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Interface Reaction between An Electroless Ni-Co-P Metallization and Sn-3.5Ag Lead-free Solder with Improved Joint Reliability

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Abstract

To address the reliability challenges brought by the accelerated reaction with the implementation of lead-free solders, an electrolessly plated Ni-Co-P alloy (3~4 wt.% P and 9~12 wt.% Co) was developed as the solder metallization in this study. Three compounds layers, $(\text{Ni,Co})_3\text{Sn}_4$, $(\text{Ni,Co})_3\text{P}$ and $(\text{Ni,Co})_{12}\text{P}_5$ are formed at the reaction interface. Nano-sized voids are visible in the $(\text{Ni,Co})_3\text{P}$ layer under TEM, but no large voids are found under SEM. This is an indication of effective diffusion barrier performance by the Ni-Co-P metallization than the binary Ni-P metallization. The influence of interfacial reaction on the solder joint reliability was reported through the evaluation of the tensile strength of micro solder joints. Upon aging at 180 °C for 600 h, the tensile strength of Ni-Co-P/Sn-3.5Ag solder joint remains high, and the failure is caused by the bulk solder necking and collapse. As a comparison, the tensile strength of Ni-P/Sn-3.5Ag solder joint drops significantly after aging for 400 h at 180 °C, and the fracture mode has shifted from ductile failure in the bulk solder to the brittle failure at the solder joint interface. The Ni-Co-P metallization, having a much slower consumption rate and improved resistance to joint strength degradation during long-term aging treatment, is a potential candidate for future microelectronic solder metallization materials.

Keywords: Electroless Ni-Co-P; Soldering; Intermetallic compounds; Diffusion; Tensile strength

1. Introduction

Cu was previously the most popular choice as the metallization for solder joining due to its excellent conductivity and good wetting performance with liquid solders [1]. However, with the

implementation of lead-free solders since July 1st 2006, new challenges for the long-term reliability of solder joints have been encountered by the industry, as commonly used lead-free solders react much faster with Cu metallization than eutectic Sn-Pb solder. This is because lead-free solders have higher Sn content and higher melting temperatures than eutectic Sn-Pb solder. Thus the reaction between Cu and lead-free solders are much faster than that between Cu and eutectic Sn-Pb solder. Cu will be completely consumed by lead-free solders quickly, leaving only intermetallic compounds (IMCs) at the interface. This would result in the degradation of mechanical strength of the solder joint [2-4]. Therefore it is well understood that Cu-based metallizations are not suitable for lead-free soldering.

Ni and Ni alloys were reported to have a much slower reaction rate with Sn as compared with Cu and Cu alloys [1, 5]. Thus over the years, Ni-based metallizations have received great attention in lead-free soldering. Among Ni-based metallizations, electrolessly plated Ni-P has been widely used for the past several decades because of its excellent uniformity, mask-less selective process, low residual stress, good solderability, and low processing cost. Accordingly, the interfacial reactions between electroless Ni-P and Sn-containing solders, along with the implication to long-term solder joint reliability, have been well studied [6-15]. During soldering with electroless Ni-P, reaction between Sn and Ni activates the transformation of amorphous Ni-P metallization into a layer of crystalline Ni₃P [16]. Since this layer has a fine columnar structure [6, 16, 17], the grain boundaries of this layer become the fast diffusion path for Ni diffusion, leading to accelerated interfacial reaction. As a result of the fast reaction, micro-sized voids are observed in the Ni₃P layer after prolonged reaction [6, 13, 17], 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 suppress the growth of the fast

diffusion path, which is the void-containing Ni_3P layer formed during soldering reaction with Ni-P metallization.

In previous studies, we have shown that incorporation of a ternary element into Ni-P can be an effective way to slow down the interface reaction by either preventing the crystallization of Ni_3P by incorporating W [18, 19] or completely avoiding the formation of Ni_3P by the addition of Sn into Ni-P [20]. In this study, we explore an electrolessly plated Ni-Co-P alloy as solder metallization. There have been some reports showing positive diffusion barrier performance using Co-containing metallizations for lead-free soldering [21-23]. Similar to Ni, Co is also reactive with Sn, and based on the Co-Sn phase diagram [24], a few IMCs may form between Co and Sn. However, Ni-Co-P phase diagram is not available. In other studies, it was reported that Ni-Co-P alloys can be a better protective coating than Ni-P due to their improved corrosion resistance and thermal stability [25,26]. Ni-Co-P alloys were also explored as the plug contact on the silicide transistor gate [27]. In the early 1990s, Ni-Co-P alloy deposit was first investigated as a diffusion barrier between an Al pad and a high-lead solder bump (95Pb-5Sn) [28]. In recent years, the electrolessly plated Ni-Co-P alloys was also investigated as the diffusion barrier layer in the ultra large-scale integration (ULSI) technology [26,29,30]. Interfacial reaction between lead-free solder and Ni-Co-P plating was reported by Daito et al. [31]. However, their 2-page report mainly looked into wetting spread area comparison among Ni-P, Co-P, and Ni-Co-P. No information on the chemical composition of the Ni-Co-P plating was available; neither were there any IMC phase identification and solder joint reliability.

The objective of this work is to study the interfacial reaction and tensile strength of solder joints between lead-free Sn-3.5Ag solder and electroless Ni-Co-P metallization after reflow and prolonged aging. Attention is laid on the interfacial IMC formation mechanism and how the

reaction affects the solder joint strength. To reveal the advantage of such a ternary alloy, a commercially available binary electroless Ni-P alloy was also investigated for comparison. Fractographic analysis on both types of failed solder joints was conducted to assist the understanding of the joint strength degradation.

2. Experimental procedures

2.1. Metallization preparation

Cu plates (99.98 wt.%) with a thickness of 6 mm were used as substrate for electroless plating of both Ni-P and Ni-Co-P. Prior to plating, the Cu plates were mechanically polished and then chemically etched with 35 vol.% nitric acid for 30 s. After that, the Cu surface was activated 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 30 mins. The obtained Ni-P coating contains 6~7 wt.% P and has a thickness of 9.7 µm. On the other hand, the electroless Ni-Co-P plating was carried out in an alkaline bath with a pH level of 10.0 at 88 ± 2 °C for 1 h. As listed in Table 1, this alkaline bath contained nickel chloride and cobalt chloride as nickel and cobalt sources, respectively. Sodium hypophosphite was used as a reducing agent along with sodium citrate, lactic acid and ammonium chloride as the complexing agents. The obtained Ni-Co-P coating contains 3~4 wt.% P and 9~12 wt.% Co, with a thickness of 9.9 µm.

2.2. Reflow and aging process

The electrolessly coated Cu plates were joined by Sn-3.5Ag solder to form Ni-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints. A thin layer of no-clean paste flux was first applied on top of the plated surface of Cu to remove the surface oxides, and then small pieces of Sn-3.5Ag solder wires with flux in core were orderly arranged on the plated surface. Alumina spacers with a thickness of around 650 μm were used to maintain a fixed and uniform thickness of solder layer in between the two joined Cu plates. The reflow soldering process was conducted in an IR reflow oven involving an initial preheating at 190 $^{\circ}\text{C}$ for 100 s, followed by reflowing at a peak temperature of 260 $^{\circ}\text{C}$ for 60 s, before finally cooling down to 120 $^{\circ}\text{C}$. After that, both types of as-reflowed solder joints were aged at 180 $^{\circ}\text{C}$ for up to 600 h to study their interfacial reactions and tensile strength upon aging.

2.3. Tensile test

Tensile test was performed using INSTRON 5567 tensile tester. Both types of solder joints were cut using a diamond cutter along the Cu plate thickness direction into micro-joints with cross-sectional dimensions around 650 $\mu\text{m} \times 650 \mu\text{m}$. Five to ten micro-joints from each reflow or aging conditions were tested to obtain the average tensile strength. The tensile test was performed with a constant crosshead speed of 0.05 mm/min to a complete fracture at room temperature.

2.4. Microstructural observation

The interfacial microstructures of both types of solder joints after reflow and prolonged aging were observed under scanning electron microscope (SEM), along with the fractured

surface of the failed solder joints under tensile test. The compositions of the interfacial compounds formed in the solder joints were analyzed using energy dispersive X-ray (EDX) incorporated in the SEM. For the cross-sectional SEM study, the samples were mounted into an epoxy mould and then mechanically grounded with SiC abrasive papers, followed by polishing with diamond pastes to a 1 μm finish. After polishing, the samples were chemical etched with 4 vol.% hydrochloride acid to reveal the microstructure. The crystal structure of the interfacial compounds during Ni-P/Sn-3.5Ag reaction has been well understood [6, 15], but the compound layers at the Ni-Co-P/Sn-3.5Ag reaction interface have clearly different compositions. Their crystal structure was identified using electron diffraction under transmission electron microscope (TEM) in the current work.

3. Results and discussion

3.1. Interfacial microstructure analysis of as-reflowed solder joints

Fig. 1(a) shows the cross-sectional micrograph of the as-reflowed Ni-P/Sn-3.5Ag solder joint. Chunky-shaped Ni_3Sn_4 is the primary IMC formed at the joint interface, and some of them have spalled into the bulk solder. The formation of Ni_3Sn_4 is due to the reaction between Sn from the solder and Ni from the Ni-P metallization. A dark layer of Ni_3P 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 [6]. A very thin ternary Ni_2SnP layer was also noticed to form in between the Ni_3Sn_4 and Ni_3P layers [10, 15].

The cross-sectional micrograph of the as-reflowed Ni-Co-P/Sn-3.5Ag solder joint is shown in Fig. 1(b). It was observed that a layer of Ni-Co-Sn compound is clearly present. Its identification will be shown later to be $(\text{Ni},\text{Co})_3\text{Sn}_4$. Unlike the case in the Ni-P/Sn-3.5Ag

reaction (Fig. 1(a)), there was no significant spallation of this $(\text{Ni,Co})_3\text{Sn}_4$ compound into the bulk solder. Underneath this layer, two unknown thinner layers were observed, one is grey and the other one is dark in colour. The grey layer partially spalled into the $(\text{Ni,Co})_3\text{Sn}_4$ layer.

3.2. Interfacial microstructure analysis of aged solder joints

Fig. 2 shows the growth of various compounds at the Ni-P/Sn-3.5Ag interface aged at 180 °C for up to 600 h. The Ni_3Sn_4 layer grew much thicker during prolonged aging, and some Ag_3Sn particles accumulated inside this layer. From Fig. 2(c), the deposited Ni-P layer was seen to be fully consumed and transformed into Ni_3P layer after 300 h of aging. The thickness of the Ni_3P layer after 300 h of aging ($\sim 4.9 \mu\text{m}$) is much smaller than that of the as-deposited Ni-P layer ($\sim 9.7 \mu\text{m}$). Such shrinkage indicates that Ni atoms have diffused out from Ni-P to form Ni_3Sn_4 during reflow and aging. It was noted that after 600 h of aging (Fig. 2(f)), the thickness of the Ni_3P layer ($\sim 4.4 \mu\text{m}$) is reduced by about 10% as compared to that after 300 h of aging ($\sim 4.9 \mu\text{m}$), while the thickness of the Ni_2SnP layer ($\sim 0.34 \mu\text{m}$) increased by about 17% as compared to that after 300 h of aging ($\sim 0.29 \mu\text{m}$). This indicates that, once the Ni-P layer is fully consumed, the Ni_2SnP layer grows at the expense of the Ni_3P layer. As the reaction proceeded upon aging, the voids in the Ni_3P layer grew both in size and number (Fig. 2).

The microstructure at the Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for up to 600 h is shown in Fig. 3. It was found that during aging, the unknown dark and grey layers grew very slowly. The thickness increase of the top $(\text{Ni,Co})_3\text{Sn}_4$ IMC layer was much slower than that of the Ni_3Sn_4 layer formed at the Ni-P/Sn-3.5Ag interface (Fig. 2). Unlike the Ni-P metallization, of which the original thickness of $9.7 \mu\text{m}$ was fully consumed after 300 h of aging, only $3.4 \mu\text{m}$ of the Ni-Co-P metallization was reacted away after 600 h of aging (Fig. 3(f)). Fig. 4 shows the

consumed thickness of Ni-P and Ni-Co-P metallizations upon aging for up to 600 h. The consumption rate of the Ni-Co-P layer is much slower than that of the Ni-P. The magnified image of the Ni-Co-P/Sn-3.5Ag interface aged at 180 °C for 600 h is displayed in Fig. 5. It was observed that the thicknesses of the unknown dark and grey layers are less than 1 µm after 600 h of aging. Moreover, it was noted that after 600 h, no voids were found in the Ni-Co-P/Sn-3.5Ag solder joint under SEM (Fig. 3(f) and Fig. 5).

From the EDX elemental mapping of the Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for 600 h (Fig. 6), it was found that the unknown dark and grey layers both consisted of Ni, Co and P elements. The composition of the unknown dark layer was measured to contain 58.9 at.% Ni, 16.2 at.% Co, and 24.9 at.% P by EDX. This composition is suggestive of (Ni,Co)₃P compound. On the other hand, the composition of the unknown grey layer was 47.4 at.% Ni, 22.1 at.% Co, and 30.5 at.% P by EDX. Such composition is suggestive of either (Ni,Co)₅P₂ or (Ni,Co)₁₂P₅ compound. For the top Ni-Co-Sn ternary compound, its composition was measured to be 41.3 at.% Ni, 3.6 at.% Co, and 55.1 at.% Sn by EDX, which is close to (Ni,Co)₃Sn₄ stoichiometry. However, the quantitative composition results from EDX are probably not very accurate, especially for the quantification of the two thin Ni-Co-P layers. Therefore electron diffraction analysis under TEM was also conducted to further identify the interfacial IMCs formed at the Ni-Co-P/Sn-3.5Ag interface. It was also observed in Fig. 5 that the grey IMC layer has partially spalled away, resulting in two grey layers (see also in Fig. 1(b) and Fig. 3). This is believed to be due to the compressive stress generated by the volume change between the reacting materials and resulting compound layer [32-34].

The TEM sample was prepared by focused ion beam (FIB) technique from the Ni-Co-P/Sn-3.5Ag solder joint aged at 180 °C for 600 h. Fig. 7 shows the TEM micrograph of the FIB

sample and the diffraction patterns from all interfacial layers formed at the Ni-Co-P/Sn-3.5Ag interface. Layer A in Fig. 7(a) is the unknown dark layer, whose diffraction pattern is given in Fig. 7(b). The diffraction analysis from this layer indicates a ring pattern of the polycrystalline tetragonal structure similar to Ni_3P . In conjunction with the composition analysis by EDX, this dark layer should be $(\text{Ni},\text{Co})_3\text{P}$, where Co is dissolved into the Ni sublattice. Moreover, it was noted that nano-sized voids formed inside the $(\text{Ni},\text{Co})_3\text{P}$ layer (Fig 7(a)). The formation of these voids is believed to be caused by the out-diffusion of Ni and Co atoms. Layer B in Fig. 7(a) is the unknown grey layer, whose diffraction pattern is given in Fig. 7(c). The diffraction analysis from this layer indicates a ring pattern of the polycrystalline tetragonal structure similar to Ni_{12}P_5 . In conjunction with the composition result from EDX, the unknown grey layer is identified to be $(\text{Ni},\text{Co})_{12}\text{P}_5$, where Co is dissolved into the Ni sublattice. Layer C in Fig. 7(a) is the Ni-Co-Sn layer, whose diffraction pattern is given in Fig. 7(d). The diffraction analysis from this layer indicates a superlattice pattern of Ni_3Sn_4 , with a series of sharp satellite spots around the fundamental Bragg spots. In conjunction with the composition result from EDX, the Ni-Co-Sn layer is confirmed to be $(\text{Ni},\text{Co})_3\text{Sn}_4$, where Co is dissolved into the Ni sublattice.

3.3. Tensile strength of solder joints

The average tensile strengths of the as-reflowed Ni-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints were 35.41 MPa and 36.26 MPa, respectively. Fig. 8 depicts the tensile strength variation with aging time for both types of solder joints for up to 600 h. The strength values with standard errors based on the 5-10 test samples for each condition are also listed in Table 2. Both types of solder joints had similar tensile strength at the as-reflowed condition. There was no significant drop in the strength of Ni-Co-P/Sn-3.5Ag solder joints upon aging for 600 h, while

the strength of Ni-P/Sn-3.5Ag solder joints decreased significantly after aging for 400 h and beyond. Therefore, solder joint with Ni-Co-P metallization is more resistant to joint strength degradation than that with Ni-P metallization during long-term aging.

3.4. Failure analysis of solder joints

The fractographic analysis of both types of solder joints were conducted under SEM to study the fracture mechanism in tensile testing upon aging. Figs. 9(a) and (b) show the cross-sectional view and fractured surface of the as-reflowed Ni-P/Sn-3.5Ag solder joints, respectively. An obvious necking occurred in the bulk solder, and the fracture surface inclined at about 45 ° to the tensile loading axis (Fig. 9(a)). Fig. 9(b) shows the fractured surface of this solder joint, and the EDX result indicates that Sn was the dominant element at the fractured surface, confirming that the fracture occurs completely in the bulk solder.

Fig. 10 shows that Ni-P/Sn-3.5Ag solder joints still experienced complete ductile failure inside the bulk solder after aging at 180 °C for up to 300 h. The entire fracture path is inside the bulk solder, similar to the as-reflowed sample. This indicates that the cohesive strength of the bulk solder is weaker than the solder interface.

However, as shown in Fig. 11, in the Ni-P/Sn-3.5Ag solder joints aged at 180 °C for 400 h and 600 h, the failure occurred completely at the solder interface. As shown in Figs. 11(a) and (c), the entire fracture path in both samples was quite flat, indicating macroscopic brittle behaviour after prolonged aging. On the fractured surfaces of the solder joints aged for 400 h and 600 h, SEM morphological observation and EDX compositional analysis both indicate the presence of Ni_3Sn_4 and solder materials, revealing that the brittle fracture occurred at the Ni_3Sn_4 /Sn-3.5Ag interface. This means that in the Ni-P/Sn-3.5Ag solder joints after aging for 400 h and beyond,

the adhesion between the Ni_3Sn_4 IMC and the solder becomes the weakest link. The weakening of the Ni_3Sn_4 /solder interface is believed to be attributed to the stress originated by the volume mismatch between the Ni_3Sn_4 IMC and the solder, and such stress increases with growth of the Ni_3Sn_4 layer [14]. Besides, as shown in Fig. 2, upon aging for a longer duration, the Ni_3Sn_4 /solder interface became more flat due to the tendency of reducing the interface area. The smoothed Ni_3Sn_4 /solder interface loses the mechanical interlocking as compared with the uneven Ni_3Sn_4 /solder interface in the as-reflowed solder joints and the solder joints undergoing shorter aging durations [14]. Thus, such flattened Ni_3Sn_4 /solder interface could be a contributing factor towards the shift of failure path from inside the bulk solder to the Ni_3Sn_4 /solder interface. It was noted that the voids in the Ni_3P layer grew both in number and size upon aging (Fig. 2), and the presence of voids should in theory weaken the Ni_3P layer itself. However, the Ni_3P layer was not observed to be the weakest connection at the entire joint interface region, probably because other locations degrade much faster than the Ni_3P layer. However, the interface weakening could still be attributed to the voids in the Ni_3P layer, which has accelerated the interface reaction.

As shown in Fig. 12(a), an obvious necking occurred in the bulk solder in the as-reflowed Ni-Co-P/Sn-3.5Ag solder joints, and the fracture surface inclined at about 45° to the tensile loading axis. Fig. 12(b) shows the fractured surface of this solder joint, and Sn was found to be the dominant element at the fractured surface by EDX analysis, thus the fracture occurred completely in the bulk solder.

Fig. 13 shows that the Ni-Co-P/Sn-3.5Ag solder joints still experienced complete ductile failure inside the bulk solder after aging at 180°C for up to 600 h. This means there is no serious degradation in the interface region after such a prolonged reaction. As a comparison, in the Ni-

P/Sn-3.5Ag solder joints, the fracture path shifted from the bulk solder to the Ni_3Sn_4 /solder interface after aging for 400 h (Fig. 11).

3.5. Diffusional formation mechanism of IMCs at the Ni-Co-P/solder interface

From the area mapping result of the Ni-Co-P/Sn-3.5Ag interface aged at 180 °C for 600 h (Fig. 6), it was clearly seen that P atoms remain in the $(\text{Ni,Co})_{12}\text{P}_5$ and $(\text{Ni,Co})_3\text{P}$ layers. In contrast, Ni and Co atoms both diffuse out from the Ni-Co-P metallization layer to form $(\text{Ni,Co})_3\text{Sn}_4$. The signal from Sn was observed to terminate at the $(\text{Ni,Co})_3\text{Sn}_4/(\text{Ni,Co})_{12}\text{P}_5$ interface, and such signal was undetected in the $(\text{Ni,Co})_{12}\text{P}_5$ layer, indicating that Sn atoms did not diffuse through the $(\text{Ni,Co})_{12}\text{P}_5$ layer. It was also noticed that after such a prolonged reaction, Cu atoms still remained in the substrate as neither $(\text{Cu,Ni})_6\text{Sn}_5$ nor $(\text{Ni,Cu})_3\text{Sn}_4$ compounds were detected. This suggests that Ni-Co-P is an effective barrier to prevent the inter-diffusion between Cu and Sn.

Fig. 14 schematically illustrates the diffusional formation mechanism of the interfacial IMCs at the Ni-Co-P/Sn-3.5Ag interface. Based on the elemental analysis, P atoms in the Ni-Co-P remain in the metallization layer during interfacial reaction. The continuous growth of the $(\text{Ni,Co})_3\text{P}$ IMC attracts Ni and Co atoms to diffuse out from the Ni-Co-P metallization layer. The depletion of Ni and Co from the surface of the Ni-Co-P metallization leads to the formation of $(\text{Ni,Co})_3\text{P}$ compound which has been explained before as the “solder reaction-assisted crystallization” [16]. In this case, instead of forming the Ni_3P -type compound alone, Ni_{12}P_5 -type compound also forms, and due to the presence of Co, the compound takes the form of $(\text{Ni,Co})_{12}\text{P}_5$. It is believed that $(\text{Ni,Co})_3\text{P}$ forms at the beginning of the reaction, and as a

consequence of the continued out-diffusion of Ni and Co atoms from this layer, part of this layer is transformed to $(\text{Ni,Co})_{12}\text{P}_5$.

According to the Ni-P phase diagram [35], it is understood that all three types of compounds, namely Ni_3P , Ni_5P_2 and Ni_{12}P_5 , are thermodynamically stable. After Ni_3P , the next phase to be formed should be Ni_5P_2 in a continuously varied composition profile, as it is the second P-rich phase. However, in our experiment, $(\text{Ni,Co})_5\text{P}_2$ compound was not detected. Duh's group reported that with further reaction at the Ni-P/Sn-3Ag-0.5Cu interface, Ni_3P would transform to Ni_{12}P_5 which is the third P-rich phase in the Ni-P phase diagram, whereas the formation of Ni_5P_2 was hindered [36-39]. Since both Ni_{12}P_5 and Ni_3P have the same tetragonal crystal structure, while Ni_5P_2 has a hexagonal structure [40], it was argued that the transformation of Ni_3P to Ni_{12}P_5 is attributed to their similarity in crystal structure [37,39]. The formation of Ni-Co-P compounds, which is due to the dissolution of Co atoms into the Ni sublattice of the Ni-P compounds, does not alter the original crystal structures of the Ni-P compounds because Ni and Co have very similar atomic radius. The same argument for Ni-P compounds should apply for the three types of Ni-Co-P compounds in the current study. As a result, with further reaction at the Ni-Co-P/Sn-3.5Ag interface, $(\text{Ni,Co})_3\text{P}$ transforms to $(\text{Ni,Co})_{12}\text{P}_5$ due to their similarity in crystal structure, while the formation of $(\text{Ni,Co})_5\text{P}_2$ is hindered.

At the Ni-P/Sn-3.5Ag interface, micro-sized voids were observed inside the Ni_3P layer under SEM observation (Fig. 2). In contrast, at the Ni-Co-P/Sn-3.5Ag interface, no voids were observed under SEM. However, nano-sized voids were observed inside the $(\text{Ni,Co})_3\text{P}$ layer at the Ni-Co-P/Sn-3.5Ag interface under TEM (Fig 7(a)). The fine columnar structure of the Ni_3P layer makes it a fast diffusion path for Ni atoms during the Ni-P/Sn-3.5Ag interfacial reaction [6].

Consequently, when the net Ni flux diffuses out from the Ni-P layer to form Ni_3Sn_4 , the accumulation of lattice vacancies in the Ni_3P layer would lead to accelerated nucleation and growth of voids to micro-size after prolonged reaction. Unlike the Ni_3P layer formed at the Ni-P/Sn-3.5Ag interface, the $(\text{Ni},\text{Co})_3\text{P}$ layer formed at the Ni-Co-P/Sn-3.5Ag interface does not display a columnar structure, and this could be due to the overall slow interface reaction. Co is generally less reactive with Sn to form Co-Sn IMC, as it has a less negative free enthalpy of formation than Ni. For example, $\Delta H_f(\text{Co}_3\text{Sn}_2) = -10 \text{ kJ/mol}$ and $\Delta H_f(\text{Ni}_3\text{Sn}_2) = -33 \text{ kJ/mol}$ [22]. Therefore the incorporation of Co slows down the formation of $(\text{Ni},\text{Co})_3\text{Sn}_4$ as compared with the formation of Ni_3Sn_4 when no Co is present. Since Ni_3P formation is directly correlated with Ni_3Sn_4 IMC formation (as a result of the solder reaction induced crystallization), the presence of Co has resulted in slow growth rate for all the interface compounds. As a consequence, a much reduced metallization consumption rate was observed, and the void growth inside the $(\text{Ni},\text{Co})_3\text{P}$ layer have to take a much longer time.

4. Conclusions

In this work, an electrolessly plated Ni-Co-P alloy (3~4 wt.% P and 9~12 wt.% Co) was developed as an alternative Ni-based metallization for lead-free soldering. The interfacial reaction and tensile strength of solder joints between Sn-3.5Ag solder and electroless Ni-Co-P metallization after reflow and prolonged aging were investigated. With the comparison with electroless Ni-P metallization (6~7 wt.% P), the following conclusions are made based on the investigation:

1. Three types of compounds, $(\text{Ni},\text{Co})_3\text{Sn}_4$, $(\text{Ni},\text{Co})_3\text{P}$ and $(\text{Ni},\text{Co})_{12}\text{P}_5$, are formed during the Ni-Co-P/Sn-3.5Ag interfacial reaction.

2. During soldering reaction, the consumption of the Ni-Co-P metallization layer was greatly reduced compared with Ni-P, making the Ni-Co-P layer a promising candidate as the diffusion barrier for lead-free soldering.
3. The as-reflowed Ni-Co-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints had comparable tensile strength. The strength of Ni-P/Sn-3.5Ag solder joints decreased significantly after 400 h of aging while the strength of Ni-CoP/Sn-3.5Ag solder joints remained high after 600 h of aging. Therefore, the long-term reliability of solder joints with Ni-Co-P metallization is significantly improved as compared with solder joints with Ni-P metallization.

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Table Captions

Table 1. Composition of the plating bath for electroless Ni-Co-P.

Table 2. Tensile strengths of Ni-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints upon aging at 180 °C for up to 600 h.

Table 1. Composition of the plating bath for electroless Ni-Co-P.

Components of plating bath	Concentration
NiCl ₂	10 g/L
CoCl ₂	4 g/L
NaH ₂ PO ₂ · H ₂ O	16 g/L
Na ₃ C ₆ H ₅ O ₇ · 2H ₂ O	40 g/L
NH ₄ Cl	30 g/L
Lactic acid	4.5 ml/L

Table 2. Tensile strengths of Ni-P/Sn-3.5Ag and Ni-Co-P/Sn-3.5Ag solder joints upon aging at 180 °C for up to 600 h.

Aging Time (hour)	Tensile Strength (MPa)	
	Ni-P/Solder Joint	Ni-Co-P/Solder Joint
0 (as-reflowed)	35.41 ± 2.85	36.26 ± 1.12
100	32.75 ± 1.38	33.64 ± 1.39
200	31.75 ± 1.36	33.51 ± 1.07
300	31.32 ± 0.43	33.99 ± 0.71
400	22.69 ± 1.36	33.64 ± 0.93
600	22.46 ± 0.99	33.52 ± 1.27

Figure Captions

Fig. 1. Back-scattered SEM images showing IMCs formed in (a) as-reflowed Ni-P/Sn-3.5Ag solder joint and (b) as-reflowed Ni-Co-P/Sn-3.5Ag solder joint.

Fig. 2. Back-scattered SEM images showing IMCs at the Ni-P/Sn-3.5Ag interface after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, (e) 500 h, and (f) 600 h.

Fig. 3. Back-scattered SEM images showing IMCs at the Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, (e) 500 h, and (f) 600 h.

Fig. 4. Consumption of Ni-P and Ni-Co-P metallizations upon aging for 600 h. Notice that the Ni-P metallization with an original thickness of 9.7 µm was fully consumed after 300 h of aging.

Fig. 5. Magnified back-scattered SEM image showing IMCs at the Ni-Co-P/Sn-3.5Ag interface after aging at 180 °C for 600 h.

Fig. 6. EDX elemental mapping analysis of the Ni-Co-P/Sn-3.5Ag interface aged at 180 °C for 600 h: (a) SEM image, (b) mapping for Ni, (c) mapping for Co, (d) mapping for P, (e) mapping for Cu, (f) mapping for Ag, and (g) mapping for Sn. Elemental concentration decreases with decreasing colour intensity.

Fig. 7. (a) Cross-sectional TEM micrograph of the Ni-Co-P/Sn-3.5Ag solder joint aged at 180 °C for 600 h (TEM sample preparation was done by focused ion beam (FIB) technique), diffraction patterns from (b) $(\text{Ni,Co})_3\text{P}$, (b) $(\text{Ni,Co})_{12}\text{P}_5$, and (d) $(\text{Ni,Co})_3\text{Sn}_4$ layers.

Fig. 8. Tensile strengths of both Ni-Co-P/Sn-3.5Ag and Ni-P/Sn-3.5Ag solder joints after aging for up to 600 h.

Fig. 9. (a) Cross-sectional view and (b) fractured surface of the as-reflowed Ni-P/Sn-3.5Ag solder joint.

Fig. 10. Cross-sectional view of Ni-P/Sn-3.5Ag solder joint after aging at 180 °C for (a) 100 h, (b) 200 h, and (c) 300 h.

Fig. 11. (a) Cross-sectional view and (b) fractured surface of the Ni-P/Sn-3.5Ag solder joint after aging at 180 °C for 400 h. (c) Cross-sectional view and (d) fractured surface of the Ni-P solder joint after aging at 180 °C for 600 h.

Fig. 12. (a) Cross-sectional view and (b) fractured surface of the as-reflowed Ni-Co-P/Sn-3.5Ag solder joint.

Fig. 13. Cross-sectional view of Ni-Co-P/Sn-3.5Ag solder joint after aging at 180 °C for (a) 100 h, (b) 200 h, (c) 300 h, (d) 400 h, and (e) 600 h.

Fig. 14. A schematic illustration of the diffusional formation mechanism of IMCs between the Ni-Co-P metallization and Sn-3.5Ag solder.

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