

Effects of Fe on the Kirkendall Void Formation of Sn-3.5Ag-xFe/Cu Solder Joints

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Abstract

Ternary Sn-3.5Ag-xFe solders with varying amount of Fe; 0.1, 0.5, 1.0, and 2.0 wt. % were reacted with Cu UBM which was electroplated using SPS additive and characteristics of Kirkendall void formation at the solder joints were investigated. Results indicate that the propensity to form Kirkendall voids at the solder joint decreased with the Fe content. It showed that Fe dissolved in the Cu UBM and reduced the segregation of S atoms to the Cu₃Sn/Cu interface, which suppressed the nucleation of Kirkendall voids at the interface.

1. Introduction

Recently, Kirkendall void formation at the solder joints has been a critical issue in the microelectronics industry, and many experimental works have used Pb-free solder alloys [1-6]. Currently, Yu et al. [6-8] proved that residual S, coming from SPS (bis-sodium sulfopropyl-disulfide, C₆H₁₂O₆S₄Na₂) additive to the Cu electroplating solution, was segregated to the Cu₃Sn/Cu interface and accelerated the nucleation of voids [6], and those nucleated voids grew due to the tensile stress arising from the Kirkendall effect [7]. In our previous work, Sn-3.5Ag-0.5X (X=Zn, Mn, Cr) solders were reacted with Cu to suppress Kirkendall void formation at the Cu₃Sn/Cu interface [8]. Furthermore, Kim and Yu [9] showed that Ag alloyed solders also had an effect on suppressing S segregation at Cu₃Sn/Cu interface. We explained that adding sulphide forming elements to the solder could reduce the interfacial segregation of S, and suppressed Kirkendall void nucleation. The suppression of Kirkendall void would improve the drop impact resistance. However, Fe is also known as the sulphide forming element and the effect of Fe on Kirkendall void formation is still unknown. This is a continuation of the work on the effects of sulphide forming element on the Kirkendall void formation. Here, Sn-3.5Ag-xFe ternary alloys with varying amounts of Fe reflowed over the Cu UBM which was electroplated using SPS in the bath (3.0×10^{-5} M), and characteristics of Kirkendall void formation and S segregation to the Cu₃Sn/Cu interface were analyzed.

2. Experimental Procedure

Ternary Sn-3.5Ag-xFe (where x = 0.1, 0.5, 1.0, and 2.0 wt. %) solders with varying amounts of Fe denoted as 0.1Fe, 0.5Fe, 1.0Fe and 2.0Fe specimens respectively, were prepared by mixing and melting high purity (99.99%) metal powders in a quartz tube under a 10^{-3} torr vacuum. Two high purity (99.99%) Cu blocks (8×2×2mm) were polished, ultrasonically

cleaned, and subsequently jointed using solders as shown in Fig. 1. One of the Cu blocks had an electroplated Cu film (20μm) on the joining side, and the electroplating was conducted in a Cu bath containing 3.0×10^{-5} M of SPS. Joining them was performed by immersion of the two blocks in the liquid solder bath (260°C) for 1 minute. Then, the joined Cu blocks were taken out of the solder bath, air cooled, and subsequently aged at 150°C. Intermetallic compounds (IMC) at the solder joint were analyzed using back-scattered scanning electron microscopy (SEM).

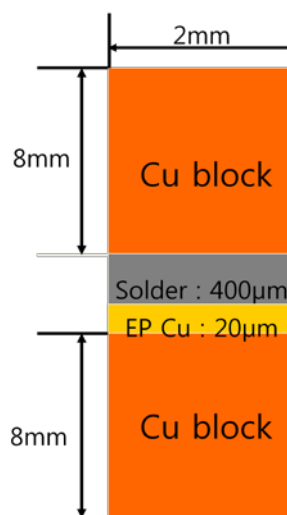


Fig. 1. A schematic diagram of specimens used for SEM analyses.

3. Results

3.1. Interface microstructures

As-reflowed specimens

Cross-sectional SEM images of as-reflowed Sn-3.5Ag-xFe/Cu solder joints are presented in Fig. 2. It can be seen that Cu₆Sn₅ IMC formed at the joint

interface after a reflow, while chunky FeSn_2 formed in the solder matrix as shown in Fig. 2. However, Kirkendall voids did not form at the solder joint in the as-reflowed condition. Subsequent isothermal aging at 150°C for 120 h, Kirkendall voids were hardly found not only in the Cu_3Sn layer but also at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface (less than 20%) regardless of Fe contents in the solder.

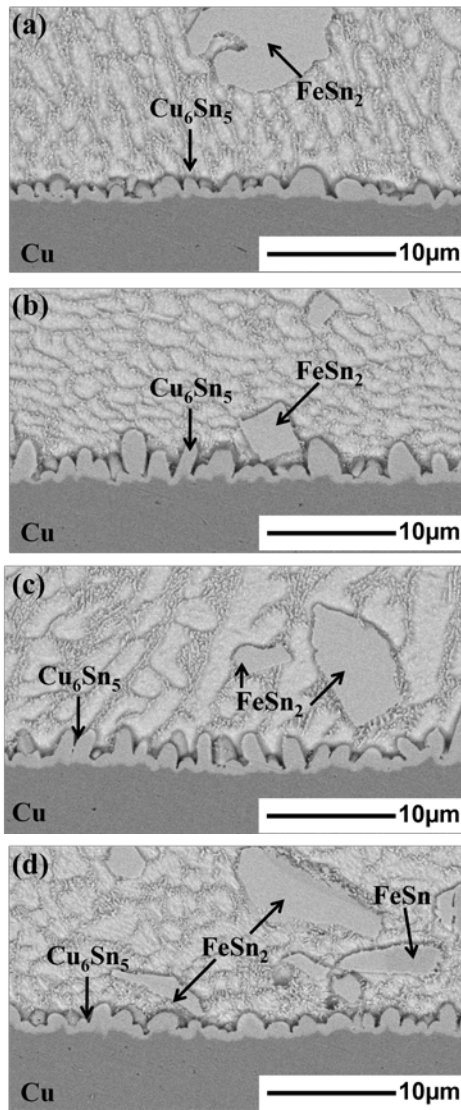


Fig. 2. SEM micrographs of as-reflowed (1min at 260°C) solder joints made of (a) 0.1Fe, (b) 0.5Fe, (c) 1.0Fe and (d) 2.0Fe.

Aged specimens: 240 h at 150°C

With further aging, Cu_6Sn_5 and Cu_3Sn developed as shown in Fig. 3, and the initially scallop-shaped Cu_6Sn_5 IMC became flatter. All specimens contained Kirkendall voids, and those were highly localized at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface due to the segregation of S coming from the SPS additive in the Cu electroplating bath. This is consistent with the result of Yu et al. [7] on Sn-3.5Ag/Cu joint. The

characteristics of IMC formation were pretty much the same among specimens except that Kirkendall voids were covered more than 50% of the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface in the case of 0.1Fe and 0.5Fe specimens as shown in Figs. 3(c) and (d). In contrast, in the case of 1.0Fe and 2.0Fe specimens, Kirkendall voids were significantly suppressed at $\text{Cu}_3\text{Sn}/\text{Cu}$ interface

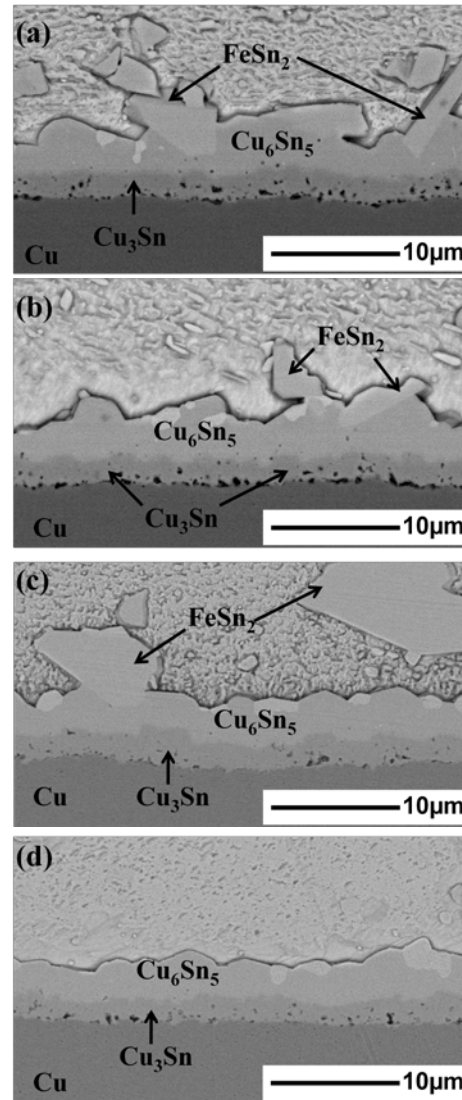


Fig. 3. Cross-sectional BSE images of (a) 0.1Fe joint, (b) 0.5Fe joint, (c) 1.0Fe joint and (d) 2.0Fe joint after aged for 240 h at 150°C .

Aged specimens: 960 h at 150°C

At extended aging times, Cu_6Sn_5 and Cu_3Sn thickened simultaneously except 0.1Fe joint. In all specimens, the total IMC thickness (δ_{tot}) increased after aging of 960 h at 150°C . However, the Cu_3Sn layer of the 0.1Fe joint became much thinner than that of other joints as shown in Fig. 4. Furthermore, in the 0.1Fe and 0.5Fe specimens, the interface of $\text{Cu}_3\text{Sn}/\text{Cu}$ appeared almost saturated with Kirkendall voids, while Kirkendall voids nucleated at the

Cu₃Sn/Cu interface of the others more or less increased.

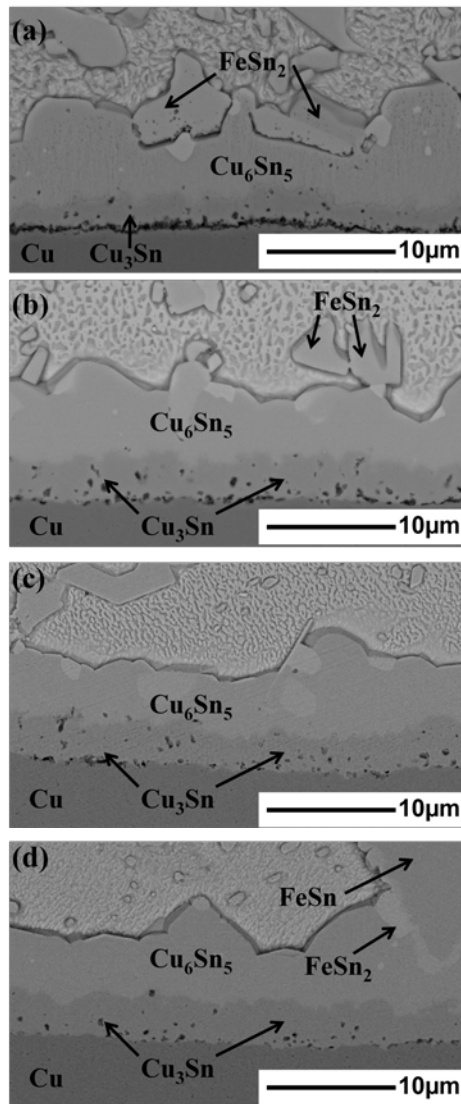


Fig. 4. Cross-sectional BSE images of (a) 0.1Fe joint, (b) 0.5Fe joint, (c) 1.0Fe joint and (d) 2.0Fe joint after aged for 960 h at 150°C.

Growth kinetics of interfacial IMC growth

Variations of IMC thickness (δ_{tot}) with the aging time are presented in Fig. 5(a), and it can be seen that δ_{tot} increased proportionally with $t^{1/2}$, which means that the growth of IMC was diffusion-controlled process. It should be noted that there were little differences in δ_{tot} among the four specimens, suggesting that IMC thickening was not greatly affected by the Fe content of the solders. However, thickening of Cu₃Sn could be explained by the correlation with the nucleation of Kirkendall voids at the Cu₃Sn/Cu interface as shown in Fig. 5(b). It was reported [7] that thickness of Cu₃Sn (δ_{Cu_3Sn}) did not

increased further after the Kirkendall voids fully covered the interface of Cu₃Sn/Cu. It can be ascribed that Kirkendall voiding reduced the Cu flux into IMC, thereby Cu₃Sn should be the Cu source for Cu₆Sn₅, which means converting Cu₃Sn to Cu₆Sn₅. Thus, δ_{Cu_3Sn} would inversely correlate with the tendency of Kirkendall void formation at the interface of Cu₃Sn/Cu.

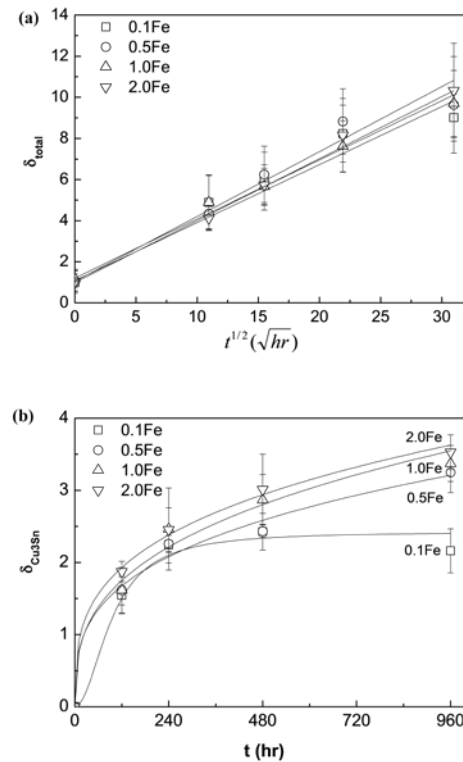


Fig. 5. Thickness variations of (a) total IMC and (b) Cu₃Sn with the ageing time at 150°C.

3.2. Characteristics of Kirkendall void formation

Generally, the voided fraction of the interface was measured from the SEM micrographs of polished specimens [10] and the line fraction of voids on the Cu₃Sn/Cu (L) was measured as shown in Fig. 6. Since Fe is a sulphide forming element ($\Delta G_f^0 = -138.7 \text{ J/mol}$ for FeS) [11], the propensity increased with the Fe content dissolved in the solder and in the Cu UBM. It can be stated that Fe atoms dissolved in the Cu UBM played a role as a S scavenger and reduced the interfacial segregation of S. Thermodynamically, the amount of Fe dissolved in the Cu solid solution increased with the Fe content in the solder up to the solubility limit of Fe in Cu (X_{Fe}^B).

Until now, the effects of the Fe content on the Kirkendall void formation at the Cu₃Sn/Cu interface were analyzed from the perspective of S scavenging.

In classical temper-embrittlement problems, notch sensitive mechanical properties, fracture toughness or Charpy V notch energy, have been enhanced by scavenging of embrittling elements, thereby suppressing the interfacial segregation of impurity elements. The drop impact resistance which is a notch sensitive property also would be improved by alloying Fe which suppressed Kirkendall void formation. In that context, the beneficial effect of Fe on the Kirkendall void formation is expected to have mitigated the effect on the drop impact resistance, when SPS was used in the Cu electroplating process.

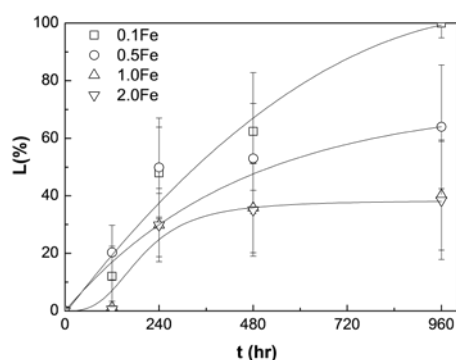


Fig. 6. Variations of line fraction of voids at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface with the ageing time measured from polished SEM.

4. Conclusion

1. Increasing the Fe content of Sn-3.5Ag-xFe solders had little effects on the total IMC thickness, but it significantly suppressed the Kirkendall void formation at the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface in Sn-3.5Ag-xFe/Cu solder joints

2. After aging of 960 h at 150°C , in 0.1Fe specimen, Cu_3Sn thickness decreased due to the reduced Cu flux from the Cu UBM to the IMC layer by Kirkendall voids fully covered the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface.

3. Line fractions of Kirkendall voids from the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface were smaller for the 1.0Fe and 2.0Fe specimens compared to the others.

4. Alloying Fe to the solder would improve the drop impact resistance by scavenging embrittling elements which are deleterious to the notch sensitive mechanical properties.

ACKNOWLEDGMENT

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