Evolution Modes and Self-healing Phenomenon of Kirkendall Voids at the Sn/Cu Solder Joints

Shaofeng Yang, Mengjia Xu and Chun Yu

Abstract The evolution process of Kirkendall voiding was investigated by employing pure Sn solder and Cu films electroplated with a low current density. It is found that the Kirkendall voids (KVs) did not form until a certain period after the formation of Cu_3Sn layer. The period length is determined by the holding temperature. Moreover, after growing to a high density, the KV-density decreased obviously. Therefore, the voiding process includes three stages, namely, incubation, formation/growth, and healing, under a low impurity level condition. Low level impurities prolong the incubation period of KVs, which is also largely determined by the temperature. The incubation stage of KV as aged at 150 °C is much longer than that aged at 180 °C. At low impurity level, the KV evolution accesses the healing stage instead of cracks and openings, which can be explained by the accelerated decline rate of J_{Cu} compared to J_{Sn} when the IMC layer grows thicker.

Keywords Self-healing · Lead-free solder · Electroplating · Aging
Interface defects

1 Introduction

Kirkendall void (KV) was usually visible at the Cu_3Sn/electroplated Cu (EPC) interface due to acute reaction between the Sn-based solder and the copper during solid state. Since a considerable amount of KVs decrease the contact area of the interface, and therefore weakens the mechanical and electrical properties,

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this reliability issue has been attracting a lot of concerns [1–5]. The formation mechanisms, as well as the factors impacting the formation and evolution of KVs have been widely investigated through experimental and theoretical methods [6, 7]. Moreover, a lot of methods have be proposed to suppress or mitigate KVs, such as, adding sulfide-forming elements into the solder [8], annealing upon the EPC before soldering [9], optimizing electroplating process [10], changing the microstructure of the copper film [11, 12], and so on.

Kirkendall voiding is sensitive to the impurities incorporated into the Cu film during electroplating [7–10]. Because the incorporated impurities block the vacancy annihilation sites, promoting unbalanced diffusion and leading nucleation and growth of voids due to vacancy supersaturation. The higher the impurity level, the more serious the Kirkendall voiding would develop, and vice versa. It is generally conformed that the density of the KVs increases with the aging time, and the KVs gradually coalesce into bigger voids after a long aging period, even extent to cracks or a big opening if the electroplating condition is serious [13]. On the other hand, Liu et al. reported the phenomenon of appearance and disappearance of the KVs in annealed solder joints [14]. They contributed the disappearance of KVs to the volume exchange between the Sn and the vacancies. Recently, Borgesen et al. found that the density of KVs did not increase straightly with the aging time, but reached a peak and then dropped down [15]. According to the limited reports, we speculate that self-healing of KVs is possible in the solder joints [16–18]. In fact, we observed this phenomenon during accelerated thermal aging process. In this work, the self-healing mechanism was primarily interpreted, and the evolution process of Kirkendall voiding was concluded. This work is beneficial in understanding the different Kirkendall voiding behaviors.

2 Materials and Experiments

The experiments were carried out using commercial Sn (99.99%) as solder, and electroplated Cu film as the substrate. The electroplating solution is $H_2SO_4 + CuSO_4 + Cl^{-}$+PEG. For this solution, the impurity level increases with applied current density. In order to observe the self-healing phenomenon during a short period, the impurity density should be limited to a low level. It could be realized by using electroplating parameter of 1.7 mA/cm^2 current density [19, 20], and the deposit thickness is 10 μm. The solder joints were prepared by directly melting solders on the electroplated Cu surface at 260 °C. Prior to the soldering process, the solder and substrate were deoxidized and degreased in 5 wt% NaOH and 5 vol.% HCl solutions sequentially, rinsed in deionized water after each step, and treated with flux. Subsequently, isothermal aging processes were performed for the as soldered joints under 150 and 180 °C, respectively. Then the samples were mounted in epoxy and metallurgically polished. The interfacial microstructures were observed by using a scanning electron micro-scope (SEM), the composition of IMC layer was determined by the energy dispersive spectroscopy (EDX).

3 Results and Discussions

The interfacial morphologies of the as soldered and aged Sn/EPC joints are presented in Fig. 1. A typical result was obtained that, a scallop-like Cu_6Sn_5 layer formed due to liquid/solid reaction, no KV at the Cu_6Sn_5/Cu interface was observed at this scale, as shown in Fig. 1a1. After aged at 180 °C for 1 day, as shown in Fig. 1a2, it is observed that small but few KVs at the Cu_3Sn/Cu could be.

Distinguished at the present scale, the average size of the KVs is 0.1 μm, and the line density is 1.2%. A considerable amount of KVs were distinctly detected after 3 days, as shown in Fig. 1a3, the average size of the KVs increases to 0.5 μm. This result is consistent to other reports, or the KVs grow denser and larger with aging time [1, 20, 21]. However, KV-density decreases obviously as aged for 7 days (Fig. 1a4), and the average size of the KVs drops down to 0.2 μm. Liang et al. explicitly declared that the formation and growth of KVs include four stages, namely, incubation, nucleation, growth and healing, through a phase field theoretical calculation [22]. However, in our experimental work, it is difficult to distinguish the nucleation stage from the growth process. Hence, we simply unify the two stages as formation/growth period. As a result, the evolution process of KVs includes incubation stage, formation/growth stage, and healing stage. At the incubation stage, the KV is hardly to be observed. While at the formation/growth stage, the KVs emerge and become bigger and denser. And at the healing stage, both the density and dimension of the KVs drop down.

To further confirm that the formation and growth of KVs really experience the above three stages, the solder joints were endured 150 °C isothermal aging. As shown in Fig. 1b1, after aged at 150 °C for 5 days, the Cu_3Sn IMC layer was about 2 μm, while KVs were still not clearly observed. The result depicts that KVs were not always formed just after the formation of the Cu_3Sn layer, and we define this period as KV incubation stage. However, a considerable amount of KVs were observed after aged for 10 days (Fig. 1b2), the average size of the KVs is 0.2 μm. Further, the KV-density increased greatly as the aging time was prolonged to 20 days (Fig. 1b3), and the average size of the KVs grows to 0.3 μm. This period is the so-called formation/growth stage. Again, the KV-density decreased greatly after aged at 150 °C for 30 days, as shown in Fig. 1b4, while the thickness of Cu_3Sn layer increased to about 5 μm. It indicates that the KV evolution accesses to the healing stage.

Hence, according to the above results, under the conditions of this work, the evolution process of KVs at a low impurity level could be concluded as three stages, namely, incubation period, formation/growth period, and self-healing period. Previous investigations mostly focused on the second period, i.e., formation/growth period. The one reason is that this stage is important for the reliability of solder joints. At this period, the solder joint is weak in mechanical properties and electrical properties due to less adhesion area. Another reason is that the evolution process of KVs at the Cu_3Sn/Cu interface does not always experience the whole three stages. For example, in a high purity Cu/Sn joint, the KVs were seldom found

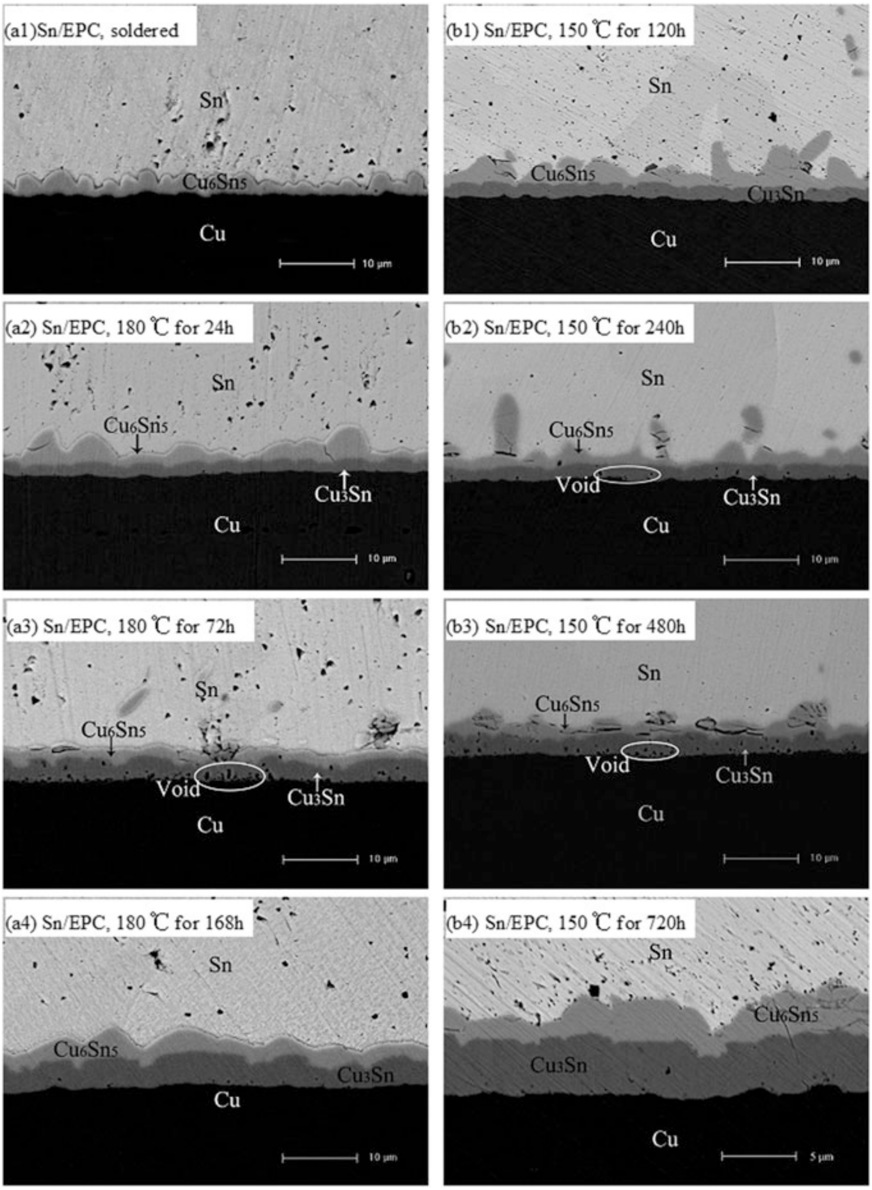


Fig. 1 Interface evolution process of Sn/EPC joints under different aging temperature

even the Cu_3Sn layer was thick enough. As shown in Fig. 2, that reflects the interface micro-structures of the Sn/HP Cu joints. A layer of scallop-like Cu_6Sn_5, which was identified by EDS, formed at the interface just after soldering, as depicted in Fig. 2a. During isothermal aging at 150 °C, a Cu_3Sn layer started to

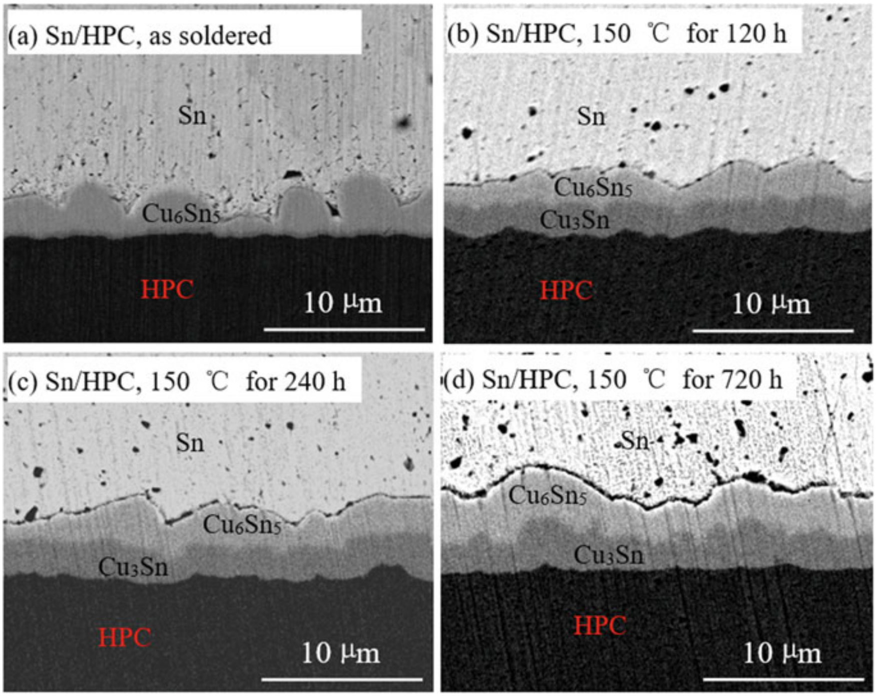


Fig. 2 Interface evolution process of Sn/HPC joint

emerge at the interface of Cu_6Sn_5/Cu. It is observed that the new layer grew much quicker than the Cu_6Sn_5 layer did. Even after aging for 120, 240 and 720 h, as presented in Figs. 2b–d, no void could be distinguished at the HP Cu/Cu_3Sn interface. While at this moment, the thickness of Cu_3Sn layer exceeds that of Cu_6Sn_5. It is reported that the growth of Cu_3Sn is also a root cause of the Kirkendall voiding [16]. However, according to this result, even the Cu_3Sn layer has a quick growth rate, it is still not a dominant factor accounting for the Kirkendall voiding in pure Sn/pure Cu diffusion couple.

It can be deduced according to the evolution rule that the KVs spent a much long incubation period. Basically, at the incubation period, vacancies generated and gathered, to form the initial voids in nano-size. This period was related to inter-diffusion flux and impurities induced by electroplating. If there does not exist impurities, the incubation period of KVs would take a much long time, like that observed in pure Sn/pure Cu couple [21]. While, as high level impurities were introduced, the KVs could be detected even at the Cu_6Sn_5/Cu interface just during soldering [23]. It indicates that Kirkendall voiding experienced a very short incubation stage under a serious condition. In this work, the impurity level is low due to a low electroplating current density, and the incubation period could be observed. Moreover, the duration of incubation period is obviously correlated to the aging temperature. As we observed that, the formation of KV initiated at 5 days as aged at 150 °C, while as aging temperature was enhanced to 180 °C, the KV formed at 1 day.

Similarly, the healing period also affected by impurity and aging conditions. The KV moved to the self-healing period within a shorter aging time at a higher aging temperature. On the other hand, the self-healing period was not observed until interface opening, under a tough electroplating condition [2, 19, 20]. Since the two periods have obviously different characteristics relative to the second period, further investigations should be conducted.

Therefore, combining the previous investigations and analysis, a flow chart reflecting the evolution process of KV could be drawn, it is presented in Fig. 3. The chart indicates that the Kirkendall voiding would lead to three evolution modes. The first mode, the KV remains the incubation stage in a very long term, only the evolution process of the IMC layer can be observed, as shown in Fig. 3b, 3c1 and 3e1. This is an idea state from reliability consideration. And it can be realized by purifying the Cu substrate, or adding minor alloying elements into the solder. The second mode, as shown in Fig. 3b, 3c2–3e2, the KV firstly experiences the incubation stage, and then goes into the formation/growth stage, while at last, it accesses the healing stage. For the third evolution mode, the KV experiences the both incubation and formation/growth stages. However, with the KVs grow up, they coalesce each other, and develop to cracks, even a big opening, as shown in Fig. 3e3. It is difficult to distinguish the healing process for this mode.

Figure 4 depicts the density change with aging time, corresponding to the above mentioned three evolution modes. Under a good condition, such as high purity copper substrate, not so high aging temperature or other loading conditions, the density of KVs mainly keeps to near zero, it corresponds to mode I. However, under a tough condition (means high impurity level), the density of KVs reaches to

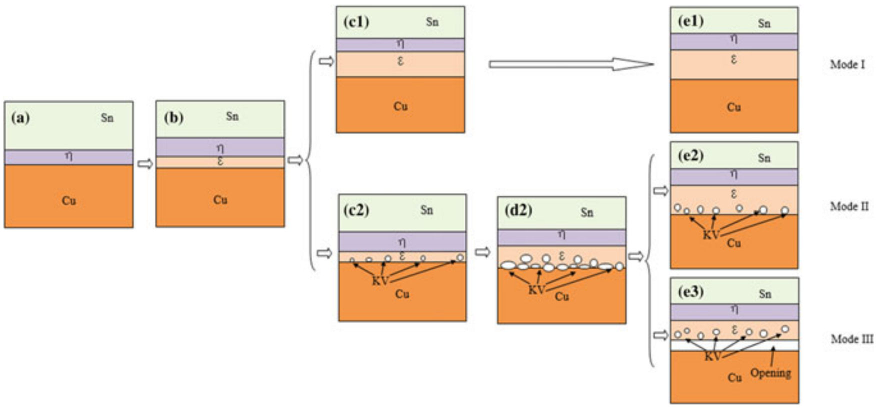
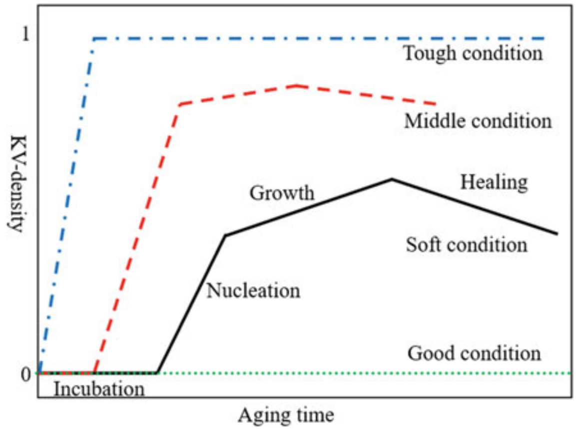


Fig. 3 Evolution modes of Kirkendall voids. **a** Is the as soldered joint; **b**, **c1**, and **e1** represent the incubation stage; **c2** and **d2** represent the formation/growth stage; **e2** represents the healing stage; and **e3** indicates the KV developing to crack or opening

Fig. 4 Density change versus aging time at different condition



1 within a short time, it corresponds to mode III. Between these two conditions, the density of KVs increases firstly, and then drops down, it corresponds to mode II. In order to distinguish the different voiding mode, and find reasonable way to avoid the disadvantage effect of KVs, it is necessary to clearly define the critical conditions.

Upon the possibility of KV healing, we give the following explain. It is well known that the IMC layer is controlled by diffusion function, and Kirkendall voiding is induced by unbalanced diffusion at the reaction interface. So, both IMC layer and KV are governed by atom diffusion. The growth of Cu_3Sn layer mainly contributes to reactions $Cu_6Sn_5 \rightarrow 2Cu_3Sn + 3Sn$ at Cu_6Sn_5/Cu_3Sn interface, and $Sn + 3Cu \rightarrow Cu_3Sn$ at Cu_3Sn/Cu interface. While, the growth of Cu_6Sn_5 layer is resulted from reactions, $2Cu_3Sn + 3Sn \rightarrow Cu_6Sn_5$ at the Cu_6Sn_5/Cu_3Sn interface, and $6Cu + 5Sn \rightarrow Cu_6Sn_5$ at the Cu_6Sn_5/solder interface. According to Fig. 1, the growth rate of Cu_3Sn layer was much quicker than that of Cu_6Sn_5. It indicates that the reactions promoting Cu_3Sn formation dominates at the interfaces. In our previous investigation, we analyzed the shifting process of the reaction interface. It was found that the Cu_3Sn/Cu interface shifts much quicker to the Cu substrate, relative to the Cu_6Sn_5/solder interface shifting toward the solder in the Sn/Cu joints [24]. The results indicate that relatively acute reaction occurred at the Cu_3Sn/Cu interface. And this acute reaction should contribute to large Sn flux continuous migrating to the Cu_3Sn/Cu interface.

Generally, at Cu/Cu_3Sn interface, unbalanced diffusion generates a vacancy flux, i.e., $J_v = J_{Cu}$-J_{Sn}, where J_v is vacancy flux, J_{Cu} is Cu flux shifting to solder side, J_{Sn} is Sn flux toward Cu_3Sn/Cu from solder. If the Cu flux migrating out of the Cu_3Sn/Cu interface (J_{Cu}) is farther bigger than that moving in, large J_v would be induced. The vacancies would then condense into microvoids. J_{Cu} is around 1.5 times of J_{Sn} at early thermal aging stage as aged at 150–180 °C [24]. Moreover, the ratio of J_{Cu}/J_{Sn} increases with temperature. Hence, kirkendall voids are prone to be formed at the initial thermal aging stage, the higher the aging temperature, the quicker the

KVs are formed. This is also the reason why Kumar et al. [25] and Paul [26] found that the KVs were formed at the Sn-based solder/pure Cu as aged at 215 °C, but seldom at the joints aged at temperature less than 200 °C. As the IMC layer grows thicker and thicker, both J_{Cu} and J_{Sn} decrease. Interestingly, the decrease rate of J_{Cu} is quicker than that of J_{Sn} [24]. Therefore, the formation rate of vacancy decreases gradually at the Cu_3Sn/Cu interface. Since the formation and growth of KV mostly contribute to the vacancy, the KV is then suppressed. At certain aging time, J_{Cu} would be nearly equal to J_{Sn}. Hence, the KV will be moved to the self-healing stage. In addition, high dense KVs formed at the Cu_3Sn/Cu interface also sever as the barrier of Cu diffusing towards the solder. Therefore, with the formation and growth of KVs, the number of Cu atoms, or J_{Cu} diffusing out of the Cu_3Sn/Cu interface would further decrease.

4 Conclusion

Summarily, we observed that the Kirkendall voiding experienced the incubation period, formation/growth period, and self-healing period at the pure Sn/electroplated Cu joints by employing an electroplating process with a low impurity level. In addition, the duration times for the three periods were affected by the aging temperature. The incubation stage of KV is much longer as aged at 150 °C, compared to 180 °C. The KV moved to the self-healing period within a shorter aging time at a higher aging temperature. Moreover, the KV has three types of evolution modes, determined by the impurity level of the Cu substrate and loading conditions. Low level impurities prolong the time it takes to incubate KVs. However, High impurity level would result in KVs growing up and coalescing, and developing to cracks and even a big opening eventually. At certain impurity level, the KV evolution accesses the healing stage after experiencing the incubation stage and the formation/growth stage.

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