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Communications

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 Au protective layer during storage time and to prevent a rapid soldering reaction with the Cu layer.^{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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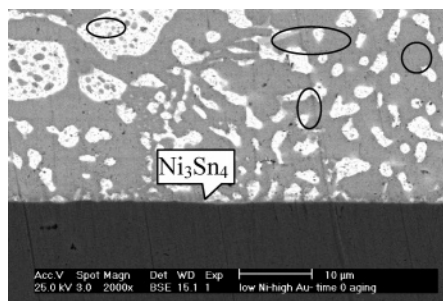


Figure 1. Typical interfacial structure of solder joints just after reflow. Inside the ellipses, needle-shaped AuSn_4 are visible.

well as the underlying mechanism of the complex Au-containing IMCs formation at the solder interface.

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 N_2 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 $^\circ\text{C}$ 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 $^\circ\text{C}$ 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 Ni_3Sn_4 binary IMC (BIMC) at the interface since the entire Au metallization layer is dissolved into the molten solder. Only needle-shaped AuSn_4 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 in the as-reflow condition. There has been no dissimilarity revealed among the differences in the Ni layer thicknesses. However, after 500–1000 h of aging at 150 $^\circ\text{C}$, a distinctly different interfacial microstructure was observed depending on the Ni layer thickness.

Figure 2 shows the interfacial microstructure of solder joints after 500 h aging at 150 $^\circ\text{C}$ for (a) a thick Ni layer and (b) a thin Ni layer. A new layer of $(\text{Au},\text{Ni})\text{Sn}_4$ has nucleated and grown on the Ni_3Sn_4 IMC layer in samples having a thick Ni layer (Figure 2a). Many other investigators have also reported the same interfacial structures.^{16–21} As

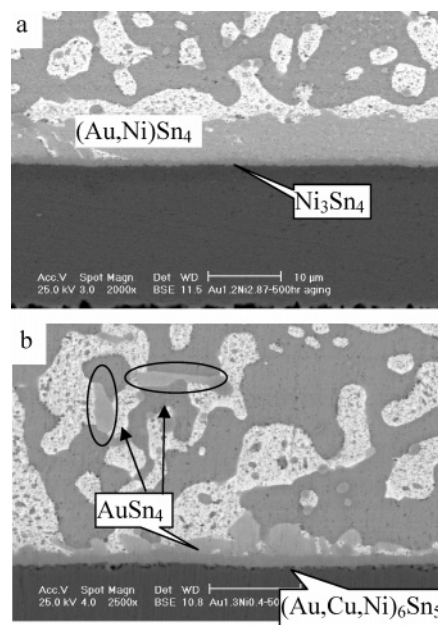


Figure 2. Interfacial structure of the solder/bond pad interfaces after 500 h aging at 150 $^\circ\text{C}$ for a thick Ni layer (a) and a thin Ni layer (b).

aging progresses, both $(\text{Au},\text{Ni})\text{Sn}_4$ and Ni_3Sn_4 grow thicker by taking Sn atoms from the solder neighboring the interface. As a consequence, a continuous Pb-rich layer is formed adjacent to the $(\text{Au},\text{Ni})\text{Sn}_4$ layer as seen in Figure 2a. On the other hand, the interfacial structure of the solder interface with a thin Ni layer, shown in Figure 2b, is totally different from the case of the thick Ni layer. Hence, there is no $(\text{Au},\text{Ni})\text{Sn}_4$ layer. The chemistry and morphology of the interfacial IMC is very different from that of the thick Ni metallization. Due to Cu diffusion, the layer-type morphology of $(\text{Au},\text{Ni})\text{Sn}_4$ no longer exists; instead, AuSn_4 is detected with a spherical morphology (Figure 2b). Underneath the AuSn_4 sphere, a complex quaternary $(\text{Au},\text{Ni},\text{Cu})_6\text{Sn}_5$ 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 $(\text{Au},\text{Ni})\text{Sn}_4$ has been observed after 500 h aging at 150 $^\circ\text{C}$ (Figure 3a), there is no Au-containing layer attached at the interface after 1000 h of aging at 150 $^\circ\text{C}$ (Figure 3b). $(\text{Au},\text{Ni})\text{Sn}_4$ has been transformed to AuSn_4 and lifted up from the interface. At the interface, the Ni_3Sn_4 layer no longer exists; instead, it is converted to $(\text{Au},\text{Cu},\text{Ni})_6\text{Sn}_5$ (Figure 3b). In the sample with a 0.7- μm Ni layer aged for 500 h at 150 $^\circ\text{C}$, it has been found that the Ni layer has just been consumed in some locations and also the Ni_3Sn_4 layer has started to convert to $(\text{Cu},\text{Ni})_6\text{Sn}_5$ in those locations. During the following 500 h aging, $(\text{Cu},\text{Ni})_6\text{Sn}_5$ has been transformed to $(\text{Au},\text{Cu},\text{Ni})_6\text{Sn}_5$ along with a new phase of Cu_3Sn 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

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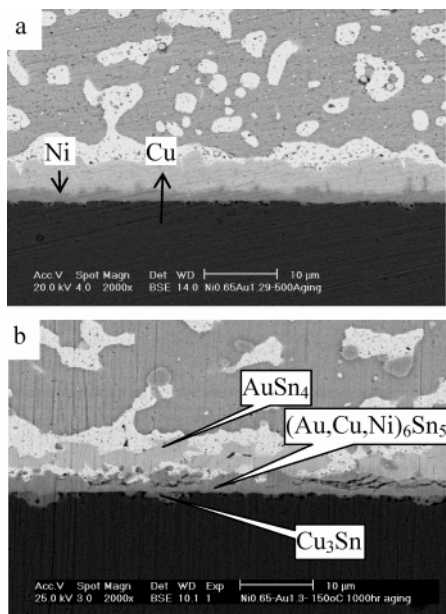


Figure 3. Interfacial structure of solder/bond pad interfaces for 0.7- μm -thick Ni layer samples after aging at 150 °C for (a) 500 h and (b) 1000 h with the thick Au layer.

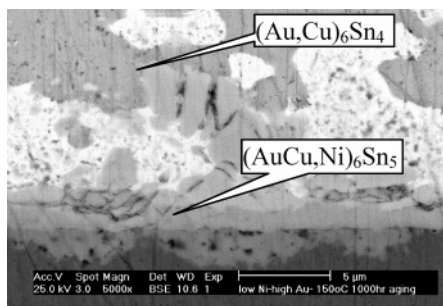


Figure 4. Interfacial structure of a solder/bond pad interface for 0.35- μm thick Ni layer samples after aging at 150 °C for 1000 h with a thick Au layer.

Cu. Cu diffusion continues in the upward direction and changes the microchemistry of AuSn_4 to $(\text{Au},\text{Ni},\text{Cu})\text{Sn}_4$ at first and later on $(\text{Au},\text{Ni},\text{Cu})\text{Sn}_4$ is transformed to $(\text{Au},\text{Ni},\text{Cu})_6\text{Sn}_5$. 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 $(\text{Au},\text{Cu})_6\text{Sn}_5$ was found instead of any AuSn_4 in the solder and $(\text{Au},\text{Ni},\text{Cu})_6\text{Sn}_5$ was found instead of $(\text{Au},\text{Ni})\text{Sn}_4$ at the interface.

The Ni solubility limit in the AuSn_4 phase is approximately 12 at. % at 150 °C, and thus the $(\text{Au},\text{Ni})\text{Sn}_4$ phase is a ternary AuSn_4 -base compound with a high Ni solubility.¹¹ From thermodynamic calculations, it has been estimated that the dissolution of Ni into AuSn_4 decreases its Gibbs free energy (Figure 5), and this decrease is the driving force for AuSn_4 to seek Ni at the interface, resulting in the migration of Au.¹⁵ Due to the slight solubility (<0.3 wt %) and the fast diffusion of Au in the eutectic SnPb at 150 °C, the AuSn_4 intermetallics in the bulk solder reconfigure to form a $(\text{Au},\text{Ni})\text{Sn}_4$ compound at the interface where Ni is available. $(\text{Au},\text{Ni})\text{Sn}_4$ forms as a layer-type morphology between the Pb-phase and the Ni_3Sn_4 IMC layer. It has been reported elsewhere that

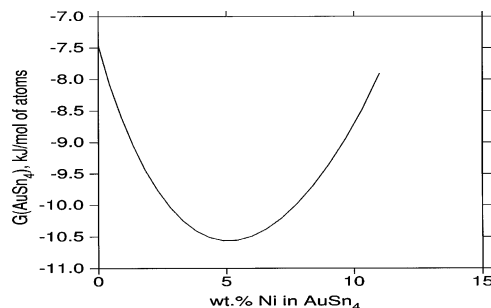


Figure 5. Estimated Gibbs energy of the line compound $(\text{Au},\text{Ni})\text{Sn}_4$ as a function of Ni content at 160 °C.²⁰

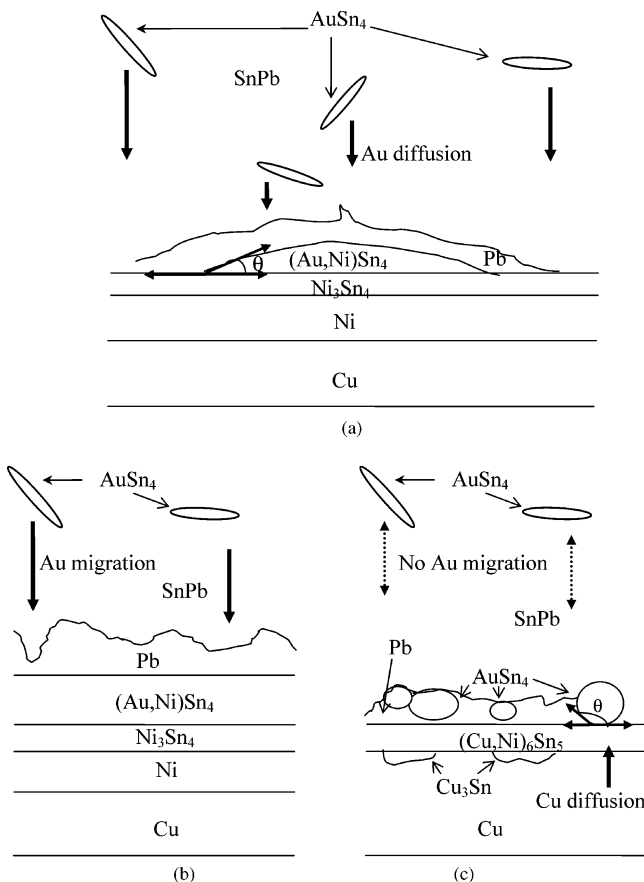


Figure 6. Schematic diagrams of the interfacial energies between different phases at the BGA SnPb solder interface. (a) Starting with a growth of the $(\text{Au},\text{Ni})\text{Sn}_4$ layer at the early stage of aging; (b) the interface of a bond pad of a thick Ni layer, after a prolonged aging; (c) the interface of a bond pad of a thin Ni layer, after a prolonged aging.

within 48 h the continuous layer of $(\text{Au},\text{Ni})\text{Sn}_4$ forms on the Ni_3Sn_4 IMC layer.^{16–19} Now the important question is why do we not see any continuous layer of $(\text{Au},\text{Ni})\text{Sn}_4$ for the thin Ni layer containing samples even when the Au layer is thick?

It has been reported by Hung and Duh²² 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 $(\text{Au},\text{Cu})\text{Sn}_4$ grains to some extent. However, during aging the Ni layer is consumed to form Ni_3Sn_4 and $(\text{Au},\text{Ni})\text{Sn}_4$. For the case of

the thin Ni layer, once the Ni layer is consumed totally the Cu underneath reacts with the Ni_3Sn_4 very quickly. Due to the Cu diffusion, the Ni_3Sn_4 BIMC transforms to $(\text{Cu,Ni})_6\text{Sn}_5$ TIMC, which is thermodynamically more stable.²² The tendency of $(\text{Cu,Ni})_6\text{Sn}_5$ TIMC formation is so strong that when all the Ni_3Sn_4 BIMC is consumed, it takes further Ni from the $(\text{Au,Ni})\text{Sn}_4$ layer resulting in AuSn_4 nodules. It is interesting to note that once the Ni_3Sn_4 layer is consumed totally by forming the $(\text{Cu,Ni})_6\text{Sn}_5$ 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 $(\text{Au,Ni})\text{Sn}_4$ layer which is also confirmed by many other investigators.^{16–21,23–25} While $(\text{Au,Ni})\text{Sn}_4$ exists in a layer-type morphology with the Pb-phase on one side and with the Ni_3Sn_4 layer on the other side, from these experiments it has been found that AuSn_4 cannot exist in a layer morphology with the newly formed $(\text{Cu,Ni})_6\text{Sn}_5$ layer. Surface energy considerations can help to understand this phenomenon clearly. To form a layer of $(\text{Au,Ni})\text{Sn}_4$ on the Ni_3Sn_4 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:

$$\gamma^{\text{Pb/Ni}_3\text{Sn}_4} = \gamma^{(\text{Au,Ni})\text{Sn}_4/\text{Ni}_3\text{Sn}_4} + \gamma^{\text{Pb}/(\text{Au,Ni})\text{Sn}_4} \cos \theta \quad (1)$$

When $\theta \rightarrow 0$, eq 1 can be written as follows:

$$\gamma^{\text{Pb/Ni}_3\text{Sn}_4} = \gamma^{(\text{Au,Ni})\text{Sn}_4/\text{Ni}_3\text{Sn}_4} + \gamma^{\text{Pb}/(\text{Au,Ni})\text{Sn}_4} \quad (2)$$

which indicates $\gamma^{\text{Pb/Ni}_3\text{Sn}_4} \geq \gamma^{\text{Pb}/(\text{Au,Ni})\text{Sn}_4}$ and $\gamma^{\text{Pb/Ni}_3\text{Sn}_4} \geq \gamma^{(\text{Au,Ni})\text{Sn}_4/\text{Ni}_3\text{Sn}_4}$.

For the thin Ni layer, a $(\text{Cu,Ni})_6\text{Sn}_5$ layer has been found instead of a Ni_3Sn_4 layer and AuSn_4 nodules instead of a

$(\text{Au,Ni})\text{Sn}_4$ layer as shown in Figure 6c. Thus using the same relation of γ

$$\gamma^{\text{Pb}/(\text{Cu,Ni})_6\text{Sn}_5} = \gamma^{\text{AuSn}_4/(\text{Cu,Ni})_6\text{Sn}_5} + \gamma^{\text{Pb}/\text{AuSn}_4} \cos \theta \quad (3)$$

Considering $\theta \rightarrow 180^\circ$ and putting the value of $\theta = 180^\circ$, eq 3 can be written as follows:

$$\gamma^{\text{Pb}/(\text{Cu,Ni})_6\text{Sn}_5} = \gamma^{\text{AuSn}_4/(\text{Cu,Ni})_6\text{Sn}_5} - \gamma^{\text{Pb}/\text{AuSn}_4} \quad (4)$$

which indicates $\gamma^{\text{Pb}/(\text{Cu,Ni})_6\text{Sn}_5} \leq \gamma^{\text{AuSn}_4/(\text{Cu,Ni})_6\text{Sn}_5}$ and $\gamma^{\text{AuSn}_4/(\text{Cu,Ni})_6\text{Sn}_5} \geq \gamma^{\text{Pb}/\text{AuSn}_4}$.

The above analysis shows that $(\text{Au,Ni})\text{Sn}_4$ has a lower interfacial energy with Ni_3Sn_4 , whereas AuSn_4 has a higher interfacial energy with $(\text{Cu,Ni})_6\text{Sn}_5$. However, both $(\text{Au,Ni})\text{Sn}_4$ and AuSn_4 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 $(\text{Au,Ni})\text{Sn}_4$ on the Ni_3Sn_4 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 $(\text{Au,Ni})\text{Sn}_4$ and Ni_3Sn_4 by forming AuSn_4 nodules and a $(\text{Cu,Ni})_6\text{Sn}_5$ layer at the interface. While $(\text{Au,Ni})\text{Sn}_4$ can exist in a layer-type morphology with the Pb-phase on one side and with the Ni_3Sn_4 layer on the other side, these experiments show that AuSn_4 cannot exist in a layer morphology with the newly formed $(\text{Cu,Ni})_6\text{Sn}_5$ layer. This study suggests that $(\text{Au,Ni})\text{Sn}_4$ has a lower interfacial energy with Ni_3Sn_4 , whereas AuSn_4 has a higher interfacial energy with $(\text{Cu,Ni})_6\text{Sn}_5$. However, both $(\text{Au,Ni})\text{Sn}_4$ and AuSn_4 have lower interfacial energies with Pb.

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