Transmission Electron Microscopy of Interfaces in Joints between Pb-Free Solders and Electroless Ni-P*¹

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Microstructures of joints between a Ni-8 mass%P UBM (under bump metallization) and three different Pb-free solders, *i.e.*, Sn-Ag, Sn-Ag-Cu and Sn-Ag-Cu-Bi were studied by transmission electron microscopy. The phases formed near the joint interfaces as well as inside the solders during soldering were identified on the basis of electron diffraction and EDX analysis without ambiguity. In the Ni-P under bump metallization near the interface with the solders, P-denuded Ni-20 mass%P layer was observed, where a high density of columnar voids were formed. Also, in Ni(Cu) SnP intermetallic, which is adjacent to the P-denuded Ni-20 mass%P, a high density of spherical voids were observed. These voids degrade the joint strength. Change of the above microstructures during thermal cycling between 253 K and 453 K was also observed.

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1. Introduction

Recently Pb free solders have attracted much attention as substitutes for the conventional Pb-Sn eutectic solders in order to cope with environmental issues.¹⁾ The microstructure of solders joints has been studied mostly using scanning electron microscopy (SEM),²⁾ the spatial resolution of which is low. Transmission electron microscopy (TEM) provides a higher spatial resolution to observe the structure of the layers in a solder joint directly. Although TEM observation is a very powerful tool, it is only very recently that analysis of solder joints using TEM was carried out. One of the obvious reason for this is that preparation of a thin foil specimen of a solder joint for TEM analysis is extremely difficult with the conventional technique available hitherto, because the joint includes materials with low-melting points. However, recently a novel technique, a focused ion beam (FIB) technique, has been successfully applied to preparing a TEM foil specimen of a solder joint.³⁻⁶⁾ Matsuki, Ibuka and Saka⁶⁾ carried out a comprehensive analysis on the microstructure of Pb-Sn eutectic solder joints. More recently TEM observations of Pb-free solders have been carried out by Kariya *et al.*⁷⁾ However, their observations did not clarify the detailed structure of the solder joints. The aim of the present study is to identify, by a comprehensive TEM observations, the layers of alloys formed at joints between different Pb-free solders and an electroless Ni-P under bump metallization

(UBM) on a Cu interconnect in a plastic ball grid array (BGA) package. Microstructures changes during thermal cycling between 253 and 453 K was also observed to provide information on changes of microstructure in storage and/or field service.

2. Experimental Procedures

Samples were prepared from a device package on a printed circuit board for an interposer. Three different types of solders, *i.e.*, Sn-Ag, Sn-Ag-Cu and Sn-Ag-Cu-Bi, were used. These chemical compositions are summarized in Table 1. As shown in Fig. 1, the under bump metallizations (UBM) are composed of a Cu land, 5 μ m thick Ni-8 mass%P and nominally 50 nm thick Au films. The Cu and Ni-8 mass%P films were plated by electroless deposition, and the Au film formed by substitution plating. The temperature profile for the soldering process is shown in Fig. 2.

Thin foil specimens for TEM observation were prepared using a focused ion beam (FIB) apparatus (Hitachi FB-2000). TEM observations were carried out in two microscopes, *i.e.*, a Hitachi 9000NAR and a Hitachi H-1250ST, at accelerating voltages of 300 kV and 1000 kV, respectively. Elemental analysis was also carried out using energy dispersive X-ray (EDX) analysis using an electron beam probe of the diameter of 5 nm.

The intermetallic compounds which are likely to be

Table 1 Samples used in this study.

Sn-Ag	Sn-3.5 mass%Ag/Ni-8 mass%P
Sn-Ag-Cu	Sn-3.5 mass%Ag-0.75 mass%Cu/Ni-8 mass%P
Sn-Ag-Cu-Bi	Sn-3.5 mass%Ag-0.75 mass%Cu-3.0 mass%Bi/Ni-8 mass%P

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Fig. 1 Schematic illustration of the cross section of a solder/UBM joint. The mechanism of the pull test is also shown.

Fig. 2 The temperature profile for the soldering process.

formed in a solder joint are summarized in Table 2, together with β -Sn. As can be seen from Table 2, most of these compounds have large lattice parameters and complex crystal structures. This often makes it impossible to identify the crystal structure from a single electron diffraction pattern. Therefore, diffraction patterns along different incident electron beam orientations were taken to identify the crystal structure without ambiguity. A relatively wide area, approximately $15\text{ }\mu\text{m}$ wide, was thinned in order to reduce noises from the surrounding areas for EDX analysis.

Some of the Sn-Ag-Cu-Bi solder joints were subjected to thermal cycles between 253 K and 453 K up to a maximum of

250 cycles, and the bond strength measured by a pull test using a bond tester PC2400. Here, a ϕ 0.3 mm Cu rod was held with a jig just on top of a solder ball to be examined, and then the jig is heated at 563 K. When the solder ball melted, the Cu rod fell into the molten solder ball and joins. Then, the jig was cooled to 322 K by air, the Cu rod was pulled out and the load at which the joint was fractured was defined as its pull load. For each cycle, 10 samples were examined to measure the pull load. The microstructures were examined by TEM.

3. Results and Discussion

3.1 Microstructure and EDX analysis

3.1.1 As-joined structure (Sn-Ag/Ni-P)

Figures 3(a) and (b) shows a microstructure of solder joint of Sn-Ag/Ni-P to UBM, at a low magnification, and concentration profiles of Sn, Ni, Ag and P, obtained at points 1–9 by EDX analysis, across the joint, respectively. Figure 3(c) shows the joint at a higher magnification. Au was not detected at any point by EDX elemental analysis. This indicates that Au, which had sat on top of the Ni-P layer before soldering, diffused into the solder and/or Ni-P layer during the mounting of a solder ball. As can be seen from Fig. 3(b), it was confirmed that at least 6 different regions were present, *i.e.*, Ni-8 mass%P (points 1 and 2), Ni-20 mass%P (point 3), a region composed of Ni, Sn and P (hereafter referred to as Ni-Sn-P) (point 4), a region composed of Ni and Sn (hereafter referred to as Ni-Sn) (points 5, 6 and 7), region composed of Ag and Sn (hereafter referred to as Ag-Sn) (point 8) and Sn (point 9). A high density of columnar voids and spherical voids are present in Ni-20 mass%P and Ni-Sn-P, respectively. These voids are quite similar to voids formed at a solder joint between Ni-8 mass%P and the Pb-Sn eutectic solder.^{4,6)}

3.1.2 As-joined structure (Sn-Ag-Cu/Ni-P)

Figures 4(a) and (b) shows a solder joint of Sn-Ag-Cu/Ni-P, at a low magnification, and concentration profiles of P, Ni, Cu, Ag and Sn, obtained at points 1–12 by EDX analysis, across the joint, respectively. Figure 4(c) shows the joint at a higher magnification. In addition to Ni-8 mass%P (points 1, 2 and 3), Ni-20 mass%P (point 4) and Sn (points 10 and 11), which were formed in the Sn-Ag/Ni-P joint, Ni-Sn-Cu-P (point 5), Cu-Ni-Sn (points 6, 7, 8 and 9) and Cu-Sn (point 12) were confirmed to be present. In Cu-Sn-Ni layer, the concentration of Sn increases with the distance from the Ni-P substrate. Again, a high density of columnar and spherical

Table 2 Intermetallic compounds likely to be formed at a solder/Ni-P interface.

Phase	Bravais Lattice	Space group	Lattice parameters (nm, degree)	JCPDS Card #
β -Sn	tetragonal	I41/amd(141)	$a = 0.5831, c = 0.318$	4-0673
Ni ₃ P	tetragonal	I-4(82)	$a = 0.8952, c = 0.4388$	34-0501
Ni ₂ SnP	orthorhombic	<i>Pmma</i> (62)	$a = 1.282, b = 0.3594, c = 0.50896$	78-0236
Ni ₃ Sn ₄	monoclinic	<i>C2/m</i> (12)	$a = 1.2290, b = 0.4054, c = 0.517, B = 103.9^\circ$	4-0845
Ni ₃ Sn ₂	hexagonal	<i>P63/mmc</i> (194)	$a = 0.407, c = 0.515$	6-0414
Ni ₄₈ Sn ₅₂	orthorhombic	<i>Pbam</i> (55)	$a = 2.445, b = 0.520, c = 0.409$	26-1289
η -Cu ₆ Sn ₅	hexagonal	<i>P63/mmc</i> (194)	$a = 0.42062, c = 0.50974$	47-1575
Ag ₃ Sn	orthorhombic	<i>Pmmn</i> (59)	$a = 0.5968, b = 0.47802, c = 0.51843$	44-1300

Fig. 3 (a) Low-magnification TEM of a joint between Sn-Ag solder and Ni-P UBM. (b) Concentration profiles of Sn, Ag, Ni and P. (c) High-magnification TEM of the joint.

Fig. 4 (a) Low-magnification TEM of a joint between Sn-Ag-Cu solder and Ni-P UBM. (b) Concentration profiles of Sn, Ag, Cu, Ni and P. (c) High-magnification TEM of the joint.

voids was observed in Ni-20 mass%P and Ni-Sn-Cu-P.

3.1.3 As-joined structure (Sn-Ag-Cu-Bi/Ni-P)

Figures 5(a) and (b) shows a solder joint of Sn-Ag-Cu-Bi/Ni-P, at a low magnification, and concentration profiles of P, Ni, Cu, Ag, Bi and Sn, obtained at points 1–16 by EDX analysis, across the joint, respectively. Figure 5(c) shows the concentration profile of Bi in more detail. Figure 5(d) shows the joint at a higher magnification. Setting aside the distribution of Bi, Ni-8 mass%P (points 1 and 2), Ni-20 mass%P (point 3), Ni-Sn-Cu-P (point 4), Ni-Sn-Cu (points 5–8), Sn (points 9–13 and 15) and Cu-Sn (points 14 and 16) were identified. In Ni-Sn-Cu, the concentration of Sn at points 5, 6 and 7 is clearly lower than that at point 8. This suggests strongly that the phase present at points 5, 6 and 7 is different from that at point 8. Thus, the former will be

called Ni-Sn-Cu (Sn poor) and the latter Ni-Sn-Cu (Sn rich) hereafter.

Bi exists mostly in Sn (points 9–13 and 15), and virtually does not exist in Cu-Sn (points 14 and 16) and Ni-P (points 1–4). Furthermore Bi concentration in Ni-Sn-Cu (points 5–8) is quite low. Again, a high density of columnar and spherical voids are observed in Ni-20 mass%P and Ni-Sn-Cu-P.

3.1.4 Microstructure after thermal cycling

Figures 6(a) and (b) shows microstructures of Sn-Ag-Cu-Bi solder joints after 20 and 250 cycles in a temperature range between 253 K and 453 K. Ni-Cu-Sn-P exists just above Ni-20 mass%P layer in a way similar to the as-joined state, but, Ni-20 mass%P layer is much thinner. This is especially true for the case of 250 cycles. Figure 7 shows concentration

Fig. 5 (a) Low-magnification TEM of a joint between Sn-Ag-Cu-Bi solder and Ni-P UBM. (b) Concentration profiles of Sn, Ag, Cu, Ni, Bi and P. (c) Concentration profile of Bi expressed in more detail. (d) High-magnification TEM of the joint between Sn-Ag-Cu-Bi solder and Ni-P UBM.

Fig. 6 Microstructure of a joint subjected to thermal cycling up to 20 cycles (a) and 250 cycles (b).

profiles obtained after 250 cycles. Again, neglecting Bi, Ni-8 mass%P (point 1), Ni-20 mass%P (point 2), Ni-Sn-Cu (Sn-poor) (points 3–5), Ni-Sn-Cu (Sn-rich) (point 6), Sn (points 7–8, 10, 11) and Ag-Sn (point 9) were identified.

3.1.5 Summary of microstructure and EDX analyses

The aforementioned results may be summarized as follows:

1) Sn-Ag/Ni-P joint:

There exist 3 layers between a Ni-8 mass%P UBM and a Sn-Ag solder in the following sequence, *i.e.*, (Ni-8 mass%P UBM)/Ni-20 mass%P/Ni-Sn-P/Ni-Sn/(Sn-Ag solder). Inside the Sn-Ag solder, Ag-Sn islands are distributed. The constitution of the solder joint is essentially similar to that of Pb-Sn eutectic solder except that Pb in the Pb-Sn solder is

replaced with Ag-Sn islands in the Sn-Ag solder.

2) Sn-Ag-Cu-(Bi)/Ni-P joint

There exist 4 layers between a Ni-8 mass%P UBM and Sn-Ag-Cu-(Bi) solders in the following sequence, *i.e.*, (Ni-8 mass%P UBM)/Ni-20 mass%P/Ni-Cu-Sn-P/Sn-poor Cu-Ni-Sn/Sn-rich Cu-Ni-Sn/(Sn-Ag-Cu-(Bi) solder). Inside the solder, Ag-Sn and Cu-Sn islands are distributed.

Bi was detected in Sn, which was the main component of the solders, and virtually not detected in Cu-Sn nor Ag-Sn islands, which were the counterparts of the eutectic structures of the solders. Furthermore, Bi concentrations in reaction products such as Ni-Sn-Cu and in Ni-P layers are quite low.

Fig. 7 (a) Low-magnification TEM of a joint between Sn-Ag-Cu-Bi solder and Ni-P UBM which was subjected to thermal cycling up to 250 cycles. (b) Concentration profiles of Sn, Ag, Cu, Ni, Bi and P.

3.2 Electron diffraction

3.2.1 Ni-8 mass%P

Figure 8(a) shows a diffraction pattern taken at Ni-8 mass%P layer. The diffraction pattern consists of continuous Debye rings, which are indexed as FCC structure with $a = 0.35$ nm. Thus, Ni-8 mass%P layer is identified as fine polycrystals of FCC-Ni, in which as large as 8 mass%P is solved.

3.2.2 Ni-20 mass%P

Figure 8(b) shows a diffraction pattern taken at Ni-20 mass% layer. Debye rings corresponding to FCC-Ni (the first two rings, *i.e.*, $\{111\}$ and $\{200\}$ rings are superimposed in Fig. 8(b)) and diffraction network corresponding to Ni_3P are evident. The key diagrams are shown in Fig. 8(c).

3.2.3 Ni-Cu-Sn-P layer

Figures 9(a) and (b) shows a diffraction pattern taken at Ni-Cu-Sn-P layer and the key diagram, respectively. The

Fig. 8 (a) Diffraction pattern obtained from the substrate Ni-8 mass%P UBM. (b) Diffraction pattern obtained from P-enriched (or Ni-denuded) Ni-P (Ni-20 mass%P) layer. Diffraction spots from Ni_3P are indicated by a network. Two circles correspond to Debye rings of $\{111\}$ and $\{200\}$ of Ni. (c) Key diagram to the spots of Ni_3P . Circles indicate Debye rings of Ni, the indices of which are underlined.

Fig. 9 (a) Diffraction pattern from Ni-Cu-Sn-P phase. (b) Key diagram to (a).

structure of this layer is identified as Ni_2SnP . However, EDX analysis indicates that this layer contains a large amount of Cu, so that it is concluded that this layer is $(\text{Ni}, \text{Cu})_2\text{SnP}$, where part of Ni is substituted by Cu.

3.2.4 Cu-Ni-Sn (Sn-poor) layer

Figures 10(a)–(f) shows diffraction patterns taken at Cu-Ni-Sn (Sn-poor) layer. Figure 10(g) shows relationship between the incident electron beam B , with which Figures 10(a)–(f) were taken, and the standard stereo projection. As can be seen from the key diagrams shown in Figures 10(a')–(f'), this layer is identified as either $\eta\text{-Cu}_6\text{Sn}_5$ or Ni_3Sn_2 . Both $\eta\text{-Cu}_6\text{Sn}_5$ and Ni_3Sn_2 have the space groups of $P63/mmc$ and their lattice parameters are very similar (*cf.* Table 2); it is impossible to distinguish between them from their electron diffraction patterns alone. However, since EDX analysis shows that the layer is much richer in Cu than Ni, it is reasonable to conclude that this layer is $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$, where Ni is substituted partly at the Cu sites. Furthermore, the diffraction patterns shown in Figs. 10(a)–(f) do not show any superlattice spots. Thus, $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$, which is a high temperature phase, must have been frozen at room temperature.

3.2.5 Cu-Ni-Sn (Sn-rich) layer

Between Cu-Ni-Sn (Sn-poor) layer ($\eta\text{-(Cu, Ni)}_6\text{Sn}_5$) and the solder, Cu-Ni-Sn (Sn-rich) layer, the Sn content of which is higher than that of $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ phase, is formed. Figures

11(a) and (b) shows diffraction patterns taken along two different orientations of the incident electron beam B . Figures 11(a') and (b') shows the key diagrams of Figs. 11(a) and (b), and the structure of Cu-Ni-Sn (Sn-rich) is identified to be the same as $\text{Ni}_{48}\text{Sn}_{52}$. Since Cu-Ni-Sn (Sn-rich) layer contains a large amount of Cu, it is concluded that this phase is $(\text{Ni}, \text{Cu})_{48}\text{Sn}_{52}$.

3.2.6 Ag-Sn island

Inside the matrices of all the solders studied, islands consisting of Ag and Sn are distributed (for example point 8 in Fig. 3(a) and 9 in Fig. 7(a)). Figure 12 shows such an island of Ag-Sn imaged at a higher magnification in the dark field mode. Figures 13(a) and (b) shows two examples of diffraction pattern, the key diagrams being shown in Figs. 13(a') and (b'). This phase is identified as Ag_3Sn . From the diffraction patterns two orientation relationships are established as follows:

$$(202)\text{Ag}_3\text{Sn} \parallel (\bar{2}\bar{1}\bar{1})\beta - \text{Sn}$$

$$[\bar{1}\bar{2}1]\text{Ag}_3\text{Sn} \parallel [10\bar{2}]\beta - \text{Sn}$$

and

$$(112)\text{Ag}_3\text{Sn} \parallel (\bar{2}\bar{1}\bar{1})\beta - \text{Sn}$$

$$[\bar{1}3\bar{1}]\text{Ag}_3\text{Sn} \parallel [10\bar{2}]\beta - \text{Sn}$$

3.2.7 Cu-Sn island

In the matrices of the Cu-containing solders, regions consisting of Cu and Sn are observed. Diffraction patterns (not shown) taken in these regions are very similar to those from Cu-Ni-Sn (Sn-poor) layer, *i.e.*, $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ phase. However, this Cu-Sn region is different from Cu-Ni-Sn (Sn-poor) layer in that Cu-Sn region is observed well far away from the solder joint and that Ni is not contained at all. Thus, it is concluded that the Cu-Sn region is $\eta\text{-Cu}_6\text{Sn}_5$ phase, and *not* $\eta\text{-(Cu, Ni)}_6\text{Sn}_5$ phase. It is formed as the primary phase when the solder freezes.

3.2.8 Summary of the solder joints

Figures 14(a) and (b) shows schematically the joints to UBM of Sn-Ag solder and Sn-Ag-Cu-(Bi) solder, respectively. The microstructure of the Sn-Ag/Ni-P joint (Fig. 14(a)) is essentially similar to that of Pb-Sn eutectic solder, except that Pb is replaced by Ag_3Sn . Neither Pb nor Ag participates in the reactions during soldering; only Sn does. By contrast, in the case of Cu-containing solders, *i.e.*, Sn-Ag-Cu-(Bi)/Ni-P (Fig. 14(b)), Cu participates in the reactions during soldering. As a result, intermetallic compounds, formed as the reaction products, are different from those formed in the cases of Sn-Ag and Pb-Sn solders.

However, from the viewpoint of diffusion of Ni and P from the Ni-P substrate, the situations in Cu-free and Cu-containing solders are similar. Matsuki *et al.*⁴⁾ have discussed formation mechanism of voids formed in Ni-20 mass%P and Ni-Sn-P, which corresponds to (Ni, Cu)-Sn-P in the case of Cu-containing solder, based on *in-situ* observation of motion of individual interfaces in a joint. They concluded that diffusion of Sn in Ni_2SnP is sluggish, while Ni can diffuse easily across Ni_2SnP . In order for Ni-Sn to keep growing, Ni must be supplied all the way from the electroless Ni-8 mass%-P. Thus, the content of Ni in the electroless Ni-8 mass%P keeps decreasing. If the supply of Ni from the

Fig. 10 (a)–(f) Diffraction patterns from (Ni, Cu)–Sn (Sn poor) phase. (a')–(f') Key diagrams to (a)–(f). (g) Relationship of the zone axes along which (a)–(f) were taken.

Fig. 11 (a), (b) Diffraction patterns from (Ni,Cu)-Sn (Sn rich) phase. (a') and (b') are key diagrams to (a) and (b).

underlying Ni-8mass%P is not sufficient, voids may be formed and grow along the diffusion path of Ni in Ni-20mass%P, leading to formation of columnar voids. The formation of spherical voids in Ni_2SnP can be explained by assuming that diffusion of Ni in Ni_2SnP is slower than in Ni-Sn. This difference in diffusivity of Ni gives rise to imbalance of supply of Ni at the $\text{Ni}_3\text{Sn}_4/\text{Ni}_2\text{SnP}$ interface, which leads to formation of spherical voids near the $\text{Ni}_3\text{Sn}_4/\text{Ni}_2\text{SnP}$ interface in Ni_2SnP . Both of these two types of void are

Fig. 12 Dark-field micrograph at higher magnification of Ag_3Sn phases dispersed in the matrix of Sn.

Fig. 13 (a) and (b) Diffraction patterns from Ag_3Sn , (a') and (b') Key diagrams to (a) and (b). Indices of Ag_3Sn are underlined. Spots denoted by * in (b) are forbidden reflections which appear as a result of the double reflection. Beam direction is normal to the $(\bar{1}\bar{2}1)$ plane for Ag_3Sn and to the $(10\bar{2})$ plane for Sn.

Fig. 14 (a) Microstructure of a joint between Sn–Ag and Ni–8 mass%P UBM. (b) Microstructure of a joint between Sn–Ag–Cu–(Bi) and Ni–8 mass%P UBM.

formed because the diffusion coefficients of the major components, *i.e.*, Ni, P and Sn, are not constant.

3.3 Strength and fracture of the joints

Figure 15 shows an electron micrograph of a joint of Sn–Ag–Cu–Ni–P fractured by a pull test. It is evident that fracture took place mostly along $(\text{Ni,Cu})_2\text{SnP}/\text{Ni-20 mass}\% \text{P}$, and occasionally inside $(\text{Cu,Ni})_6\text{Sn}_5$. Thus, it is reasonable to conclude that the columnar voids in the Ni–20 mass%P layer degrades the strength of the joint. This is in keeping with the case of Pb–Sn/Ni–P joint.

Figure 16 shows variation in the pull load as a function of the number of cycle of thermal cycling. The pull load remains

Fig. 15 Cross-sectional TEM of a Sn–Ag–Cu/Ni–P joint pulled to fracture. W denotes a protective layer of tungsten deposited prior to FIB milling and has nothing with structures of the joint.

Fig. 16 Variation in the tensile strength of a Sn–Ag–Cu–Bi/Ni–P joint as a function of the number of thermal cycle. The solid line indicates the values averaged over 10 measurements.

virtually unchanged. During thermal cycling the thickness of Ni–20 mass%P where a high density of columnar voids exist decreases dramatically. However, surprisingly the pull load remains unchanged. One possible explanation to this is that, during thermal cycling $\eta-(\text{Cu,Ni})_6\text{Sn}_5$ intermetallics also coarsen, thus canceling the improvement of the joint strength due to shrinkage of columnar voids.

4. Summary

Microstructures of interfaces of joints between Ni–8 mass%P UBM and three different Pb-free solders, *i.e.*, Sn–Ag, Sn–Ag–Cu and Sn–Ag–Cu–Bi were observed by TEM. The results obtained are as follows:

- (1) In Sn–Ag/Ni–P joint, 3 layers are formed at the joint in the following sequence, *i.e.*, (Ni–8 mass%P UBM)/Ni–20 mass%P/Ni₂SnP/Ni–Sn/(Sn–Ag solder). Inside the Sn–Ag solder, Ag₃Sn islands are distributed. The constitution of the solder joint is essentially similar to that of Pb–Sn eutectic solder except that Pb in the Pb–Sn solder is replaced with Ag–Sn islands in the Sn–Ag solder.
- (2) In Cu-containing solders, *i.e.*, Sn–Ag–Cu–(Bi), 4 layers are formed between a Ni–8 mass%P UBM and Sn–Ag–Cu–(Bi) solders in the following sequence, *i.e.*, (Ni–8 mass%P UBM)/Ni–20 mass%P/(Ni, Cu)₂SnP/ $\eta-(\text{Cu,Ni})_6\text{Sn}_5$ /(Sn–Ag–Cu–(Bi) solder).
- (3) Inside the solder, Ag₃Sn and $\eta-\text{Cu}_6\text{Sn}_5$ islands are distributed.
- (4) The following orientation relationships between Ag₃Sn and β -Sn are established

$$(202)\text{Ag}_3\text{Sn} \parallel (\bar{2}\bar{1}\bar{1})\beta - \text{Sn}$$

$$[\bar{1}\bar{2}1]\text{Ag}_3\text{Sn} \parallel [10\bar{2}]\beta - \text{Sn}$$

and

$$(112)\text{Ag}_3\text{Sn} \parallel (\bar{2}\bar{1}\bar{1})\beta - \text{Sn}$$

$$[\bar{1}\bar{3}\bar{1}]\text{Ag}_3\text{Sn} \parallel [10\bar{2}]\beta - \text{Sn}$$

- (5) Bi is detected in Sn, which is the main component of the solders, and virtually not detected in Ag₃Sn nor $\eta-\text{Cu}_6\text{Sn}_5$ islands, which are the counterparts of the eutectic structures of the solders.

- (6) Bi concentration in reaction products and the Ni–P layers is quite low.
- (7) A high density of columnar voids are formed in Ni–20 mass%P near the interface with Ni₂SnP or (Ni, Cu)₂SnP.
- (8) A high density of spherical voids are formed in Ni₂SnP or (Ni, Cu)₂SnP near the interface with Ni–Sn or Ni–Cu–Sn intermetallics.
- (9) These voids, especially columnar ones, degrade the strength of the joints.
- (10) After thermal cycling between 253 and 453 K, Ni–20 mass%P layer decreases in thickness substantially.
- (11) At the same time η -(Cu, Ni)₆Sn₅ intermetallics also coarsen during thermal cycling, and this may cancel the improvement of the joint strength due to shrinkage of columnar voids.

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