Suppressed Ni$_3$P Formation during Soldering Reaction between An Electroless Ni-Sn-P Metallization and Lead-free Sn-3.5Ag Solder

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The voids formed in the Ni$_3$P layer during reaction between Sn-based solders and Ni-P metallization is the main reason for the fast degradation of the solder joint. To suppress the formation of this layer, an electrolesslyplated Ni-Sn-P alloy was developed. After prolonged reaction, neither Ni$_3$P nor voids areformed at the reaction interface. The Ni-Sn-P metallization is consumed much slower than electroless Ni-P. The reason for the phase suppression and the overall interface reaction mechanisms were discussed.

**Keywords**: electroless Ni-Sn-P; lead-free solder; metallization; intermetallic compound; diffusion

Electrolesslyplated Ni-Phasbeen widely used as soldering metallization materials for the past several decades. Accordingly, the interfacial reactions between electroless Ni-P and Sn-containing solders, as well as the implications to long-term reliability, have been widely studied and well understood [1-9]. During soldering, reaction between Sn and Ni activates the transformation of amorphous Ni-P metallization into a layer of crystalline Ni$_3$P containing numerous voids [10]. The formation mechanism of such voids has been explained too [1]. Since the Ni$_3$P layer has a fine columnar structure [1, 10-12], diffusion of Ni throughthis layer is much faster, leading to the accelerated interfacial reaction. As a result of the fast reaction, voids nucleate and grow in the Ni$_3$P layer after prolonged reaction [1, 4-7, 12], contributing to the weakened interface and degraded reliability of the
solder joint. Therefore, in order to slow down the interfacial reaction with lead-free solders, it is necessary to avoid the formation, or suppress the growth of the fast diffusion path, the columnar Ni₃P layer. In a previous study, we developed an electroless Ni-W-P metallization which shows impressive slow-down of the interfacial reaction [13, 14]. During the Ni-W-P/Sn-3.5Ag interfacial reaction, neither Ni₃P layer nor voids were formed, so incorporation of a third element into electroless Ni-P has been proven as an effective approach to avoid the formation of Ni₃P layer during soldering reaction. According to the Ni-Sn-P phase diagram at 550 °C[15, 16], the formation of Ni₃P will be avoided when the Sn concentration is greater than ~10 wt.% (~5 at.%) when P content is around 6~7 wt.%. Instead, the composition falls into the region of (Ni + Ni₃Sn + Ni₁₂₁P₆Sn₂) at 550 °C [15]. Unfortunately the phase diagram for Ni-Sn-P is not available for lower temperatures below 550 °C due to a number of practical difficulties [17]. In such event, no thermodynamic data can be obtained at the solder reflow temperature around 260 °C. Nevertheless we could hypothesize that if the ternary phase (Ni₁₂₁P₆Sn₂) is stable at lower temperatures, the three-phase equilibrium (Ni + Ni₃Sn + Ni₁₂₁P₆Sn₂) could be maintained without the presence of Ni₃P. This principle is true, even if the three phases are not exact as what they are at 550 °C.

To test the above hypothesis, Ni-P alloy with incorporation of a high content of Sn was prepared for soldering reaction with Sn-3.5Ag. Interfacial reaction between Ni-Sn-P and Sn-3.5Ag solder after reflow and prolonged aging was studied. Electroless Ni-P was also studied under the same conditions for comparison.

Cu plates (6 mm thick, 99.98 wt.%) were used as substrate for electroless plating of both Ni-P and Ni-Sn-P. Prior to the Ni-P plating, the Cu surface was activated by using a commercial ruthenium-based pre-initiator. Electroless Ni-P plating was conducted in a commercial acidic sodium hypophosphite bath (from MacDermid) with a pH level of 5.3 at 88 ± 2 °C for 40 min. The deposited Ni-P layer contains 6~7 wt.% of P, and has a thickness of around 14 μm. Prior to the Ni-Sn-P plating, the Cu surface was activated by PdCl₂. Electroless Ni-Sn-P plating was performed in an alkaline bath with a pH level of 9.0 at 88 ± 2 °C for 30 min. The Ni-Sn-P plating bath contains nickel sulphate and sodium stannate as nickel and tin sources respectively, sodium hypophosphite as reducing agent.
along with complexing agents and buffering agents. The deposited Ni-Sn-P layer contains 6~7 wt.% of P and 19~21 wt.% of Sn, and has a thickness of around 12.1 μm.

The electrolessly coated Cu plates were joined by lead-free Sn-3.5Ag solder to form Ni-P/Sn-3.5Ag and Ni-Sn-P/Sn-3.5Ag solder joints. The reflow soldering process was conducted in a reflow oven with a peak temperature of 260 °C for 60 s, followed by solid-state aging at 200 °C for up to 200 h.

Fig. 1(a) shows the cross-sectional micrograph of the as-reflowed Ni-P/Sn-3.5Ag solder joint. Chunky-shaped Ni3Sn4 is the primary IMC formed at the joint interface, and some of them spalled into the bulk solder. The formation of Ni3Sn4 is due to the reaction between Sn from the solder and Ni from the Ni-P metallization. A dark layer of Ni3P formed within the top region of the Ni-P metallization, with a few voids present inside. The formation of these voids has been explained in previous study[1]. A very thin ternary Ni2SnP layer was also noticed to be present in between the Ni3Sn4 and Ni3P layers [6, 18]. Fig. 1(b) and 1(c) show the growth of various compounds at the Ni-P/Sn-3.5Ag interface after aging at 200 °C for 50 h and 200 h, respectively. The Ni3Sn4 layer grew much thicker upon aging, with some Ag3Sn particles accumulated inside. After aging for 50 h, the Ni-P metallization was fully consumed and transformed into Ni3P layer (Fig. 1(b)). The thickness of the Ni3P layer (~7.4 μm) is much smaller than that of the as-deposited Ni-P layer (~14 μm). Such shrinkage indicates that, Ni atoms diffuse out from Ni-P to form Ni3Sn4 during reflow and aging. After 200 h of aging, the thickness of the Ni3P layer (~5.8 μm) reduced by around 20% as compared to that after 50 h of aging (~7.4 μm), while the thickness of the Ni2SnP layer increased to around 3 times the one after 50 h of aging. This indicates that, once the Ni-P layer is fully consumed, the Ni2SnP layer grows rapidly at the expense of the Ni3P layer. There were only a few voids present in the Ni3P layer at the as-reflowed state (Fig. 1(a)); however, as the reaction proceeded upon aging, the voids in the Ni3P layer grew both in size and number (Fig. 1(b) and 1(c)). Interestingly, after the Ni-P metallization was fully consumed (Fig. 1(b) and 1(c)), instead of (Ni,Cu)3Sn4, only Ni3Sn4 formed and no voids were observed at the Cu/Ni3P interface, indicating that Cu atoms still remained in the substrate even after aging for 200 h.
For the as-reflowed Ni-Sn-P/Sn-3.5Ag solder joint, chunky-shaped Ni$_3$Sn$_4$ was formed (Fig. 1(d)). Unlike at the as-reflowed Ni-P/Sn-3.5Ag interface, there was neither Ni$_3$P layer nor voids formed at the as-reflowed Ni-Sn-P/Sn-3.5Ag interface. Thus, the hypothesis is confirmed that the formation of Ni$_3$P layer could be avoided through the design of the metallization composition. From Fig. 1(d), a thin layer of ternary Ni-Sn-P compound was also observed in between the Ni$_3$Sn$_4$ layer and the unconsumed Ni-Sn-P metallization. EDX result indicates that the newly-formed ternary Ni-Sn-P compound contains ~51 at.% Ni, ~34 at.% Sn and ~15 at.% P. It is a different type of IMC from the Ni$_2$SnP compound formed at the Ni-P/Sn-3.5Ag interface. Fig. 1(e) and 1(f) show the growth of various compounds at the Ni-Sn-P/Sn-3.5Ag interface after aging at 200 °C for 50 h and 200 h, respectively. Some Ag$_3$Sn particles were observed to accumulate inside the Ni$_3$Sn$_4$ layer. During prolonged aging, the growth of the Ni$_3$Sn$_4$ layer at the Ni-Sn-P/Sn-3.5Ag interface was much slower than that at the Ni-P/Sn-3.5Ag interface. After 50 h of aging, around 3.6 µm of the Ni-Sn-P metallization was consumed. As a comparison, the Ni-P metallization with an original thickness of around 14 µm was fully consumed after aging for 50 h (Fig. 1(b)). Even after 200 h of aging, only around 5.4 µm of the Ni-Sn-P metallization was consumed, indicating that the Ni-Sn-P metallization was consumed much slower than the Ni-P metallization. The significantly reduced consumption rate of the Ni-Sn-P metallization is consistent with the much reduced growth rate of the Ni$_3$Sn$_4$ layers compared to that at the Ni-P/Sn-3.5Ag interface. It is worth mentioning that no Ni$_3$P was observed at the Ni-Sn-P/Sn-3.5Ag interface with extended aging for up to 200 h (Fig. 1f), indicating that this phase is thermodynamically avoidable. Moreover, the growth of the Ni-Sn-P compound at the Ni-Sn-P/Sn-3.5Ag interface was negligible during aging.

The crystal structure of the newly-formed Ni-Sn-P compound at the Ni-Sn-P/Sn-3.5Ag interface was identified using electron diffraction under TEM. The cross-section sample was prepared by focused ion beam (FIB). Fig. 2 shows the TEM micrograph of the FIB sample and the diffraction pattern from the Ni-Sn-P compound. The diffraction analysis from this compound shows a typical ring pattern representing poly-crystallites within the diffraction region. By using diffraction pattern matching software (JEMS), combined with the composition result from EDX as a reference, the new phase was
identified as Ni$_{13}$Sn$_8$P$_3$ having a triclinic lattice (P1, a = 6.456 Å, b = 21.291 Å, c = 13.247 Å, $\alpha$ = 81.052°, $\beta$ = 56.260°, $\gamma$ = 68.221°)[19].

Only two interfacial compounds, Ni$_3$Sn$_4$ and Ni$_{13}$Sn$_8$P$_3$, are formed during the Ni-Sn-P/Sn-3.5Ag interfacial reaction. Since the Ni-Sn-P metallization itself contains both Ni and Sn, in order to determine whether the formation of Ni$_3$Sn$_4$ is caused by the soldering reaction between Sn from the solder and Ni from the metallization or the reaction between the existing Ni and Sn within the metallization at the reflow temperature, XRD was conducted on the as-deposited Ni-Sn-P after annealing at 260 ºC (the same as the reflow temperature). Fig. 3 shows XRD patterns of the Ni-Sn-P deposit before and after annealing at 260 ºC for 2 h. The XRD spectra were recorded between 2-theta from 30° to 80° with a fixed glancing angle of 2°. It was observed that the pattern for the as-deposited Ni-Sn-P consisted of only one broad peak with highest intensity belonging to Ni; hence, the as-deposited Ni-Sn-P had an amorphous structure. After annealing at 260 ºC for 2 h, no peaks from Ni$_3$Sn$_4$ were present in the pattern, so the Ni-Sn-P deposit still had an amorphous structure, proving that the formation of Ni$_3$Sn$_4$ cannot occur by the reaction between the Sn and Ni composition within the Ni-Sn-P metallization itself. Therefore, the formation of Ni$_3$Sn$_4$ is caused by the reaction between the Sn atoms diffusing out from the solder and the Ni atoms diffusing out from the metallization during soldering between Ni-Sn-P and Sn-3.5Ag. Meanwhile, the continuous formation of Ni$_3$Sn$_4$ during soldering reaction leads to the depletion of Ni from the surface of the Ni-Sn-P metallization.

The Ni$_{13}$Sn$_8$P$_3$ compound has not been reported in any soldering systems, and this compound thickens as reaction proceeds. Here we propose a diffusional formation mechanism based on several observations in this work. From the literatures, it has been proven that there is no out-diffusion of P atoms from the Ni-P metallization during soldering reaction. In this work, the P atoms in the Ni-Sn-P metallization are also believed to remain in the metallization layer during soldering reaction. This is probably best confirmed by comparing the compositions of the as-deposited Ni-Sn-P layer (77 at.% Ni, 10 at.% Sn and 13 at.% P) and the newly-formed Ni$_{13}$Sn$_8$P$_3$ layer (54 at.% Ni, 33 at.% Sn and 13 at.% P). Since both layers have the same P concentration, it is most likely that the Ni-Sn-P deposit is transformed into the Ni$_{13}$Sn$_8$P$_3$ compound during soldering
reaction. As the Ni and Sn concentrations in the two neighboring layers are different, we need to explain the diffusion paths for these two elements during the solder reaction.

The formation of Ni$_3$Sn$_4$ causes depletion of Ni from the surface of the Ni-Sn-P layer, so the top region of the Ni-Sn-P layer is transformed into a phase with lower Ni concentration, which is in agreement with the fact that the Ni$_{13}$Sn$_8$P$_3$ compound has a lower Ni content than the Ni-Sn-P metallization. Since the Ni$_{13}$Sn$_8$P$_3$ compound has a higher Sn content than the Ni-Sn-P deposit, it is speculated that the transformation of the Ni-Sn-P deposit into the Ni$_{13}$Sn$_8$P$_3$ compound requires Sn supply from the solder, which is similar to the formation of the Ni$_2$SnP compound during the Ni-P/Sn-3.5Ag interfacial reaction [6, 20-23]. Based on the above arguments, we believe that the polycrystalline Ni$_{13}$Sn$_8$P$_3$ compound is formed by transforming the amorphous Ni-Sn-P metallization with the aid of outward diffusion of Ni and inward diffusion of Sn during the soldering reaction.

Fig. 3 schematically illustrates the diffusional formation mechanism of IMCs at the Ni-Sn-P/Sn-3.5Ag interface. The Sn atoms diffusing out from the solder react with the Ni atoms from the Ni-Sn-P metallization to form the Ni$_3$Sn$_4$ compound. Meanwhile, the top region of the Ni-Sn-P metallization becomes Ni-depleted due to the out-diffusion of Ni to form Ni$_3$Sn$_4$. Since Sn is the faster diffusant in Ni$_3$Sn$_4$[24], some Sn atoms will also reach the Ni$_3$Sn$_4$/Ni-Sn-P interface to form the Ni$_{13}$Sn$_8$P$_3$ compound. The continued growth of Ni$_3$Sn$_4$ requires Ni supply from the Ni-Sn-P layer, so Ni atoms have to diffuse through the formed Ni$_{13}$Sn$_8$P$_3$ layer to react with the Sn atoms from the solder. The much reduced growth rate of Ni$_3$Sn$_4$ indicates that the Ni$_{13}$Sn$_8$P$_3$ layer acts as an effective barrier for Ni diffusion.

As highlighted above, the formation of the Ni$_3$P layer should be avoided to slow down the interfacial reaction. The current work to choose an electroless Ni-Sn-P alloy as the metallization material for lead-free soldering is based on the limited thermodynamic data with reasonable assumption that the formation of Ni$_3$P layer could be avoided altogether when the Sn concentration is high enough. Indeed, in the current work with Ni-Sn-P metallization, the formation of Ni$_3$P has been successfully avoided, and no voids were observed at the Ni-Sn-P/Sn-3.5Ag interface even after prolonged reaction.
In this study, an electrolessly plated Ni-Sn-P alloy (6~7 wt.% of P and 19~21 wt.% of Sn) has been developed as an alternative Ni-based metallization for lead-free soldering. Interfacial reaction between Sn-3.5Ag solder and electroless Ni-Sn-P after reflow and aging was investigated, with interfacial reaction between the same solder and electroless Ni-P (6~7 wt.% of P) under the same reflow and aging conditions as a benchmark. Only two intermetallic compounds, Ni₃Sn₄ and Ni₁₅Sn₈P₃, are formed during the Ni-Sn-P/Sn-3.5Ag interfacial reaction. The Sn atoms from the solder react with the Ni atoms from the Ni-Sn-P metallization to form Ni₃Sn₄, and as a result, the top surface of the metallization layer becomes Ni-depleted. The Sn atoms from the solder also diffuse through the formed Ni₃Sn₄ layer to reach the Ni₃Sn₄/Ni-Sn-P interface, and react with the Ni-depleted region of the Ni-Sn-P layer to form the second IMC-Ni₁₅Sn₈P₃. With successful elimination of the fast diffusion path, which is the columnar Ni₃P layer, the Ni-Sn-P metallization was consumed much slower than the Ni-P metallization. Therefore, electroless Ni-Sn-P alloy with a high Sn content is a promising metallization material for lead-free soldering.

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References

Figure captions

Fig. 1. Back-scattered SEM images showing IMCs formed in (a) as-reflowed Ni-P/Sn-3.5Ag solder joint, (b) Ni-P/Sn-3.5Ag solder joint after aging at 200 °C for 50 h, (c) Ni-P/Sn-3.5Ag solder joint after aging at 200 °C for 200 h, (d) as-reflowed Ni-Sn-P/Sn-3.5Ag solder joint, (e) Ni-Sn-P/Sn-3.5Ag solder joint after aging at 200 °C for 50 h, and (f) Ni-Sn-P/Sn-3.5Ag solder joint after aging at 200 °C for 200 h.

Fig. 2. (a) TEM micrograph showing the Ni-Sn-P/Sn-3.5Ag interfaces, and (b) the diffraction pattern from the ternary Ni-Sn-P compound region indicating its crystal structure is Ni$_{13}$Sn$_8$P$_3$.

Fig. 3. XRD patterns of the Ni-Sn-P coating before and after annealing at 260 °C for 2 h.

Fig. 4. A schematic illustration of the diffusional formation mechanisms of IMCs at the Ni-Sn-P/Sn-3.5Ag interface.
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