C. In 50In-(50-x)Sn-xZn/Cu(x = 0, 6) diffusion couples, two types of intermetallic compound layers were observed: ε-Cu_3(In,Sn) adjacent to the Cu substrate and η-Cu_2(In,Sn) adjacent to the solder, which were formed though a solid–solid diffusion reaction and solid–liquid reaction, respectively. The growth of ε-Cu_3(In,Sn) was at the expense of η-Cu_2(In,Sn). In 50In-44Sn-6Zn/Cu diffusion couple, the growth of ε-Cu_3(In,Sn) was grain-boundary diffusion controlled and n (the time constant) was 0.31. But in the 50In-50Sn/Cu diffusion couple, due to the slow growth of η-Cu_2(In,Sn), the time constant of ε-Cu_3(In,Sn) was down to 0.19. With the addition of Zn in the 50In-50Sn/Cu couple, the diffusion of Cu was alleviated. Zn exhibited high activity and moderated the dissipation of the main atoms (In/Sn) in the solder. So the growth of Cu_3(In,Sn) was suppressed significantly.

Key words: ε-Cu_3(In, Sn), η-Cu_2(In, Sn), intermetallic compound evolution, power-law relationship

INTRODUCTION

In the field of electronic packaging, In-Sn eutectic alloy is highly regarded for its good plasticity, excellent thermal conductivity and low melting point.[1,2] However, with the increasing integration of electronic components and the diversification of their application scenarios,[3,4] the reliability of In-Sn eutectic solder is challenged.

Most research shows that the reliability of solder joints is mainly affected by the IMC (intermetallic compound) formed between the solder and the substrate. The soldering properties may be affected if the IMC is too thick or fast-growing. Tsao et al.[5] reported that wicker-IMC growth can cause reliability concerns, and mainly cracks were found along the wicker-Cu_6Sn_5 IMC after ball shear tests. Numerous studies were carried out to moderate IMC growth and improve soldering performance. Alloying is a commonly used methos. Chang[6] proposed that the activation energy of IMC and its further growth can be suppressed by mechanically intermixing nano-Al_2O_3 particles into the Sn-Ag-Cu solder. Pstruś et al.[7] added appropriate amount of Indium to the Sn-Zn eutectic solder to improve its wettability. Zinc was found to be effective in improving the drop resistance of Sn-3.5Ag solder on a Cu pad.[8]

However, IMC is affected by both alloying elements and by aging temperature. Even in the same diffusion couple, the formed IMC is different. For instance, in a Sn-3.5Ag-0.5Cu/Cu diffusion couple, the initial scallop-like IMC transformed to a more planar type at low and intermediate aging temperatures, but became hump-like at high aging temperature.[9] Also, the change law of IMC thickness is influenced by the temperature. The thickness of the IMC layer depends approximately parabolically on time at high temperatures and linearly at low temperatures.[10]

Lin et al.[2] studied the growth and evolution behavior of IMC in the Sn-20In-xZn/Cu diffusion

---

(Received August 15, 2019; accepted November 14, 2019;

couple. But the situation is different in the reaction of the near-eutectic In-Sn alloy with Cu. So in this paper, the effect of Zn addition on the evolution of IMC at the near-eutectic 50In-50Sn/Cu interface was investigated at 210°C.

MATERIALS AND METHODS

50In-(50-x)Sn-xZn(x = 0, 6) was fabricated using pure indium (99.995 at.%), pure tin (99.995 at.%) and pure zinc (99.995 at.%) at 500°C by high frequency induction heating. The solder for aging was in bulk form and weighed about 0.05 g. The size of the copper substrate is approximately 15 × 15 × 0.2 mm. All bare Cu substrates were put into 30 wt.% HNO_3 solutions in sequence to remove the oxide film and other impurities on the surface, then they were cleaned by alcohol. An AMTECH-4300 type flux manufactured in the United States was used. The aging temperature was 210°C, which was about 90°C above the melting point of the alloy. Under such condition, the so-formed IMC was more stable at lower temperature.[10]

Almost all IMCs had a rapid earlier-growth stage that was chemical reaction-limited (n = 1, n is the time exponent). Usually, it doesn't last more than 5 min. At this stage, the thickness of the IMC was linear with the aging time, even if it was under high temperature.[11,12] Therefore, the key point was the mechanism judgment at the later stage. In the present case, the samples were heated for 15 min, 30 min, 45 min, 60 min, and 75 min, respectively, avoiding the influence of the first stage.

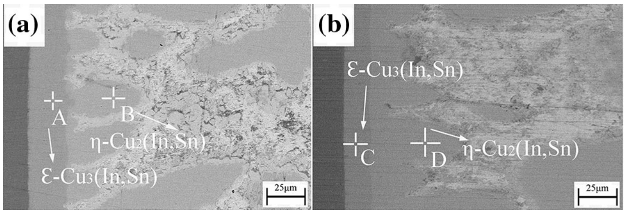

Fig. 1. EDS analysis of (a) 50In-50Sn/Cu diffusion couple and (b) 50In-44Sn-6Zn/Cu diffusion couple.

The cross-section of the sample was observed by SU8020 scanning electron microscope (SEM) equipped with attachments for energy dispersive spectroscopy (EDS). The average thickness of the IMC layer (X) can be calculated using the following equation[6]:

$$\mathrm{X} = \frac{S}{L} \tag{1}$$

where L is the IMC's length and S is the area of the intermetallic layer at the interface.

RESULTS AND DISCUSSION

Analysis of Phase Morphology and Phase Identification

The types of IMC are influenced by different factors. In the $Sn_{3.13}Ag_{0.74}CuIn/Cu$ diffusion couple, Moser et al.[13] found that the diffusion of Cu was enhanced with the addition of Indium. If the content of Indium was high enough (50 at.% or 75 at.%), a Cu-rich $Cu_{41}Sn_{11}$ phase formed near the side of the Cu substrate. Also, the aging temperature influenced the formation of IMC even in the same diffusion couple. For instance, when the aging temperature was above the melting point, a Cu-rich IMC usually formed near the Cu side[14] in the eutectic In-Sn/Cu system, which was different from the situation under the lower aging temperature.[15]

In the present case, 50In-(50-x)Sn-xZn/Cu(x = 0, 6) was aged at a temperature exceeding the melting point. The IMCs were generated at the interface of Cu and the solder as shown in Fig. 1. The points A/B/C/D (Fig. 1) were analysed by EDS, and the result showed that all IMC layers had a high Cu content (Table I).

In/Sn atoms have similar atomic sizes and crystallographic properties. Great mutual solubility between Cu-In and Cu-Sn compounds has been found in the Cu-In-Sn ternary system.[16,17] Also, Lin et al.[2] proposed that in the In-Sn-Zn/Cu diffusion couple, indium atoms were likely to substitute Sn atoms in the Cu-Sn phases. Therefore, the IMC type

Table I. The atomic ratio of Cu:(In + Sn) in 50In-(50-x)Sn-xZn/Cu(x = 0, 6) diffusion couples

	50In-50Sn		50In-44Sn-6Zn	
	Adjacent to the substrate	Adjacent to the solder	Adjacent to the substrate	Adjacent to the solder
Sn	11.36	19.41	9.06	12.77
In	10.98	17.90	10.37	16.65
Cu	77.66	62.69	68.57	62.38
Zn	–	–	11.99	8.20
Cu:(In + Sn)	3.4	1.7	3.5	2.1
IMC	$Cu_3(In,Sn)$	$Cu_2(In,Sn)$	$Cu_3(In,Sn)$	$Cu_2(In,Sn)$

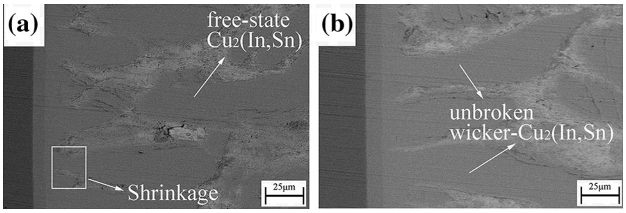

Fig. 2. The cross-section micrographs of 50In-44Sn-6Zn/Cu interfaces: (a) the shrink-break-shift process of $Cu_2(In,Sn)$ (b) the unbroken wicker-$Cu_2(In,Sn)$.

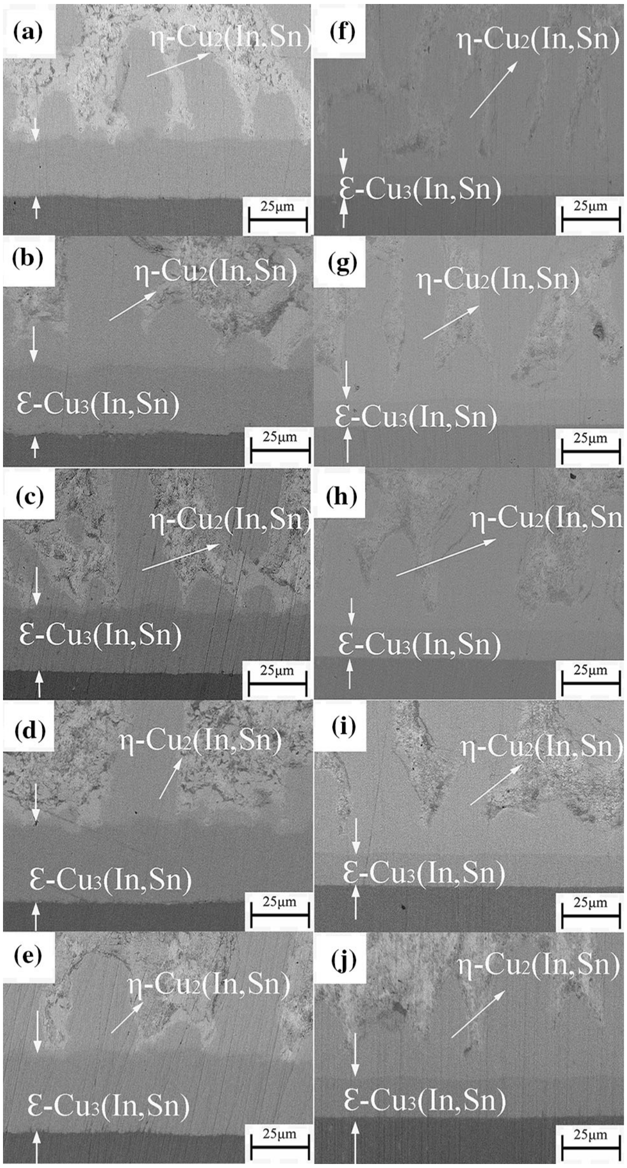

Fig. 3. Cross-section BEI micrographs of 50In-(50-*x*)Sn-*x*Zn/Cu(*x* = 0,6) at 210°C: (a–e) *x* = 0 *t* = 15, 30, 45, 75, 90 min and (f–j) *x* = 6 *t* = 15, 30, 45, 75, 90 min.

of Cu-(In,Sn) possibly depends on the atomic ratio of Cu:(In + Sn).

As shown in Table I, the two types of intermetallic compound layers were identified: $Cu_3(In,Sn)$ adjacent to the Cu substrate and $Cu_2(In,Sn)$ adjacent to the solder, which is similar to the results reported by Chuang et al.[14]

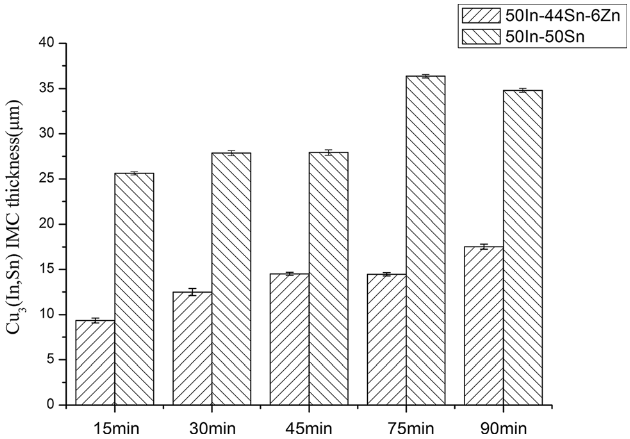

Fig. 4. The thickness of $Cu_3(In,Sn)$ in 50In-(50-*x*)Sn-*x*Zn/Cu(*x* = 0, 6) diffusion couples.

The first-formed layer was the $Cu_2(In,Sn)$ phase. It was scallop-like because of the solid–liquid interface during its solidification. The $Cu_3(In,Sn)$ phase was formed between the substrate Cu and $Cu_2(In,Sn)$, through the solid–solid diffusion. Compared with $Cu_2(In,Sn)$ phase, it was more flat (Fig. 1). Furthermore, as shown in Fig. 2, the wicker-$Cu_2(In,Sn)$ formed on outer-IMC and tended to grow into the solder. The free-state $Cu_2(In, Sn)$ was also observed (Fig. 2a).

These similar phenomena were reported often in SAG solder[18] and can be attributed to the high temperature enhancing the diffusion of Cu and Sn atoms. Thus, the concentration gradient of copper in the substrate-solder increased, causing the preferred growth of $Cu_2(In,Sn)$.[19] Also, a "breakout" mode was proposed by Chang et al.,[6] that is, a shrink-break-shift process (Fig. 2). The difference was that more unbroken wicker-$Cu_2(In,Sn)$ (Fig. 2b) existed in the present case, and some even extended to the top of the solder. So the thickness of $Cu_2(In, Sn)$ was difficult to count and the error of it was hard to control. When calculating of the IMC growth rate k and the time constant *n* (discussed later), the $Cu_2(In,Sn)$ layer was not considered.

Effect of Zn Addition on the Evolution of IMC

Numerous studies have shown that a thick IMC has a great influence on the reliability of solder joints, especially, the later-formed IMC in the double-layered structure, which usually has a high melting point and high hardness. In order to enhance the stability of the IMC layer, Kanlayasir and Sukpimai[20] decreased the thickness of the Cu_3Sn layer by adding indium into the SAC solder.

Wang et al.'s[21] research on the Sn-Ag/Cu diffusion couple showed that the growth of Cu_3Sn tended to consume the first formed IMC. Moreover, in the Cu/

Sn/Cu sandwich structure, the Cu_6Sn_5 IMC was found to be totally replaced by Cu_3Sn gradually.[22]

In the present case, it can be seen from Fig. 3a–e that with the increase of aging time, the growth rate of Cu_3(In,Sn) was significantly faster than that of Cu_2(In,Sn). After 45 min, Cu_3(In,Sn) has almost covered the Cu_2(In,Sn), only leaving the scallop-like phase. This was similar to the result of Chuang's research[14,15] that solid–solid diffusion formed Cu_3Sn IMC had higher activation energy and grew faster at high temperatures. On the contrary, the growth of Cu_3(In,Sn) was obviously inhibited by the addition of Zn (Fig. 3f–j). Under the same conditions, the thickness of Cu_3(In,Sn) in In-44Sn-6Zn/Cu was always maintained at a lower level. Even aging over 90 min, the thickness of Cu_3(In, Sn) was just half of the Cu_2(In, Sn) (Fig. 4).

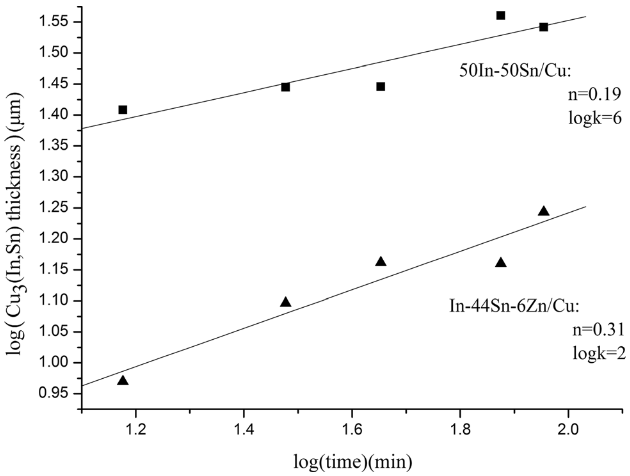

Fig. 5. Log–log plot of Cu_3(In,Sn) IMC layer thickness versus time.

In order to investigate the growth mechanism of Cu_3(In,Sn) IMC, its growth kinetics were analyzed using a power-law relationship[12,23]:

$$x = (kt)^n \tag{2}$$

Equation 2 can be expanded as follows:

$$\log x = n \log k + n \log t \tag{3}$$

where x is the IMC layer thickness, k is the growth rate, n is the time exponent and t is the soldering time.

The calculated results of time exponent n indicates different growth evolution processes: chemical reaction-limited stage (the time exponent $n = 1$), volume diffusion-controlled stage ($n = 0.5$) and grain boundary diffusion-controlled stage ($n = 0.33$).[11,24] The data in Fig. 4 were processed according to Eq. 2 to calculate the values of n and k, respectively, shown in Fig. 5.

The results showed that in the 50In-44Sn-6Zn/Cu diffusion couple, Cu_3(In,Sn) was grain-boundary diffusion controlled ($n = 0.31$). In the 50In-50Sn/

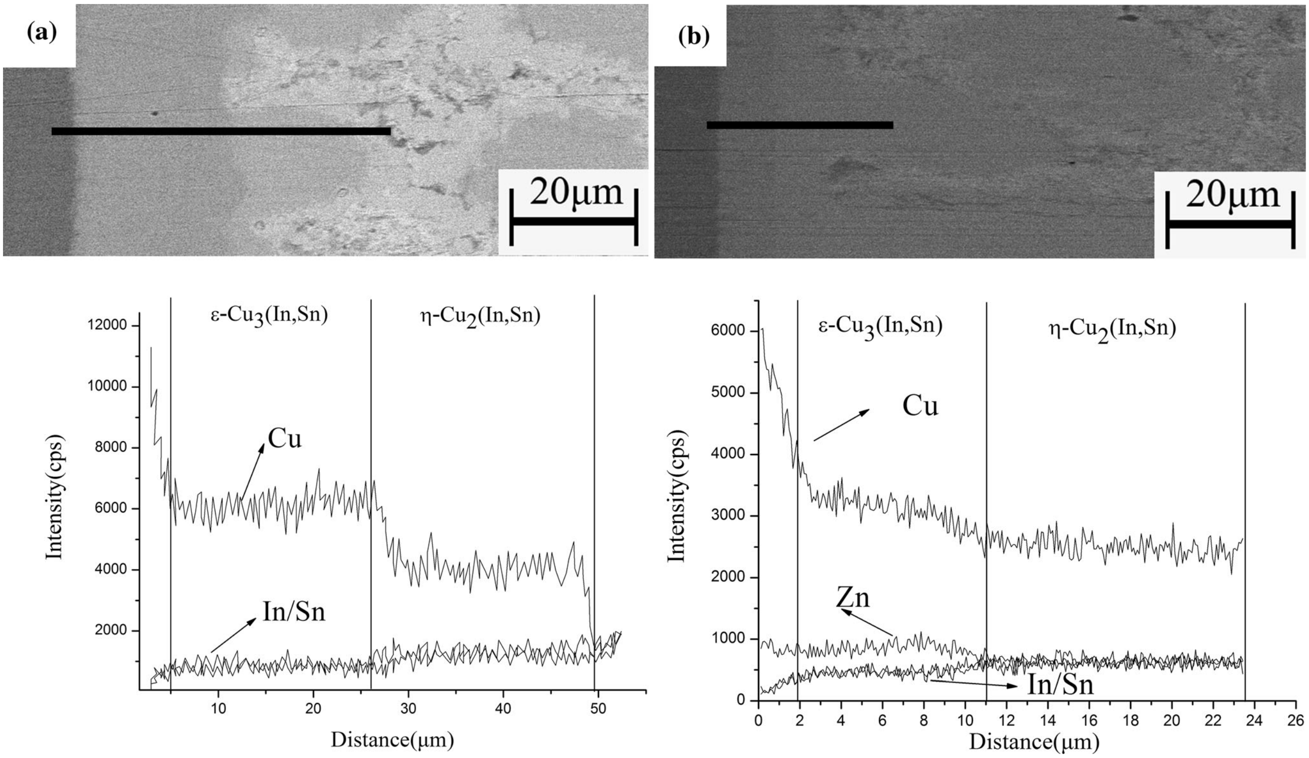

Fig. 6. Line scanning analysis of element distribution by EDS in IMC layers of In-(50-x)Sn-xZn alloys: (a) $x = 0$, aging at 210°C for 15 min and (b) $x = 6$, aging at 210°C for 15 min.

Cu diffusion couple, the value of the time exponent n did not comply with the traditional value ($n = 0.33$), and it was down to 0.19. This may be attributed to the following reason. Aging after 30 min, $Cu_3(In,Sn)$ almost covered the total $Cu_2(In,Sn)$. After that (until 90 min), the $Cu_3(In, Sn)$ advanced together with $Cu_2(In, Sn)$ to 10 μm. Therefore, the evolution of $Cu_3(In,Sn)$ was affected by the slow growth of $Cu_2(In,Sn)$. The value of n ($n = 0.19$) revealed the overall growth state of $Cu_3(In,Sn)$ and $Cu_2(In,Sn)$.

Lin et al. and Jee et al. added Zn in the solder (Sn-20In and Sn-3.5Ag, respectively) to form a Cu-Zn barrier layer in the middle of the IMC. In this way, the growth of the IMC was effectively controlled and Zn exhibited high activity.[2,8] In the present case, no barrier layer was formed, but the thickness of Cu_3Sn in 50In-44Sn-6Zn/Cu diffusion couple was also effectively mitigated. In order to explore the specific role of Zn, EDS analysis was used.

Zn diffused from the solder to the Cu substrate initially. However, after heating, the concentration gradient of Zn was changed, which ran from Cu substrate to the solder instead (Fig. 6b). In the $Cu_3(In,Sn)$ phase, Zn had a higher concentration. The results of the Table I showed that the Zn content was about 4% higher than that in $Cu_2(In, Sn)$. Moreover, the content of Zn was even higher than that of In/Sn in $Cu_3(Sn, In)$ (Fig. 6b). Zn exhibited high activity and suppressed the dissipation of the main atoms (In/Sn) in the solder. A similar result was also reported by Kang. In Sn-Ag-Cu/Cu, the accumulation of Zn atoms at the Cu_3Sn and Cu interface inhibited the growth of IMC.[25]

In the 50In-50Sn/Cu diffusion couple, between $Cu_3(Sn, In)$ and $Cu_2(Sn, In)$, the content of Cu decreased in a cliff-like manner. But with Zn addition, the decrease of Cu became smooth. This means that in $Cu_3(Sn, In)$, the content of Cu has already decreased. It can be seen from Table I that after adding Zn, the content of Cu in $Cu_3(In,Sn)$ decreased to 68%, while the Cu content of $Cu_3(In,Sn)$ in 50In-50Sn/Cu was about 78%. So, the addition of Zn effectively suppressed diffusion of Cu and slowed down the growth of IMC, especially $Cu_3(In, Sn)$. Essentially, it can be explained from the perspective that the formation of the Cu-Zn phase was more favorable than that of the Cu-Sn phase during the action. As discussed in Sarwono's research,[23] the diffusivity of Zn in solder was greater than that of Sn during soldering. The thermodynamic data at 773 K for the Gibbs free energy of Cu-Zn and Cu-Sn IMCs were 11.72 kJ/mol to 12.55 kJ/mol and 7.78 kJ/mol and 7.42 kJ/mol, respectively. Although, in our present case, the Cu-Zn phase was not formed (it was also possible that the Cu-Zn phase had decomposed under high temperature for the long reaction[2]), but the high activity and superior diffusion ability of Zn were found. As shown in Table I, the two types of intermetallic compound layers were identified to be $Cu_3(In,Sn)$ and $Cu_2(In,Sn)$ with or without Zn. But the Cu:(In + Sn) ratio of the two IMCs in 50In-44Sn-6Zn was both slightly larger than that in 50In-50Sn. This also proved that the presence of Zn trapped a small amount of Cu. So in summary, the high activity of Zn inhibited the growth of Cu-Sn IMC and caused a decrease in the further diffusion of Cu.

CONCLUSIONS

The effect of Zn addition on the evolution of IMC at the near-eutectic In-50Sn/Cu interface was investigated at 210°C. The conclusions are as follows:

(1) In the In-50Sn-xZn/Cu($x = 0$, 6) diffusion couples, two types of intermetallic compound layers were observed: $Cu_3(In,Sn)$ adjacent to the Cu substrate and $Cu_2(In,Sn)$ adjacent to the solder, which were formed though a solid–solid diffusion reaction and solid–liquid reaction, respectively.

(2) The growth of ε-$Cu_3(In,Sn)$ was at the expense of η-$Cu_2(In,Sn)$. In the In-44Sn-6Zn/Cu diffusion couple, the growth of ε-$Cu_3(In,Sn)$ was grain-boundary controlled and the time constant n was 0.31. In the In-50Sn/Cu diffusion couple, due to the slow growth of η-$Cu_2(In,Sn)$, the time constant of $Cu_3(In,Sn)$ was down to 0.19.

(3) With the addition of Zn in In-50Sn/Cu couple, the diffusion of Cu was alleviated. Zn exhibited high activity and moderated the dissipation of main atoms (In/Sn) in the solder. So the growth of $Cu_3(In,Sn)$ was suppressed significantly.

ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support provided by the Harbin Youth Reserve Talents Project [Grant Number RC2014QN017012]. The authors would like to thank Professor Chen and Professor Ma at the center for material analysis and testing, who provided experimental help.

REFERENCES

1. Y. Li, F. Wu, and Y.C. Chan, *J. Mater. Sci. Mater. Electron.* 26, 8522 (2015).
2. S.K. Lin, R.B. Chang, S.W. Chen, M.Y. Tsai, and C.M. Hsu, *J. Mater. Sci.* 49, 3805 (2014).
3. G. Yoo and J.H. Park, *J. Korean Phys. Soc.* 65, 960 (2014).
4. X. Liu, R.W. Davis, L.C. Hughes, M.H. Rasmussen, R. Bhat, C.E. Zah, and J. Stradling, *J. Appl. Phys.* 100, 013104 (2006).
5. J.C. Leong, L.C. Tsao, C.J. Fang, and C.P. Chu, *J. Mater. Sci. Mater. Electron.* 22, 1443 (2011).
6. S.Y. Chang, L.C. Tsao, M.W. Wu, and C.W. Chen, *J. Mater. Sci. Mater. Electron.* 23, 100 (2011).
7. J. Pstruś, T. Gancarz, and P. Fima, *Adv. Mater. Sci. Eng.* 2017, 1 (2017).
8. Y.K. Jee, Y.H. Ko, and J. Yu, *J. Mater. Res.* 22, 1879 (2007).

9. T. Xu, X. Hu, Y. Li, and X. Jiang, *J. Mater. Sci. Mater. Electron.* 28, 18515 (2017).
10. S. Sommadossi, W. Gust, and E.J. Mittemeijer, *Mater. Chem. Phys.* 77, 924 (2002).
11. Y. Yao, J. Zhou, F. Xue, and X. Chen, *J. Alloy Compd.* 682, 627 (2016).
12. C.H. Wang and K.T. Li, *Mater. Chem. Phys.* 164, 223 (2015).
13. P. Šebo, Z. Moser, P. Švec, D. Janičkovič, E. Dobročka, W. Gasior, and J. Pstru, *J. Alloy Compd.* 480, 409 (2009).
14. T.H. Chuang, C.L. Yu, S.Y. Chang, and S.S. Wang, *J. Electron. Mater.* 31, 640 (2002).
15. D.G. Kim and S.B. Jung, *J. Alloy Compd.* 386, 151 (2005).
16. S.K. Lin, T.Y. Chung, S.W. Chen, and C.H. Chang, *J. Mater. Res.* 24, 2628 (2009).
17. S.K. Lin, C.F. Yang, S.H. Wu, and S.W. Chen, *J. Electron. Mater.* 37, 498 (2008).
18. Y. Tang, S.M. Luo, Z.H. Li, C.J. Hou, and G.Y. Li, *J. Electron. Mater.* 47, 5913 (2018).
19. R.A. Gagliano and M.E. Fine, *JOM-US* 53, 33 (2001).
20. K. Kanlayasiri and K. Sukpimai, *J. Alloy Compd.* 668, 169 (2016).
21. D.L. Wang, Y. Yuan, and L. Luo, *J. Mater. Sci. Mater. Electron.* 23, 61 (2011).
22. L.P. Mo, F.S. Wu, C.Q. Liu, in *2015 IEEE 65th Electronic Components and Technology Conference (2015)*, pp. 1854–1858.
23. D. Sarwono and K.L. Lin, *J. Electron. Mater.* 48, 99 (2018).
24. C.H. Wang and C.Y. Kuo, *Mater. Chem. Phys.* 130, 651 (2011).
25. S.K. Kang, D. Leonard, D.Y. Shih, L. Gignac, D.W. Henderson, S. Cho, and J. Yu, *J. Electron. Mater.* 35, 479 (2006).