

# Shear Strength and Interfacial Compound of Sn–Ag–Bi–In Alloy

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Sn–3Ag–8Bi–5In solder (melting point, 461–477 K) was investigated as a lead(Pb)-free solder. In order to evaluate the solderability of the Sn–Ag–Bi–In alloy, the shear strength of soldered joint and inter-metallic compound (IMC) were investigated. As an experimental procedure, a 0.5 mm diameter solder was set on the Ni/Cu/Cr-pad of a Si-substrate. The solder ball on the pad was reflowed with Rosin Mildly Activated (RMA)-flux in air, and the reflow temperature was controlled between 483 K and 533 K. The shear strength and microstructure of the solder ball were evaluated with and without aging. The results show that the shear strength of the Sn–3Ag–8Bi–5In solder ball had the highest value of 1.69N by reflowing at 513 K for 10 s. The shear strength decreased from 1.69N to 0.95N as the IMC thickness was increased from 1.75  $\mu\text{m}$  to 1.9  $\mu\text{m}$ . Needle-shaped  $\text{Ni}_3\text{Sn}_4$  and plate-like  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  formed on the interface between the solder and the Under Bump Metallization (UBM) that was bonded for 10 s at 513 K.

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**Keywords:** Sn–3Ag–8Bi–5In, Pb-free solder, microstructure, inter-metallic compound, joint strength

## 1. Introduction

A large number of lead (Pb)-free solder alloys have been proposed as replacements for the Sn–Pb eutectic solder in electronic parts.<sup>1–3)</sup> However, most are not adequate for replacing the currently used alloy because of their high melting point, poor solderability and other problems.<sup>4,5)</sup> However, among the proposed lead-free solders, Sn–Ag–Cu alloy has been the most popular candidate and generally recognized as a substitute for lead containing solder. It has satisfactory reliability, solderability and strength compared to other lead-free solders. Even with these merits, its high melting point of almost 490 K is proving to be one shortcoming for the Sn–Ag–Cu alloy. This can cause some problems such as thermal damage to electronic parts due to the high soldering temperature, modification of the soldering equipment and *etc.* Because of these demerits, some researchers have tried to find other solder alloys with relatively lower melting point.

In order to overcome the high melting point of Pb-free solders, a Sn–Ag–Bi–In alloy has been suggested by some researchers.<sup>6,7)</sup> Although In is an expensive metal and an excessive Bi content increases the hardness of the solder, the Sn–Ag–Bi–In alloy is attractive in terms of its relatively low melting temperature compared to the Sn–Ag–Cu alloy. A lower melting temperature becomes more important in BGA and flip chips that have a high heat capacity. Limited reports on Sn–Ag–Bi–In<sup>8–11)</sup> alloys are available. In this study, the solderability of a Sn–3Ag–8Bi–5In alloy was evaluated by investigating the shear strength of the soldered joint and the inter-metallic compound on the solder interface.

## 2. Experimental

For the experimental material, a Si-substrate plated with UBM (Under Bump Metallurgy) was prepared. Subsequently, a 70 nm thick Cr and a 100 nm thick Cu layer were deposited by electron beam (EB) evaporation, and a 4  $\mu\text{m}$  thick Cu and a 2  $\mu\text{m}$  thick Ni layer were electro-plated. A 5 mm diameter

solder ball of Sn–3Ag–8Bi–5In was set on the UBM with the RMA (Rosin Mildly Activated) flux (see Fig. 1).

The solder ball on the UBM was reflowed using a flip chip bonder in air with the temperature profile given in Fig. 2. The heating and cooling rates for the soldering was 10 K/s and 5 K/s, respectively. The peak temperature was changed from 483 to 533 K with a holding time of 5–300 s, as shown in Fig. 2.

The shear strength and microstructure of the soldered joints were evaluated with and without aging. The aging treatment was carried out at 383 K for 16 days, and the shear strength was evaluated with a tip speed of 200  $\mu\text{m}/\text{s}$  and a gap to the substrate of 10  $\mu\text{m}$ . The shear test was repeated 20 times for each soldering condition and their average values were taken as the shear strengths. Inter-metallic compounds

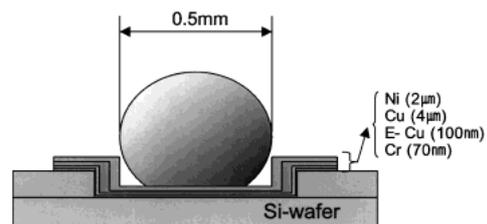


Fig. 1 Schematic illustration of the solder ball on the Ni/Cu/Cr-UBM.

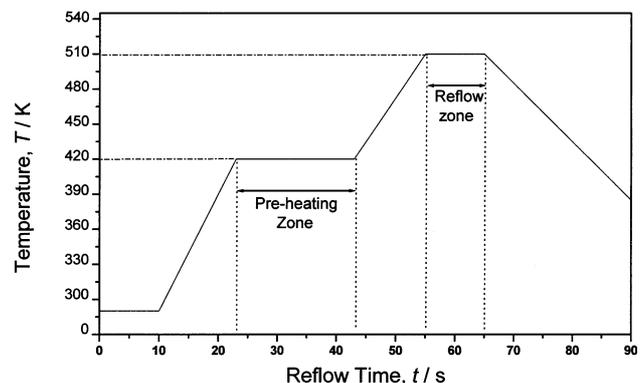


Fig. 2 Temperature profile for the reflow soldering.

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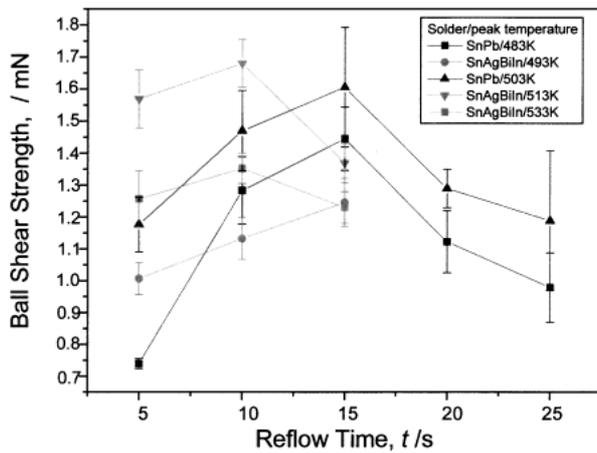


Fig. 3 Effect of reflow time on the shear strength of solder ball (substrate: UBM coated Si-wafer, solder: Sn37Pb, Sn3Ag8Bi5In).

(IMC's) at the solder/UBM interface were investigated by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), and X-ray Diffractometer (XRD).

### 3. Results and Discussion

#### 3.1 Shear strength

The effects of the reflow time and soldering temperature on the shear strength of the solder balls, Sn37Pb and Sn3Ag8Bi5In, are given in Fig. 3. The shear strength of Sn37Pb shows high values of 1.46, 1.60N by reflowing at 483 K and 503 K respectively. In the case of the Sn3Ag8Bi5In alloy, its peak soldering temperatures were determined to be 493, 513, 533 K by considering its melting ranges of 461–477 K. The shear strength of the Sn3Ag8Bi5In alloy shows highest value of 1.69N at 513 K. It is known that the bonding strength of the solder ball is affected by the thickness of the intermetallic compound, and the overgrown intermetallic compound is detrimental to joint strength.<sup>12)</sup>

In order to evaluate the relationship between the IMC thickness and the joint strength of the solder ball, the ball on the UBM was reflowed at 513 K by changing the reflow time from 10 s to 150 s. In this test, the shear strengths of the soldered balls decreased with increasing reflow time *e.g.* 1.69N at 10 s, 0.95N at 30 s, 0.90N at 60 s and 0.72N at 150 s. The IMC thicknesses for the same soldering condition were 1.75  $\mu\text{m}$  at 10 s, 1.9  $\mu\text{m}$  at 30 s, 2.01  $\mu\text{m}$  at 60 s and 2.54  $\mu\text{m}$  at 150 s. From these results, the relationship between the IMC thickness and the ball shear strength is redrawn in Fig. 4. The figure shows that the shear strength decreased drastically from 1.69N to 0.95N when the IMC thickness increased from 1.75 to 1.9  $\mu\text{m}$ . However, when the IMC thickness is greater than 1.9  $\mu\text{m}$ , the strength decreases slightly.

The Sn3Ag8Bi5In balls soldered on the UBM were aged at 383 K for 16 days, and their shear strengths were evaluated as shown in Fig. 5. The holding time at the peak soldering temperature was fixed at 10 s, which gave the highest strength (see Fig. 3). In Fig. 5 the shear strengths show relatively high values after aging for 4 or 9 days. The average strength decreases after 16 days was approximately 5% when compared to the as soldered state.

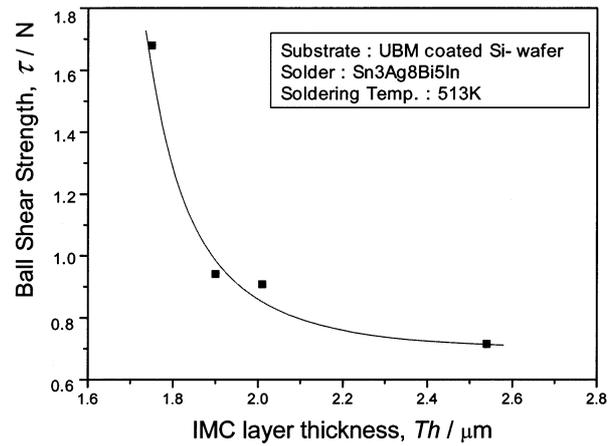


Fig. 4 Relationship between IMC thickness and shear strength of solder ball (ball diameter: 0.5 mm).

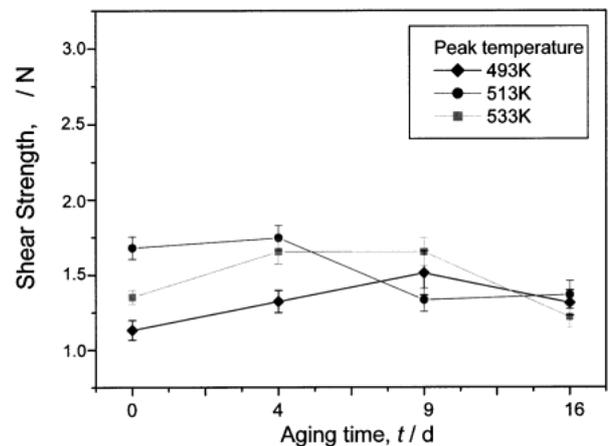


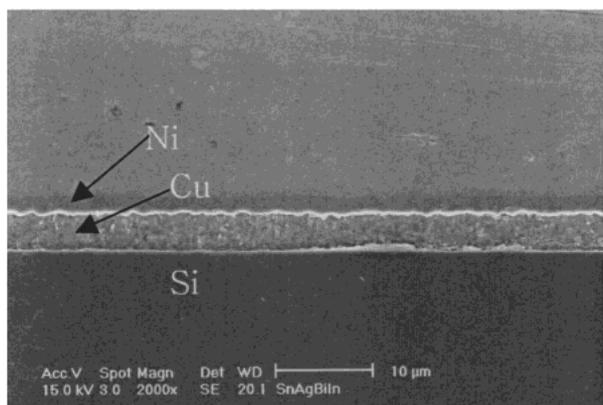
Fig. 5 Effect of aging time on the shear strength of Sn3Ag8Bi5In solder ball on UBM. (holding time at peak temperature; 10 s, aging temperature: 383 K).

#### 3.2 Microstructure

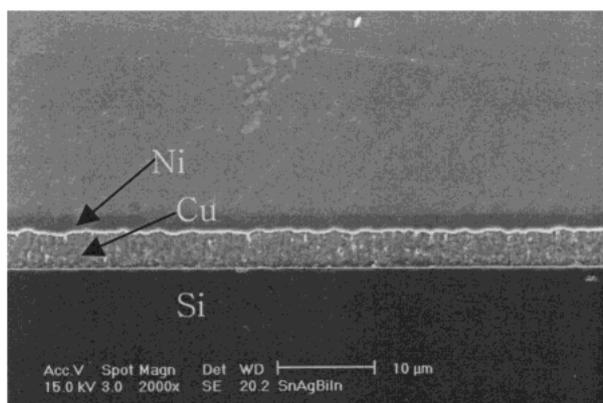
Figure 6 shows the interface between the Sn3Ag8Bi5In and UBM that was reflowed at 513 K. In Fig. 6, the Cu- and Ni-layer can be identified, and the Ni-layer appears as a gray line along the interface. The Ni-layer suppresses the formation of Sn–Cu IMC's and acts as a diffusion barrier against Cu. Therefore, Ni forms a Sn–Ni IMC such as  $\text{Ni}_3\text{Sn}_4$ , which is relatively thinner than Sn–Cu IMC.<sup>13)</sup> As shown in Fig. 6, the thickness of the Ni-barrier becomes thinner with increasing reflow time, and it appears to be consumed by a reaction with Sn to form a Sn–Ni compound.

In order to investigate the IMC between the solder and the Ni-layer in detail, the solder bulk on the IMC was removed by etching. The solder-removed IMC was observed using SEM and XRD, and Fig. 7 shows the half etched IMC and Fig. 8 shows the completely etched one.

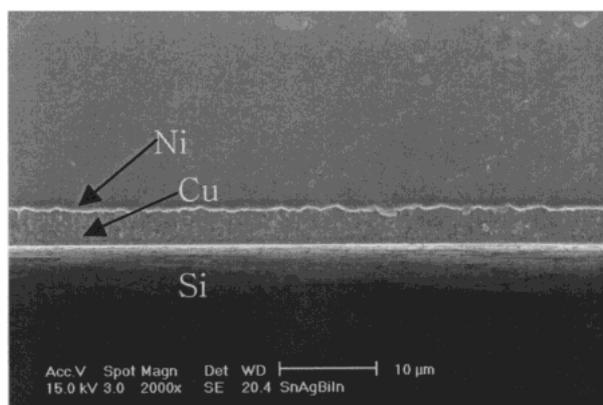
In Fig. 7, the IMC's of  $\text{Ag}_3\text{Sn}$  and  $\text{Ni}_3\text{Sn}_4$  were embedded in  $\beta$ -Sn. However, in Fig. 8 most of the IMC's were  $\text{Ni}_3\text{Sn}_4$  and  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ , and  $\text{Ag}_3\text{Sn}$  was not found. Therefore,  $\text{Ag}_3\text{Sn}$  appears to exist in a small distance away from the Ni–Sn compound layer. On the joint interface, which was soldered at 513 K for 10 s, a needle-shaped IMC was observed (see Fig. 8(a)). The chemical composition of the IMC was analyzed as 41.27 at%Ni and 58.73 at%Sn, which appears to be



(a) 30s



(b) 60s



(c) 300s

Fig. 6 Cross-section of interface between Sn3Ag8Bi5In and Ni/Cu/Cr-UBM (peak soldering temp.: 513 K).

$\text{Ni}_3\text{Sn}_4$ . XRD was used to examine the compounds on the interface more closely, and  $\text{Ni}_3\text{Sn}_4$ ,  $\text{Ag}_3\text{Sn}$  and  $\text{Cu}_6\text{Sn}_5$  were detected as shown in Fig. 9. From EDS and XRD-analysis, the needle-shaped alloy was found to be  $\text{Ni}_3\text{Sn}_4$ . This result is similar to those of Kim *et al.* who reported needle shaped  $\text{Ni}_3\text{Sn}_4$  on the interface between the solder and the Ni-layer.<sup>14</sup> In another study, both  $\text{Ni}_3\text{Sn}_4$  and  $\text{Ni}_3\text{Sn}$  IMC were observed on the interface between Sn–36Pb–2Ag and

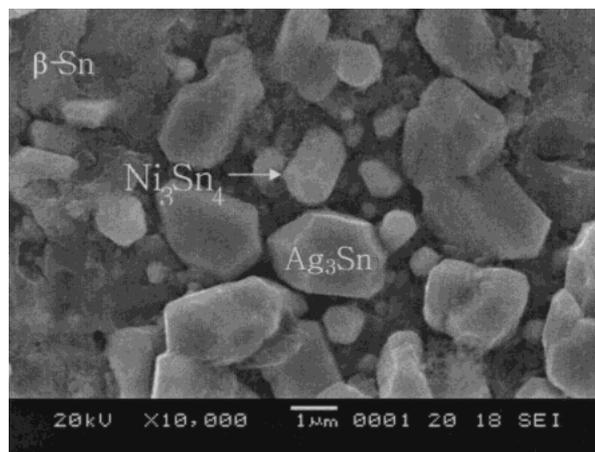


Fig. 7 Intermetallic compounds observed on the half etched interface of Sn3Ag8Bi5In/UBM. (top-viewed, peak soldering temp.: 513 K).

Au/Ni/Cu-UBM.<sup>15</sup> Dehaven *et al.*<sup>16</sup> reported that  $\text{Ni}_3\text{Sn}_4$  was unstable, and  $\text{Ni}_3\text{Sn}$  and  $\text{Ni}_3\text{Sn}_2$  were produced by holding the soldered joint for sufficient time and temperature. However, in this study,  $\text{Ni}_3\text{Sn}$  and  $\text{Ni}_3\text{Sn}_2$  were not observed, and the reason appears to be the shorter reflow time.

The plate-like IMC shown in Fig. 8(e) has the composition of 54.10 at%Sn, 40.25 at%Ni and 5.65 at%Cu, and it is suggested to be  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ . Ho *et al.*<sup>17</sup> reported that  $\text{Ni}_3\text{Sn}_4$  can be transformed to  $(\text{Cu}, \text{Ni})_3\text{Sn}_4$  by Cu-diffusion to the  $\text{Ni}_3\text{Sn}_4$  where Cu is added to the Sn–3.9Ag solder. In Figs. 8 and 9, it can see that the needle-shaped  $\text{Ni}_3\text{Sn}_4$  occupies most of the interface, and the quantity of  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  increases with increasing reflow time.

With increasing reflow time, the size of the intermetallic compound of  $\text{Ni}_3\text{Sn}_4$  and  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  becomes larger. In particular,  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  after 300 s (see Fig. 8(d)) was 2–3 times larger than that of 10 s (see Fig. 8(a)). The change in the IMC morphology appears to affect the joint strength of the solder ball. In other words, by increasing the reflow time from 10 s to 300 s, the IMC morphology and size changed as mentioned previously and the strength decreased from 1.69N to 0.8N.

Figure 10(a) shows the cross section of the interface between the Sn3Ag8Bi5In and Ni/Cu/Cr UBM that was soldered at 513 K for 10 s, and Fig. 10(b) shows the result of the EDS-analysis of Sn, Ni and Cu, which are thought to be the active elements producing the IMC's along the indicated line in Fig. 10(a). In Fig. 10(b), the left side indicates the solder and the right side indicates the UBM. In this figure, Sn- and Cu-content show higher values on solder and Cu-layer respectively. On the intermediate position between the solder and the Cu-layer, the Ni-content that originated from the Ni-barrier shows higher value. However, an unexpected small Cu-peak was found in the Sn-rich zone, as shown in Fig. 10(b). This indicates that Cu, originated from the Cu-layer, diffused through the Ni-barrier and moved into the solder. In order to determine the reason for Cu diffusion, AFM analysis was carried out on the Ni-layer (Fig. 11).

A relatively thinner position compared to other one was observed. From this result, it appears that Cu can diffuse more easily into the solder through the thinner position or other

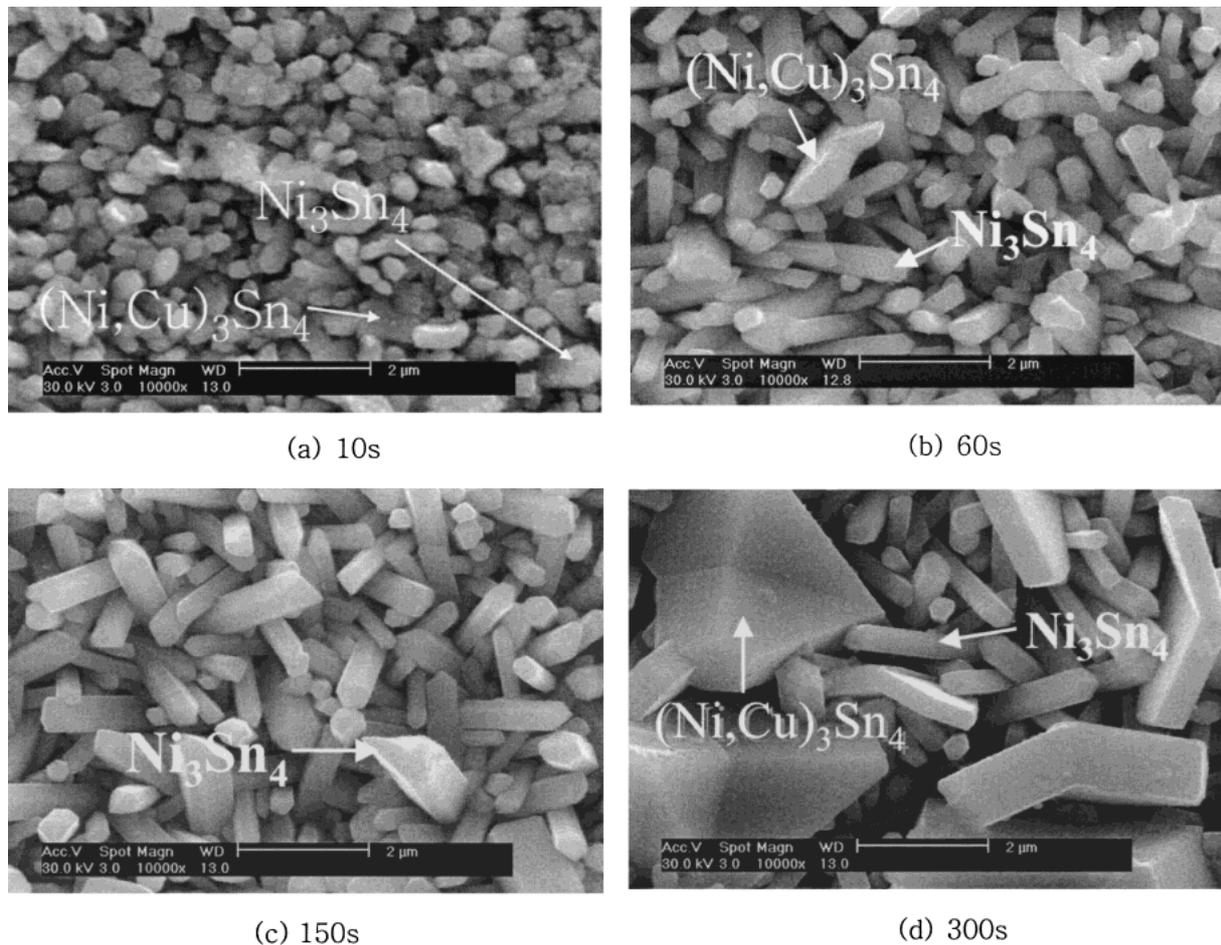


Fig. 8 Intermetallic compounds on the interface of Sn3Ag8Bi5In/UBM with reflow time (top-viewed, peak soldering temp: 513 K).

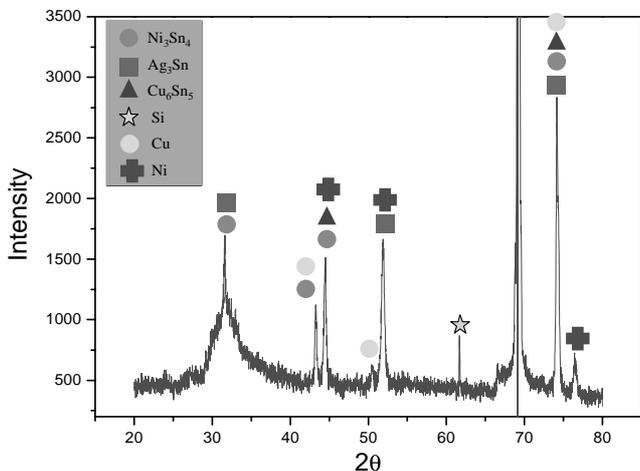


Fig. 9 X-ray diffraction pattern of the interface between Sn3Ag8Bi5In and UBM (soldering condition: 513 K, 10 s).

routes such as grain boundaries or micro-cracks in the Ni-layer.

Figure 12 shows a schematic illustration of the forming procedure of the IMC on the interface. In the initial stage of soldering (Fig. 12(a)), the  $\text{Ag}_3\text{Sn}$  compound and Bi-particle that exceeds the solid solubility gets distributed in the solder. After reflowing for 10 s, as in Fig. 12(b), needle-shaped  $\text{Ni}_3\text{Sn}_4$  and plate-like  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  were found with

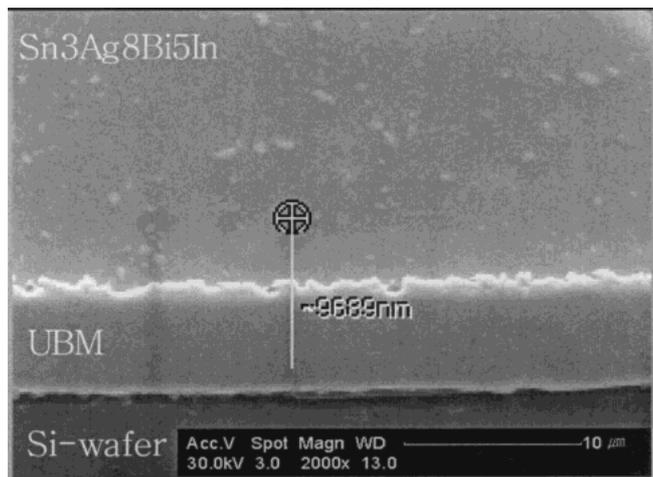
the  $\text{Cu}_6\text{Sn}_5$  on the interface. However, increasing the reflow time to more than 30 s, as shown in Fig. 12(c),  $\text{Ni}_3\text{Sn}_4$  and  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  became the dominant phases, and  $\text{Cu}_6\text{Sn}_5$  was not observed. The reason for the  $\text{Cu}_6\text{Sn}_5$  disappearance appears to be that Ni atoms around the  $\text{Cu}_6\text{Sn}_5$  diffuse into the  $\text{Cu}_6\text{Sn}_5$ , and  $\text{Cu}_6\text{Sn}_5$  transforms into  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$ . Ho *et al.*<sup>17)</sup> reported the effect of Cu on the  $\text{Ni}_3\text{Sn}_4$  transformation to  $(\text{Ni}_{1-x}, \text{Cu}_x)_3\text{Sn}_4$ . According to their result,  $\text{Ni}_3\text{Sn}_4$  changed into  $(\text{Ni}_{1-x}, \text{Cu}_x)_3\text{Sn}_4$  as a result of Cu addition into the solder, which was followed by Cu diffusion into  $\text{Ni}_3\text{Sn}_4$ . Similar work was carried out by Park *et al.*<sup>18)</sup> From these previous reports it is proposed that  $\text{Cu}_6\text{Sn}_5$  attached to the Ni-layer can change into  $(\text{Ni}, \text{Cu})_3\text{Sn}_4$  by Ni diffusion, and the Ni-layer will become the supplier of the Ni-atoms.

#### 4. Conclusion

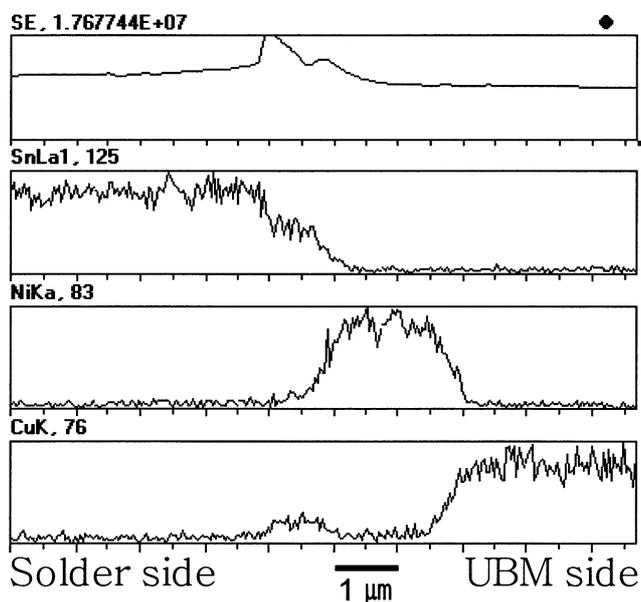
The shear strength and the interfacial compounds of a Sn-3Ag-8Bi-5In solder ball joint were investigated. A 0.5 mm diameter solder ball was set on a Ni/Cu/Cr-UBM, which was plated on the Si-wafer, and reflowed at the peak temperature of 493–533 K. The results are summarized as follows:

(1) The shear strength of the Sn3Ag8Bi5In ball shows the highest value of 1.69 N by reflowing at 513 K for 10 s, whereas that of the Sn37Pb was 1.60 N at 503 K for 15 s.

(2) The Sn-3Ag-8Bi-5In balls soldered at 493–533 K for 10 s were aged at 383 K for 16 days. The average strength



(a)



(b)

Fig. 10 Cross-sectional view (a) and line scan of EDS (b) across the interface between Sn3Ag8Bi5In and UBM (soldering condition: 513 K, 10 s).

of the joint after 16 days decreased by approximately 5% of the as soldered state.

(3) When the IMC thickness on the solder joint increased from 1.75 μm to 1.9 μm, the shear strength of the Sn3Ag8Bi5In ball decreased from 1.69N to 0.95N. However, beyond a thickness of 1.9 μm, the strength decreased slightly.

(4) Ni<sub>3</sub>Sn<sub>4</sub>, Ag<sub>3</sub>Sn, Cu<sub>6</sub>Sn<sub>5</sub> and (Ni, Cu)<sub>3</sub>Sn<sub>4</sub> were detected on the interface, and Ni<sub>3</sub>Sn<sub>4</sub> occupied the greater part of the interface.

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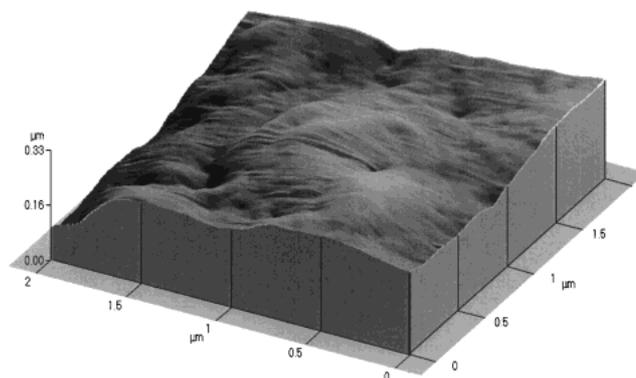
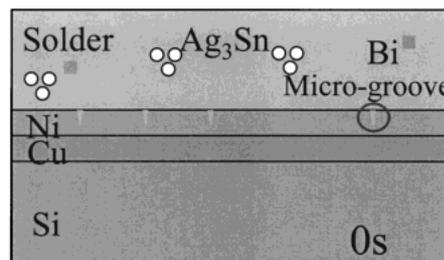
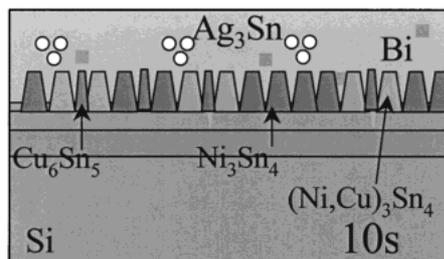


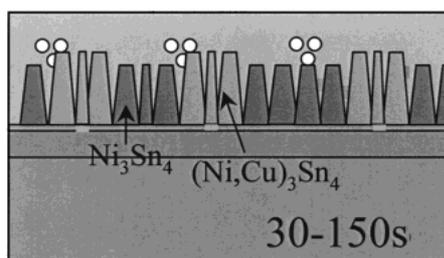
Fig. 11 Surface image of Ni-layer analyzed by AFM.



(a) initial stage



(b) 10s reflow



(c) 30 – 150s reflow

Fig. 12 Schematic illustration of IMC formation on the interface between Sn3Ag8Bi5In and Ni/Cu/Cr-UBM during reflow soldering.

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