Inhibition of interfacial embrittlement at SnBi/Cu single crystal by electrodeposited Ag film

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Electrodeposited Ag film was explored as a potential interfacial barrier to Bi segregation for suppressing the interfacial embrittlement of Cu/SnBi interconnects. The presence of Ag film introduced Ag_3Sn intermetallic layer at the interface, which effectively prevented Bi from reaching the Cu/intermetallic interface. When the persistent slip bands (PSBs) in the Cu single crystal were driven to impinge the Cu/Cu_3Sn interface, interfacial cracking was averted and instead superceded by cracking of intermetallic compounds (IMCs) at the interface.

I. INTRODUCTION

Solder interconnection is an essential part of microelectronic packaging because it not only provides the electrical connection but also ensures the mechanical bonding.[1,2] In recent years, a significant development for solder interconnection is the replacement of SnPb solders with Pb-free solders owing to environmental and health concerns.[2–4] During the soldering process, excess heat can cause a series of deleterious effects,[5,6] especially for electronic components sensitive to high temperatures, so that low soldering temperatures become necessary to avoid thermal damage in a package. In this regard, binary eutectic SnBi solder is particularly attractive because of its low melting point and narrow freezing range. Moreover, compared to the lead-free solders with high melting points, the reaction rate of SnBi solder with the metallization is slower under low-temperature reflowing. To form a solder interconnect, SnBi is typically reflow-soldered onto a device metallization.[5,7] However, for the most common metallization, Cu, a severe interfacial embrittlement develops when Bi is allowed sufficient mobility, e.g., by aging at 120 °C for 7 days, to segregate at the Cu/Cu_3Sn interface.[8,9] Because the conditions for segregation are not too far from the thermal conditions employed in manufacturing and service, the reliability of SnBi/Cu joint becomes questionable. Thus it is necessary to further investigate the interfacial brittleness and corresponding mechanisms due to segregation of Bi into the SnBi/Cu interface, which is helpful for the use of the SnBi alloy in the Cu substrate.

Herein we report an exploratory study aimed at introducing a possible diffusion barrier of Bi by inserting a thin film of Ag between SnBi solder and Cu substrate. By comparisons of Bi diffusion within different paths, we can better understand the mechanism of Bi segregation into the intermetallic compound (IMC)/Cu interface. In engineering applications, Ag is a common alloying element in a number of Pb-free solder systems, including Sn–Bi.[10] Thin Ag films are also used to preserve the solderability of the metallization by limiting oxidation at reflowing temperature.[11] In our current research, we demonstrated the effectiveness of Ag by observing crack development at the Cu/Cu_3Sn interface when dislocations in the persistent slip bands (PSBs) of a Cu single crystal subjected to cyclic deformation were pushed against the interface by repeated cyclic loading, following the approach by Zhu et al.,[12] as illustrated in Fig. 1. It is well known that the plastic strain always localized within PSBs in both copper polycrystals and single crystals, which caused fatigue damage and crack initiation during cyclic deformation. It is expected that the PSBs can introduce a high local plastic strain to the interface between the Cu substrate and the IMCs for a better understanding of the intrinsic brittle or ductile cracking feature of the interfaces.

II. EXPERIMENTAL

The Cu single crystal was grown from oxygen-free/high-conductivity (OFHC) Cu of 99.999% purity by the Bridgman method in a horizontal furnace. Some

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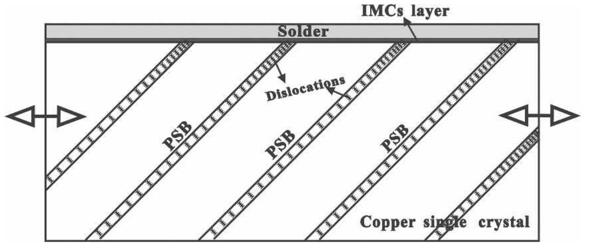

FIG. 1. Illustration of the interaction of PSBs with the interface between the SnBi solder and Cu single crystal.

rectangular specimens with a size of 50 mm × 6 mm × 5 mm were spark-cut from the Cu single-crystal plate. Specimen surfaces were mechanically ground and then carefully electropolished. A film Ag layer of about 2–3 μm was then electroplated on the selected area of the specimen surface. The electroplated Ag surface was carefully polished and then rinsed in water and alcohol. Upon air drying, a commercial eutectic 58Bi–42Sn solder paste was dispersed on the top surface of two kinds of specimens, those with or without those without electroplated Ag film. The specimens were then heated in an electric oven, where the reflow temperature was controlled at 180 °C for 1 min to melt solder paste and evaporate the rosin flux before the specimens were cooled down in air. The as-reflowed SnBi/Cu single crystal specimen was isothermally aged at 120 °C for 7 days, which was previously reported to induce Bi segregation at the Cu/Cu_3Sn interface.[8,9] For comparison, the specimen with the electroplated Ag film was aged at 120 °C for 9 days. Before fatigue tests, all specimens were mechanically polished for microstructural observations on the solder, interface, and Cu single crystal. The specimens were cyclically deformed in a push–pull manner under a constant axial plastic strain amplitude of 10^{-3} at room temperature. The interfacial microstructures before and after aging and the surface of the fatigued specimens were observed with a LEO (Oberkochen, Germany) Super35 scanning electron microscope (SEM) equipped with energy-dispersive x-ray spectroscopy (EDX).

III. RESULTS AND DISCUSSION

Figure 2(a) shows the interfacial microstructure between SnBi solder and Cu single crystal in the as-reflowed condition. During the reflowing process, Cu reacted selectively with the liquid Sn to form a thin layer of Cu_6Sn_5 intermetallic compound phase. The thickness of the IMC layer is about 1–2 μm. After aging for seven days, the microstructure of solder was obviously coarsened and the interfacial IMC phase grew to about 6–7 μm, as shown in Fig. 2(b). A thinner Cu_3Sn IMC also became evident between Cu and Cu_6Sn_5. Because Bi does not form an IMC phase with Cu, the residual Bi from eutectic SnBi solder had to accumulate along the IMC/solder interface. These observations are consistent with previous studies on SnBi and SnPb solder on Cu substrate.[8,9,13] For the Cu substrate with electroplated Ag film, the liquid Sn first reacted with the Ag film during the reflow process to form a planar-like IMC layer of

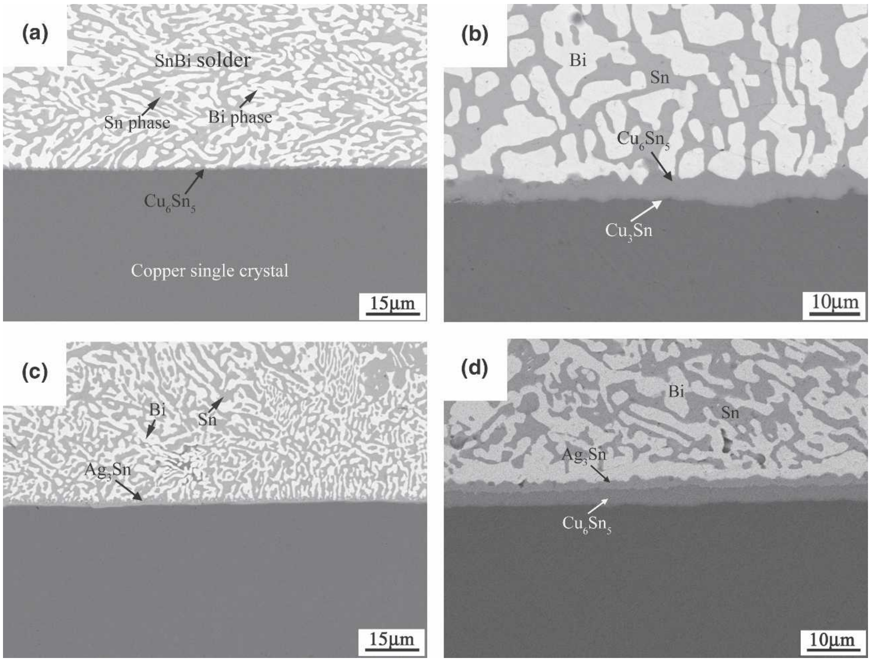

FIG. 2. SEM back-scattered electron micrographs of IMCs morphology at the interfaces between SnBi and Cu single crystal: (a) as-reflowed, (b) aged at 120 °C for 7 days; at the interface between SnBi and the Cu single crystal with an electroplated Ag film: (c) as-reflowed, and (d) aged at 120 °C for 9 days.

about 3 μm, as shown in Fig. 2(c). EDX analysis indicates that the atom percentage of Ag and Sn elements in the interfacial layer is approximately equal to 3:1, close to the ratio in the Ag_3Sn phase. After aging for 9 days, it is noted that the Ag layer was completely consumed, and the Sn atoms diffused through the Ag_3Sn layer to react with Cu, forming a layer of Cu_6Sn_5 phase, as shown in Fig. 2(d). The Cu_6Sn_5 layer grew rather rapidly, so that a large amount of Sn was consumed, leaving a Bi-rich zone upon the Ag_3Sn layer.

During cyclic deformation, PSBs were activated on the polished Cu single-crystal surface, and the dislocations inside the PSBs were forced to impinge the Cu_3Sn/Cu interface. The shear stress along PSBs is inclined about 45° with the interface, which generates equal stress components parallel and perpendicular to the IMC/Cu interface. For the specimen without the electroplated Ag film, as shown in Fig. 3(a), the cracks initiated and propagated exactly along the Cu_3Sn/Cu interface, resulting in a brittle interfacial IMC/Cu fracture after only 300 cycles. Evidently, the fracture toughness of the Cu_3Sn/Cu interface should be much lower than that of the IMC layer. Figure 3(b) exhibits a quite flat and smooth fracture surface (on IMC side), characteristic of brittle fracture. According to previous work,[8,9] this severe interfacial embrittlement is due to the segregation of Bi atoms into the IMC/Cu interface, which disrupts the local Cu atomic arrangement at the interface. The similar cases were also widely reported in Cu (Bi) alloys.[14–17]

When the cyclic deformation was applied to the SnBi/Cu single crystal joint with the electroplated Ag film, no brittle fracture of the Cu_3Sn/Cu interface was found even after 5,000 cycles. Instead, the cracks started at the intersection sites of PSBs with the interface and propagated nearly perpendicular to the interface within the IMC layers, as shown in Fig. 3(c), which indicates the fracture

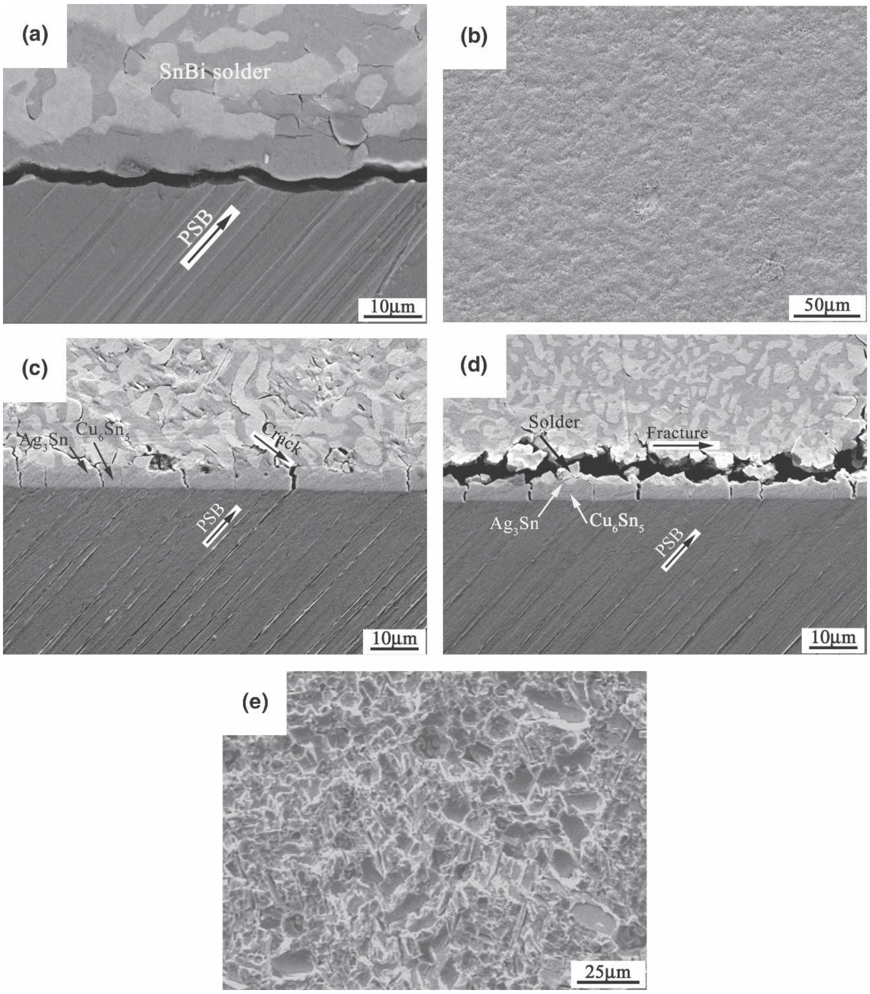

FIG. 3. Fatigue damage at the interface of SnBi/Cu single crystal produced by striking the interface with PSBs: (a) brittle fracture along the IMC/Cu single crystal interface after 300 cycles, (b) fracture surface of the IMC side; at the interface of SnBi/Cu single crystal with an electroplated Ag film: (c) crack initiation at the intersection of PSBs with the interface after 5,000 cycles, (d) fracture along the solder/IMC interface after 8,000 cycles, and (e) fracture surface with ductile tear bands.

toughness of the IMC layer should be lower than that of the IMC/Cu interface. With further cyclic deformation, the cracks continued to develop on the other side of the IMC, along the interface of solder and Ag_3Sn layer, as shown in Fig. 3(d). Unlike the brittle fracture along Cu_3Sn/Cu interface, the crack growth along the solder and IMC interface generally represents a more ductile fatigue process with higher resistance, as known in the as-reflowed SnBi/Cu and SnAgCu/Cu couples.[9,12] The fracture surface (on the side of IMC) is shown in Fig. 3(e). It consists of a few ductile tear bands and fracture surfaces of residual Bi phase, which suggests that most crack propagation was essentially within the solder close to the intermetallic phase. From these results, it is evident that there is a significant transition of interfacial fracture mode under a microscale loading when the Cu substrate was electroplated a thin Ag film. In other words, the Bi-induced embrittlement at the interface was effectively inhibited by inserting a thin Ag film.

From the microstructural observations in Figs. 2(c) and 2(d), it is noted that the Ag_3Sn layer separated the Bi atoms from the Cu and Cu_6Sn_5 phase, in the as-reflowed as well as the aged states. In the case of SnBi/Cu without an electroplated Ag film,[8,9] the Bi atoms could readily reach the IMC/Cu interface. Therefore, it can be reasonably assumed that the Bi diffusing through the Ag_3Sn IMC layer in the present case should be a more difficult process. To determine whether the Bi atoms have reached the Ag_3Sn/Cu_6Sn_5 interface, x-ray photoelectron spectroscopy (XPS) was used to detect the Bi concentration at the interface. When the solder layer and Ag_3Sn layer were selectively etched away by acetic acid solution, the Cu_6Sn_5 grains (gray contrast) and some residual Ag_3Sn granules (bright contrast) are clearly seen in Fig. 4(a), indicating that the site is on the interface of Ag_3Sn and Cu_6Sn_5. The surface was first bombarded by Ar ions for 5 min in a high vacuum to remove oxide before XPS analysis. Figure 4(b) shows the XPS spectra obtained from the exposed surface; no detectable Bi elements could be found at the interface. XPS results suggest that the Bi atoms did not diffuse through the Ag_3Sn layer to reach the Ag_3Sn/Cu_6Sn_5 interface. Without Bi influx, it is impossible for Bi atoms to segregate into the interface of IMCs layer and Cu substrate. Thus it is evident that the Ag_3Sn layer served as a barrier to the Bi segregation into the interface. Of course, the present Ag_3Sn layer may be only one of typical IMCs where the diffusion of Bi atoms can be effectively blocked off. In general, it seems that the Bi segregation into the interface may be heavily dependent on the type of IMC path, in which the diffusion of Bi is determined by the factors of IMC, including the crystal structure, morphology, element diffusion mechanism, and so on.

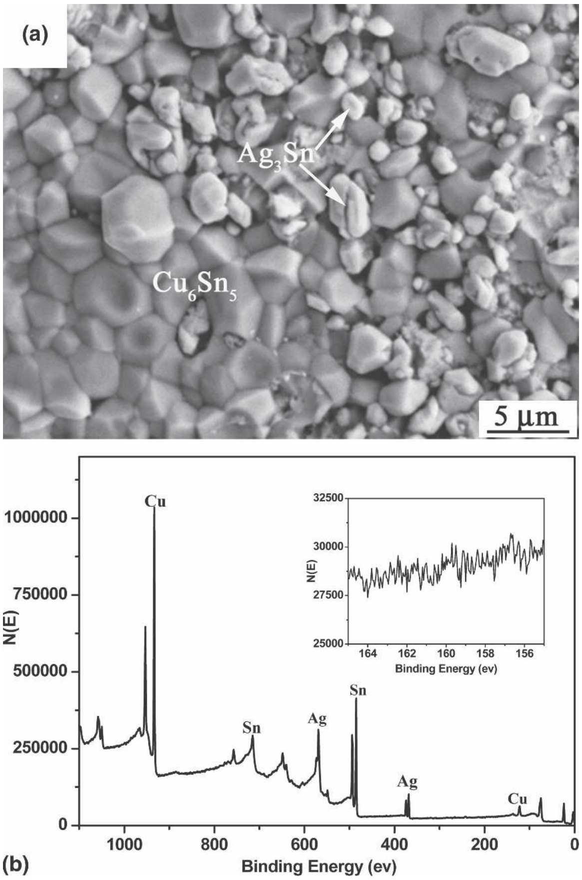

FIG. 4. (a) Top surface morphology at the Ag_3Sn/Cu_6Sn_5 interface after chemical removal of the solder and Ag_3Sn layer; (b) XPS spectra of the top surface at the Ag_3Sn/Cu_6Sn_5 interface.

IV. CONCLUSIONS

In summary, after striking the interface with PSBs, the fatigue damage at the interface between a SnBi solder and a Cu single crystal was examined at the microscopic scale. Aged SnBi/Cu single-crystal couples exhibited a Bi-induced brittle fracture along the interface of IMC and Cu substrate, whereas insertion of an electroplated Ag film at the interface resulted in a switch in the fracture mode to a ductile fracture along the interface of the IMC and solder layer. Such a beneficial effect of the Ag film was shown to derive from blockage of Bi segregation to the Cu/intermetallic interface by the Ag_3Sn layer between the SnBi solder and Cu_6Sn_5. It is thought that the segregation of Bi into the IMC/Cu interface is closely related with the type of IMC path.

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