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Letter

Interfacial reactions of Sn/Ag/Cu tri-layer on a deformed polyimide substrate

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ABSTRACT

Sn/Ag/Cu tri-layer structure was frequently encountered in microelectronic solder joints. In flexible microelectronics, the Sn/Ag/Cu tri-layer structure was usually subjected to strain when the plastic substrate was deformed. This study investigated the Sn/Ag/Cu interfacial reactions on a polyimide substrate subjected to compressive and tensile strain. Under both strain conditions, the Sn/Ag/Cu tri-layer structure was replaced by the multi-layer structure of Sn/Ag_3Sn/Cu_6Sn_5/Cu_3Sn/Cu after 150 and 200 °C of aging. However, blocky Cu_6Sn_5 was formed at the Sn/Ag_3Sn interface subjected to compressive strain but rarely observed at that subjected to tensile strain, revealing that strain was an influential factor to the Sn/Ag/Cu interfacial reactions.

1. Introduction

Flexible microelectronics receive much attention during the past years because of many advantages such as flexibility, light weight, small package volume, and so forth [1,2]. Flexible printed circuit board (PCB) is an important and essential component in this industry. Flexible PCB is generally composed of a plastic substrate (for example, polyimide) coated with a conductive metal (Cu) trace. To prevent the Cu trace from excessive oxidation during storage, a surface finish layer is usually coated on its surface. Immersion Ag is a promising choice of surface finish because it offers better coplanarity and is also feasible to wire-bonding process [3,4]. Also, the cost of immersion Ag is lower compared to conventional Au-containing finish layer.

Solid-state bonding rather than high-temperature reflow is a common technique to join the integrated-circuit chips to a flexible PCB [5] in order to avoid possible high-temperature damage on plastic substrate. During solid-state bonding, the solders do not melt and consequently the immersion Ag layer remains on the Cu metallization, forming a solder/Ag/Cu tri-layer solder joint. This is different from conventional reflow process, in which the entire Ag layer melts by molten solder and the bonding is finished by a solder/Cu bi-layer joint. We have investigated the tri-layer Sn/Ag/Cu interfacial reactions under solid-state aging [6] and found that this kind of interfacial reaction exhibited very distinct behavior compared to conventional Sn/Cu bi-layer system.

Flexible PCBs are usually bended in order to reduce the packaging volume, making the solder joints subject to strain. Therefore, it is of interest to investigate the Sn/Ag/Cu tri-layer interfacial reactions under the influence of strain. In this present study, flexible PCBs coated with Ag and Sn were bended upward or downward, making the Sn/Ag/Cu interface subject to tensile or compressive strain, respectively. Formation and growth behavior of the reaction products at the interface were investigated and correlation with different strain conditions was also discussed.

2. Materials and methods

A commercial flexible PCB, a 25-μm thick polyimide coated with a 30-μm thick Cu layer, was used as the substrate. An immersion Ag layer was deposited on the Cu layer by immersing the flexible PCB in a commercial plating solution at 58 °C. Two immersion times were set, 10 and 40 min, and the thicknesses of the resultant Ag layers were 0.63 and 1.75 μm, respectively. Then, a 15-μm thick Sn layer was electrodeposited on the Ag layer. The flexible PCBs were stuck on the inner side or outer side of a semi-cylinder quartz tube with a diameter of 1.6 cm. As shown in Fig. 1, the Sn/Ag/Cu tri-layer was subjected to compressive strain as the flexible PCB was stuck on the inner (concave) side. On the contrary, the Sn/Ag/Cu tri-layer was subjected to tensile strain as the flexible PCB was stuck on the outer (convex) side. Solid-state aging was conducted by placing the deformed flexible PCBs stuck on the quartz tubes into an oven at 150 and 200 °C for 12–168 h. Another set of samples without deformation were also aged as a reference.

After aging, the samples were removed from the oven and treated metallographically. The samples were mounted in epoxy resin, followed by grinding and polishing respectively with sandpapers and fine Al_2O_3 suspensions in the direction perpendicular to the Sn/Ag/Cu interface. The samples were microetched for clear observation. Field-emission scanning electron microscopy (FESEM) was used to observe the microstructure of the cross-sections of the Sn/Ag/Cu interface. The compositions of intermetallics were determined using energy dispersive X-ray spectrometer (EDX).

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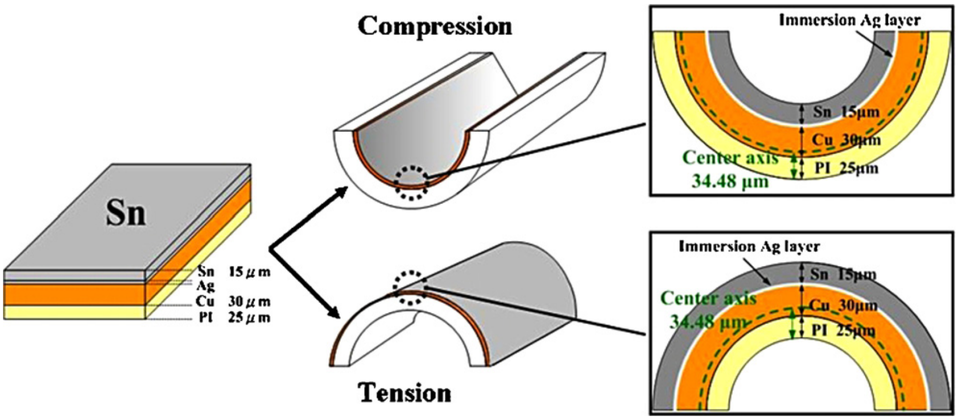

Fig. 1. Schematic showing the strain conditions of deformed flexible PCBs.

3. Results and discussion

Fig. 2 shows the SEM images of the Sn/Ag/Cu interface with 0.63-µm thick immersion Ag layer after aging at 150 °C, where (a) and (b) are the samples subjected to compressive strain and (c) and (d) subjected to tensile strain. From Fig. 2(a), a discontinuous Ag_3Sn layer was formed by consuming the entire immersion Ag after 24 h of aging. Also, Cu_6Sn_5 and Cu_3Sn were formed at the Ag_3Sn/Cu interface. These three intermetallics coexisted at the interfaces of the samples subjected to compressive and tensile strain. The Cu_6Sn_5 and Cu_3Sn phases presented continuous layered structure but the Ag_3Sn phase transformed into discontinuous island-shaped structure upon increasing the aging time. One noticeable thing is that blocky Cu_6Sn_5 was formed at the Sn/Ag_3Sn interface subjected to compressive strain after 120 h of aging. In contrast, no blocky Cu_6Sn_5 was observed at the interface subjected to tensile strain after aging up to 168 h. The blocky Cu_6Sn_5 grew along the grain boundary of Sn, as seen in Fig. 2(b). Formation of blocky Cu_6Sn_5 was also observed in the samples subjected to compressive strain as the aging temperature was raised to 200 °C and the immersion Ag layer was thickened to 1.75 µm, as seen in Fig. 3.

Understanding of dominant diffusing species is essential and helpful in the discussion of interfacial reactions. In general, Cu is considered to be the dominant diffusing species in the binary Sn/Cu interfacial reaction because Cu can diffuse interstitially in the Sn lattice [7]. However, this is not completely true in our case. At the early stage of aging, Ag_3Sn was formed first by the Sn/Ag interfacial reaction. This phase could be taken as a marker which separated Sn and Cu. If Cu is the dominant diffusing species, Cu would diffuse through Ag_3Sn to the Sn side (probably via the grain boundaries inside Ag_3Sn) and reacted with Sn to form Cu_6Sn_5 at the Sn/Ag_3Sn interface. However, a layered Cu_6Sn_5 phase was observed on the other side of the Ag_3Sn layer (the Ag_3Sn/Cu interface), as seen in Figs. 2 and 3, indicating that the diffusion of Sn also contributed to the growth of Cu_6Sn_5 and was very likely to dominate because the layered Cu_6Sn_5 phase was apparently the primary product compared to the locally formed blocky Cu_6Sn_5 phase. On the contrary, the growth of blocky Cu_6Sn_5 at the Sn/Ag_3Sn interface was con-

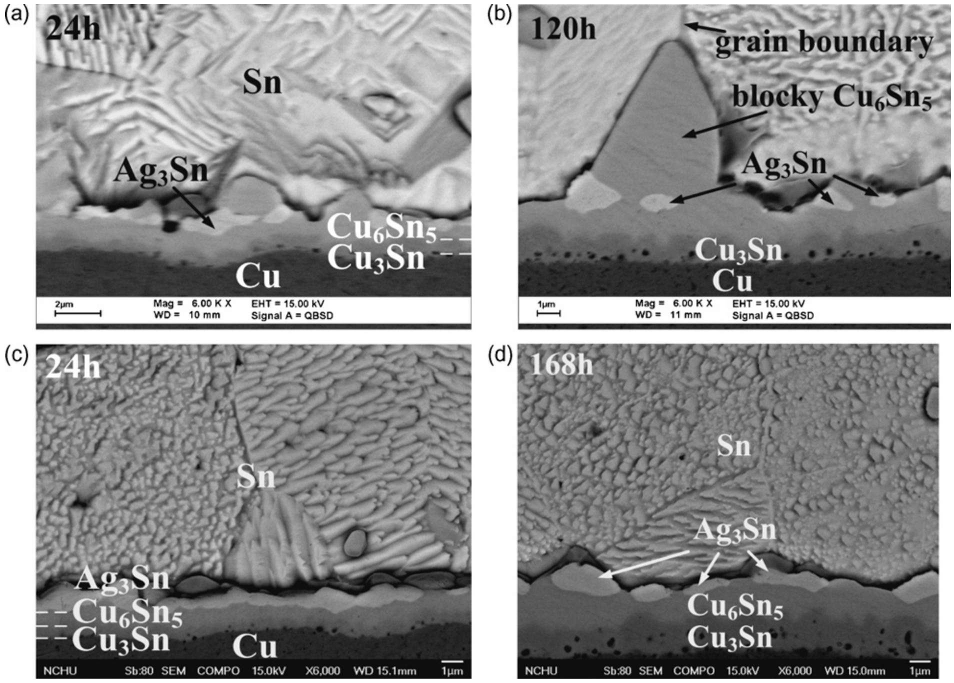

Fig. 2. SEM images of the Sn/Ag/Cu interfaces with 0.63-µm thick immersion Ag layer after aging at 150 °C, where (a) and (b) are the samples subjected to compressive strain and (c) and (d) subjected to tensile strain.

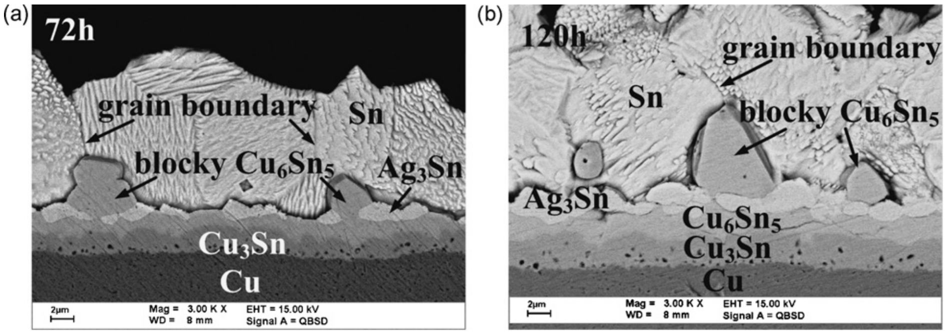

Fig. 3. SEM images of the Sn/Ag/Cu interfaces subjected to compressive strain: (a) with 0.63-µm thick immersion Ag layer after aging at 200 °C for 72 h and (b) with 1.75-µm thick immersion Ag layer after aging at 150 °C for 120 h.

trolled by the diffusion of Cu. The primary growth mechanism of this blocky Cu_6Sn_5 was grain boundary diffusion because it grew along the grain boundaries of Sn. In addition, the formation of Cu_3Sn at the Cu_6Sn_5/Cu interface was a result of the phase transformation of Cu_6Sn_5 by incorporating Cu atoms from the Cu side. In other words, the growth of Cu_3Sn was controlled by the diffusion of Cu into the Cu_6Sn_5 phase. Formation of Kirkendall voids in Cu_3Sn (near the Cu side) also evidenced that Cu was the dominant diffusing species for the Cu_3Sn growth.

In our previous study, we also observed the formation of blocky Cu_6Sn_5 in the samples without deformation [6]. Compared to the results obtained in this present study, the tensile strain appeared to have effects on inhibiting the formation of blocky Cu_6Sn_5. In other words, the Cu diffusion toward Sn was retarded when the Cu layer was subjected to tensile strain. To have a detailed understanding of the strain effect on the Cu diffusion, we should figure out first what is the driving force for the diffusion of Cu toward Sn. In general, concentration gradient is the most common driving force for atomic diffusion in the interfacial reaction systems, and it exists in our samples no matter the Sn/Ag/Cu tri-layers were subjected to compressive or tensile strain. So, if the blocky Cu_6Sn_5 phase was formed in the samples subjected to compressive strain, it should be also formed in the samples subjected to tensile strain. However, the blocky Cu_6Sn_5 phase was rarely observed in the samples subjected to tensile strain, indicating that there should be other driving force for the diffusion of Cu toward Sn. Intrinsic compressive stress due to the formation of layered Cu_6Sn_5 phase was attributable to the driving force. When Sn diffused to the Cu side and reacted with Cu to form layered Cu_6Sn_5, volume expansion occurred due to volume change, $\Delta V = V_{\mathrm{Cu6Sn5}} - 6\,V_{\mathrm{Cu\,(with\,5Sn)}} = +75.41\ \mathrm{cm}^3/\mathrm{mol}$ [8]. This volume expansion would result in intrinsic compressive stress at the Ag_3Sn/Cu interface, inducing the Cu diffusion toward Sn in order to release the compressive stress. Therefore, the blocky Cu_6Sn_5 phase was formed in the samples subjected to compressive strain because the intrinsic compressive stress still existed and even increased by the extrinsic compressive strain due to sample deformation. However, the blocky Cu_6Sn_5 phase was rarely observed in the samples subjected to tensile strain because the extrinsic tensile strain might neutralize the intrinsic compressive stress, diminishing the driving force for Cu diffusion.

4. Conclusions

Ag_3Sn was formed at the interface first, and then layered Cu_6Sn_5 and Cu_3Sn were formed at the Ag_3Sn/Cu interface. Blocky Cu_6Sn_5 was also observed locally at the Sn/Ag_3Sn interface subjected to compressive strain but was rarely observed at that subjected to tensile strain, revealing that the strain effect had significant effects on the Sn/Ag/Cu interfacial reaction. By taking Ag_3Sn as a marker in the Sn/Cu interdiffusion, the formation of Cu_6Sn_5 at the Ag_3Sn/Cu interface was attributed to the diffusion of Sn, while the blocky Cu_6Sn_5 formation at the Sn/Ag_3Sn interface was dominated by the diffusion of Cu. The absence of blocky Cu_6Sn_5 at the interface subjected to tensile strain suggested that the tensile strain could retard the diffusion of Cu toward Sn.

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