Interfacial Reaction Phenomena of Sn–Pb Solder with Au/Ni/Cu Metallization

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Eutectic Sn–Pb alloy is still used as a primary solder composition for electronic applications. The soldering pad on ball grid array (BGA) substrates usually has a trilayer Au/Ni/Cu metallization. The outermost Au layer serves to protect the bond pad from corrosion and oxidation as well as to increase solderability.1,2 The Ni layer serves the purpose of a diffusion barrier to inhibit the out-diffusion of Cu to the solder.3–8 This Au coating dissolves very quickly into the molten solder during reflow and precipitates as AuSn4 in the matrix of the solder upon cooling, while the Ni reacts with the molten Sn–Pb to form a thin Ni3Sn4 intermetallic compound (IMC) layer at the interface.9–11 It is surprising that after the BGA package is subjected to several hundred hours of solid-state aging at 100–150 °C, most of these AuSn4 needlelike precipitates migrate to the Ni interface and form a continuous layer of (Au,Ni)Sn4 over the Ni3Sn4 layer.

However, it is interesting to note that the re-deposition of (Au,Ni)Sn4 on Ni3Sn4 does not occur in Pb-free solder joints during solid-state aging.12–14 In a Pb-free solder, the dissolution of Ni is higher because of the higher solubility of Ni and also because of the higher reflow temperature usually employed during Pb-free soldering process. Thus, dissolved Ni may stabilize atomic Au or Au-containing IMCs inside the solder. Zeng and Tu reported another concept where they tried to discuss the role of Pb in Sn–Pb solder to obtain a (Au,Ni)Sn4 layer between the Ni3Sn4 layer and the Pb layer in terms of interfacial energy with each other.15 This present investigation attempts to study the relationship of the effect of Ni layer thickness on the redeposition of (Au,Ni)Sn4 as

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A solder mask-defined copper bond pad on a BGA substrate was used as a base for electrodeposition of Au and Ni. The thickness of the Ni layer was varied from 0.35 to 2.8 μm. The thickness of Au was kept at 1.3 μm. Commercially available BGA solder balls of Sn (36wt %)/Pb (2wt %)/Ag were used for this study. The solder mask-opening diameter was 600 μm and the diameter of the BGA solder ball before melting was 760 μm. After being dipped into the flux, solder balls were placed on the Au/Ni/Cu bond pads and reflowed in a N₂ atmosphere reflow oven. A schematic diagram of the soldering process on a BGA substrate is shown in ref 16. The peak reflow temperature was 225 °C and the time above the melting point of the solder alloy was 30 s. Immediately after the reflow, the substrates were subjected to aging at 150 °C for times up to 1000 h. After the aging test for each readout point, cross-sectioned samples were prepared to study interfacial microstructures. The scanning electron microscope (SEM) used for this study was a Philips XL 40 FEG equipped with energy-dispersive X-ray analysis (EDX).

A typical interfacial structure of the solder joints just after reflow shows only the Ni₃Sn₄ binary IMC (BIMC) at the interface since the entire Au metallization layer is dissolved into the molten solder. Only needle-shaped AuSn₄ BIMC is distributed throughout the bulk solder for the joints where a thick Au layer was used (Figure 1). No ternary IMC (TIMC) has been noticed either at the interface or in the bulk of the solder joint with a 0.7-μm Ni layer aged for 500 h at 150 °C, it has been found that the Ni layer has just been consumed in some locations and also the Ni₃Sn₄ layer has no longer exists; instead, AuSn₄ is detected with a spherical morphology (Figure 2b). Underneath the AuSn₄ sphere, a complex quaternary (Au,Ni,Cu)₆Sn₅ IMC is noticeable.

With an increase of aging time, changes have been noticed according to the Ni layer thickness. For example, for the solder joint with a 0.7-μm Ni layer, although a continuous layer of (Au,Ni)Sn₄ has been observed after 500 h aging at 150 °C (Figure 3a), there is no Au-containing layer attached at the interface after 1000 h of aging at 150 °C (Figure 3b). (Au,Ni)Sn₄ has been transformed to AuSn₄ and lifted up from the interface. At the interface, the Ni₃Sn₄ layer no longer exists; instead, it is converted to (Cu,Ni)₆Sn₅ (Figure 3b). In the sample with a 0.7-μm Ni layer aged for 500 h at 150 °C, it has been found that the Ni layer has just been consumed in some locations and also the Ni₃Sn₄ layer has started to convert to (Cu,Ni)₆Sn₅ in those locations. During the following 500 h aging, (Cu,Ni)₆Sn₅ has been transformed to (Au,Cu,Ni)₆Sn₅ along with a new phase of Cu₃Sn between the IMC layer and the Cu pad.

As the Cu pad underneath the interface is much thicker than the Ni layer or interfacial IMCs, it acts as a source of

Cu. Cu diffusion continues in the upward direction and changes the microchemistry of AuSn\textsubscript{4} to (Au,Ni,Cu)Sn\textsubscript{4} at first and later on (Au,Ni,Cu)\textsubscript{6}Sn\textsubscript{5}. For the solder joint with the thinnest Ni layer (0.35 μm), it has been found that Cu diffused to the solder region at a faster rate leaving behind Ni. Figure 4 shows the interfacial microstructure of a solder joint for a 0.35-μm Ni layer and 1.3-μm Au layer after aging at 150 °C for 1000 h, where (Au,Cu)\textsubscript{6}Sn\textsubscript{5} was found instead of any AuSn\textsubscript{4} in the solder and (Au,Ni,Cu)\textsubscript{6}Sn\textsubscript{5} was found instead of (Au,Ni)Sn\textsubscript{4} at the interface.

The Ni solubility limit in the AuSn\textsubscript{4} phase is approximately 12 at. % at 150 °C, and thus the (Au,Ni)Sn\textsubscript{4} phase is a ternary AuSn\textsubscript{4}-base compound with a high Ni solubility.\textsuperscript{11} From thermodynamic calculations, it has been estimated that the dissolution of Ni into AuSn\textsubscript{4} decreases its Gibbs free energy (Figure 5), and this decrease is the driving force for AuSn\textsubscript{4} to seek Ni at the interface, resulting in the migration of Au.\textsuperscript{15} Due to the slight solubility (<0.3 wt %) and the fast diffusion of Au in the eutectic SnPb at 150 °C, the AuSn\textsubscript{4} intermetallics in the bulk solder reconfigure to form a (Au,Ni)Sn\textsubscript{4} compound at the interface where Ni is available. (Au,Ni)Sn\textsubscript{4} forms as a layer-type morphology between the Pb-phase and the Ni\textsubscript{3}Sn\textsubscript{4} IMC layer. It has been reported elsewhere that within 48 h the continuous layer of (Au,Ni)Sn\textsubscript{4} forms on the Ni\textsubscript{3}Sn\textsubscript{4} IMC layer.\textsuperscript{16–19} Now the important question is why do we not see any continuous layer of (Au,Ni)Sn\textsubscript{4} for the thin Ni layer containing samples even when the Au layer is thick?

It has been reported by Hung and Duh\textsuperscript{22} that a limited amount of Cu diffuses through the Ni layer during reflow soldering which they termed “solder reaction assisted diffusion”. A thinner Ni layer makes easier diffusion of Cu toward the solder during reflow. This diffused Cu dissolves in the solder and might stabilize Au as (Au,Cu)Sn\textsubscript{4} grains to some extent. However, during aging the Ni layer is consumed to form Ni\textsubscript{3}Sn\textsubscript{4} and (Au,Ni)Sn\textsubscript{4}. For the case of

the thin Ni layer, once the Ni layer is consumed totally the Cu underneath reacts with the Ni3Sn4 very quickly. Due to the Cu diffusion, the Ni3Sn4 BIMC transforms to (Cu,Ni)6Sn5 TIMC, which is thermodynamically more stable.22 The tendency of (Cu,Ni)6Sn5 TIMC formation is so strong that when all the Ni3Sn4 layer is consumed, it takes further Ni from the (Au,Ni)Sn4 layer resulting in AuSn4 nodules. It is interesting to note that once the Ni3Sn4 layer is consumed totally by forming the (Cu,Ni)6Sn5 layer, there is a chemical change as well as a physical change of the Au-containing compound which occurs simultaneously. It is noticed that the Pb-phase envelops the (Au,Ni)Sn4 layer which is also confirmed by many other investigators.16–21,23–25 While (Au,Ni)Sn4 exists in a layer-type morphology with the Pb-phase on one side and with the Ni3Sn4 layer on the other side, from these experiments it has been found that AuSn4 cannot exist in a layer morphology with the newly formed (Cu,Ni)6Sn5 layer. Surface energy considerations can help to understand this phenomenon clearly. To form a layer of (Au,Ni)Sn4 on the Ni3Sn4 layer as shown in Figure 6(a and b), consider the following relation of γ (interfacial energy per unit area) for the thick Ni layer interface:

\[ \gamma_{\text{PbNi}} = \gamma_{\text{AuNiSn4NiSn4}} + \gamma_{\text{PbAuNiSn}} \cos \theta \]  

(1)

When θ → 0, eq 1 can be written as follows:

\[ \gamma_{\text{PbNi}} = \gamma_{\text{AuNiSn4NiSn4}} + \gamma_{\text{PbAuNiSn}} \]  

(2)

which indicates \( \gamma_{\text{PbNi}} \geq \gamma_{\text{AuNiSn4NiSn4}} + \gamma_{\text{PbAuNiSn}} \) and \( \gamma_{\text{PbNi}} \geq \gamma_{\text{AuNiSn4NiSn4}} \).

For the thin Ni layer, a (Cu,Ni)6Sn5 layer has been found instead of a Ni3Sn4 layer and AuSn4 nodules instead of a (Au,Ni)Sn4 layer as shown in Figure 6c. Thus using the same relation of γ

\[ \gamma_{\text{Pb(AuNi)Sn4}} = \gamma_{\text{AuSn4/CuNiSn3}} + \gamma_{\text{Pb/AuSn4}} \cos \theta \]  

(3)

Considering θ → 180° and putting the value of \( \theta = 180^\circ \), eq 3 can be written as follows:

\[ \gamma_{\text{Pb(AuNi)Sn4}} = \gamma_{\text{AuSn4/CuNiSn3}} - \gamma_{\text{Pb/AuSn4}} \]  

(4)

which indicates \( \gamma_{\text{Pb(AuNi)Sn4}} \leq \gamma_{\text{AuSn4/CuNiSn3}} \) and \( \gamma_{\text{AuSn4/CuNiSn3}} \geq \gamma_{\text{Pb/AuSn4}} \).

The above analysis shows that (Au,Ni)Sn4 has a lower interfacial energy with Ni3Sn4, whereas AuSn4 has a higher interfacial energy with (Cu,Ni)6Sn5. However, both (Au,Ni)Sn4 and AuSn4 have a lower interfacial energy with Pb. It should be pointed out here that this finding is solely based on these experimental findings, as yet no quantitative measurements have been reported elsewhere of these interfacial energies. Only Zeng and Tu15 have reported similar approach when they attempted to explain why there is no evidence of a brittle continuous layer of (Au,Ni)Sn4 on the Ni3Sn4 layer for the Pb-free system.

In summary, the thinner Ni layer in Au/Ni/Cu metallization facilitates Cu diffusion into the interface. The role of Cu in the interfacial reaction during solid-state aging is very significant. It changes the microchemistry and morphology of the (Au,Ni)Sn4 and Ni3Sn4 by forming AuSn4 nodules and a (CuNi)6Sn5 layer at the interface. While (Au,Ni)Sn4 can exist in a layer-type morphology with the Pb-phase on one side and with the Ni3Sn4 layer on the other side, these experiments show that AuSn4 cannot exist in a layer morphology with the newly formed (Cu,Ni)6Sn5 layer. This study suggests that (Au,Ni)Sn4 has a lower interfacial energy with Ni3Sn4, whereas AuSn4 has a higher interfacial energy with (Cu,Ni)6Sn5. However, both (Au,Ni)Sn4 and AuSn4 have lower interfacial energies with Pb.

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