Microstructural Evolution of Joint Interface between Eutectic 80Au–20Sn Solder and UBM

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The soldering behaviour of the eutectic Au–Sn alloy on two kinds of under bump metallurgy was studied in relation to time and temperature. For a Ni substrate, two types of the intermetallic compounds were observed at the joint: (Au,Ni)₂Sn₂ and (Au,Ni)₃Sn. As the soldering temperature increased, the shape of the (Au,Ni)₂Sn₂ grains generally changed from a long, thin rod-type to a short, thick type. The degree of buildup of the interfacial intermetallic compounds was similar up to 32 min, even if the soldering was conducted at three different temperatures between 300°C and 400°C. In addition, the reaction of the eutectic Au–Sn solder with the sputtered under bump metallurgy (Al/Ni/V/Au) was studied at 300°C. By 20 s of soldering, the protective Au layer was dissolved away and the Ni(V) layer started to dissolve into the solder. Thus, some of the Au reacted with the Al underlayer to form the Au₃Al phase, which was accompanied by volume expansion at the joint. The (Au,Ni)₂Sn₂ layer was then lifted up, and several interlocked (Au,Ni)₃Sn₂ grains were broken and separated at weak points along the joint interface. In this way, the joint interface was separated from the Si chip, and a resultant failure occurred in the device.

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1. Introduction

The investigation into the use of Pb-free solders as a replacement for the commonly used Pb–Sn solders has been initiated by environmental concerns over the use of lead in microelectronic packaging applications.¹,² In general, high-tin alloys are available as lead-free solder alloys. However, only a few of the alloys that can replace high-Pb solders have high melting temperatures. One strong candidate is the eutectic 80Au–20Sn solder by weight (71Au–29Sn by molar content); as shown in Fig. 1, this hard solder has an attractive melting point of 280°C.³ In addition, the yield strength of this solder is about the same as the yield strength of Cu.

When considering the use of eutectic Au–Sn solder, the first concern is the stress caused by the thermal expansion mismatch. Although the eutectic Au–Sn solder has no fatigue problem because of its hardness, the stresses that develop in typical bonded structures do not incur plastic deformation.

Eutectic Au–Sn solder has been successfully used for highly reliable die attach and fluxless soldering in optoelectronic packaging.⁴,⁵ This type of solder has high thermal and electrical conductivity, corrosion resistance, no thermal fatigue and the possibility of fluxless soldering. Traditionally, a system of Ti/Pt under bump metallurgy (UBM) has been used for eutectic Au–Sn soldering.⁶,⁷ In this case, the interaction between the Pt and Sn creates an excessive buildup of intermetallic compounds (IMCs), such as PtSn and PtSn₄.⁸ Therefore, the Au–Sn ratio in the solder changes to a more Au-rich composition, which significantly increases the liquidus temperature for the Au–Sn alloy. As a result, a nonuniform joint structure is formed, and this structure degrades the performance of the bonded chip.

In view of the degradation, several research efforts have been attempted to replace the Pt-based UBM. Nickel is an attractive replacement for the diffusion barrier metal because, as the Au–Ni phase diagram suggests, the solubility of Ni in Au is limited at soldering temperatures and Au and Ni fail to dissolve into each other below 100°C.⁹ Moreover, in contrast to Pt, Ni dissolves into an Sn-based solder at a low rate and it has higher thermal and electrical conductivities than other barrier metals, such as Cr and Pt.¹⁰,¹¹ Of course, the difference in thermal conductivity and electrical conductivity between Ni and Cr or Pt may not be important in this application because the layers are thin and the resulting

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difference in thermal resistance and electrical resistance can be ignored. Furthermore, a part of the Ni layer turns in the IMC layer after the soldering process.

Song et al. studied how the Au–Sn solder joint interacts on Cu and later replaced the UBM with a Cu/Ni/Au multilayer. Because they used typical electroless Ni plating, their work involved phosphorus (P). Moreover, they focused on the microstructure of the solder alloy itself rather than on the joint interface.

Our aim is to clarify the microstructural evolution of the eutectic Au–Sn solder’s joint interface. We conducted two kinds of experiments. Firstly, we examined the microstructural evolution of the IMCs between the eutectic Au–Sn and the pure Ni substrate (which contained no phosphorus) with respect to different soldering times and temperatures. Secondly, we studied how the eutectic Au–Sn solder reacted over time with sputtered UBM (Al/Ni(V)/Au) at 300°C.

2. Experimental Procedures

The eutectic 80Au–20Sn solder alloys were prepared from Au and Sn metals of purity higher than 99.9 percent. The samples were encapsulated in quartz tubes under vacuum, and then melted and mechanically mixed. We shaped the molten alloy into a wire-type specimen by injecting it through a fine hole (0.5 mm in diameter) and quenching it in water. We then cut the specimen into 1.1 mm lengths and converted it into a spherical shape (750 μm in diameter) by dropping it in silicone oil at 320°C.

In the first experiment, we put the spherical specimens on a Ni substrate (with a purity higher than 99.9 percent and a thickness of 0.5 mm), after first polishing the substrate with 1 μm of diamond paste and cleaning it with an acetone and ethanol solution. We then conducted sessile drop experiments in air by using rosin mildly activated flux. Next, we did soldering over time with sputtered UBM (Al/Ni(V)/Au) at 300°C.

In the second experiment, we used a trilayer of the Al/Ni(V)/Au structure as the UBM on an Si chip with a 1 μm thick Al metal pad, as shown in Fig. 2. We then sputtered the Al layer with a thickness of 0.4 μm and the Ni(V) layer with a thickness of 0.8 μm. To coat the top Au layer to a thickness of 0.18 μm, we immersed it in the Au coating solution. In addition, the Ni layer contained 7 at% V to reduce the magnetic interference during the sputtering process. Next, we conducted the sessile drop experiments in silicone oil to ensure temperature homogeneity without having to use rosin mildly activated flux. Finally, we performed the soldering at 300°C for periods ranging from 5 s to 5 min.

In both experiments, we examined the cross-sectional microstructure of the solder joint by using a scanning electron microscope (SEM) operated at 10 kV in a back scattered electron detector mode. In addition, to analyze the composition of the IMCs, we used an energy dispersive X-ray (EDX) operated at 20 kV. We found that the spatial resolution was approximately 1 μm diameter near the target point, and we determined the compositions by averaging more than five measurements. To observe a cross section of each layer of the IMCs, we divided the area of the layers by the width of the image. Furthermore, to measure the thickness of each layer, we used more than five SEM micrographs and we took into account the protruding particles. The error bars were determined as one standard deviation.

3. Results and Discussion

3.1 Microstructural evolution at the interface of a eutectic Au–Sn solder joint on a Ni substrate

Figures 3 and 4 show typical SEM micrographs of solder joints. Figure 3 shows a eutectic Au–Sn solder on a Ni substrate after soldering at 300°C for 1, 8 and 32 min, while Fig. 4 shows the results of soldering at 400°C. The interfacial IMCs seemed to grow initially as layer-type compounds and then coarsened with prolonged soldering. After a closer look, however, we found that the merged rod-type IMC particles formed a layer. Many IMC particles, which look like islands, were actually cross sections of the rod-type IMC particles grown randomly from different locations on the interface. It is difficult to determine the true shape of the IMC particles solely on the basis of the cross-sectional micrographs. We tried taking top view micrographs of the solder joint after we had etched away the remaining solder but the etching process was unsuccessful. Nonetheless, as the soldering temperature increased, the morphology generally changed from a long, thin rod-type to a short, thick type. In particular, as seen in Fig. 4(c), the island-type particles in the solder matrix seem to be cross sections of hexagonal cylinders that have been cut at a certain angle, thereby implying that the IMC particles (IMC1 in Fig. 5) take on the shape of a hexagonal cylinder.

As shown in Fig. 5, the microstructure inside the solder is lamellar and, as expected from Fig. 1, it must be composed of AuSn (δ-phase) and Au3Sn (μ-phase). The bright constituent in the eutectic microstructure is the μ-phase, whereas the darker one is the δ-phase. After soldering the specimen at 400°C for 32 min, we found two types of IMCs, marked IMC1 and IMC2, near the joint interface. To measure their compositions, we used EDX (Table 1).

As expected, we identified the bright phase of the lamellar structure as Au3Sn. The IMC1 phase was (AuNi)3Sn2 and the IMC2 phase was (AuNi)2Sn. According to Fig. 6, the tie line from the liquid eutectic Au–Sn solder composition is directed toward the Ni3Sn2 phase, whereas the Ni3Sn phase is located in the middle of the tie line that connects Ni3Sn2 to
We suggest, therefore, that the \((\text{Au,Ni})_3\text{Sn}_2\) phase is initially formed when the liquid eutectic Au–Sn solder reacts with the Ni substrate, and that the \((\text{Au,Ni})_3\text{Sn}\) phase is formed when the preformed \((\text{Au,Ni})_3\text{Sn}_2\) phase reacts with the Ni substrate. This kind of explanation is similar to that of Ronka et al., who used a phase diagram to predict a microstructural evolution of IMCs at the interface of the solder joint.\(^{15}\) On the other hand, Song et al. observed no \((\text{Au,Ni})_3\text{Sn}\) phase but only the \((\text{Au,Ni})_3\text{Sn}_2\) and \(\text{Au}_5\text{Sn}\) (\(\zeta\)) phases, which were present probably because of the short reflow time and the low reflow temperature.\(^{12,13}\) The reflow in their study included an exposure of 75 s above 280 °C, with a peak temperature of 315 °C.

Figure 7 shows the growth behaviour of IMC1 (excluding IMC2 in Fig. 5). The IMC1 thickness increases with soldering time, but the soldering temperature has a weaker effect on thickness than the soldering time. The joint interface shows an IMC1 buildup with a similar thickness. As long as the soldering time is the same, the difference in thickness is smaller than 1 µm.

The growth of IMCs is unlikely to be controlled by just one mechanism. Commonly, the growth of IMCs is affected by several factors such as soldering temperature, the number of diffusion paths or channels in the IMC layer, and the compositional difference between the solder and the IMCs. In the case of fine-grained intermetallics, grain boundary diffusion is regarded as dominant for the growth of the interfacial layer.

As shown in Figs. 3 and 4, the lateral size of the rod-type intermetallic grains at 300 °C is much smaller than the grains.
soldered at 400 °C. Thus, at lower temperatures, many empty channels exist among the small intermetallic grains, and these channels can accelerate the growth of the intermetallics. At 400 °C, the reaction rate is thermally activated but there are fewer diffusion paths or channels because of the grain coarsening effect. As a result, the growth rate of IMCs is retarded. This retardation probably explains why the thickness of IMC1 is similar even if they are soldered at three different temperatures between 300 and 400 °C.

Song et al. observed that, for aging at 200 °C, the growth rate of the interfacial layer in the eutectic Au–Sn solder bump on Ni is only about half the growth rate of the interfacial layer in the same solder bump on Cu. Subsequently, we focused on liquid-state soldering of the same alloy at higher temperatures up to 400 °C, and we observed that the growth in the kinetics of the interfacial IMCs was retarded.

### 3.2 Microstructural evolution at the interface of a eutectic Au–Sn solder joint on Al/Ni(V)/Au

New UBM was used in this test. Figure 8 shows the cross-sectional microstructure of the joint interface after we had soldered the eutectic Au–Sn solder on Al/Ni(V)/Au at 300 °C for periods of 20 s to 5 min. As shown in Fig. 5, the bright constituent in the eutectic Au–Sn solder is Au5Sn (ζ-phase) and the dark constituent is AuSn (δ-phase). Compared with Fig. 5, the large islands of the ζ-phase in Fig. 8(a) seem to have been caused by the Au that dissolved from the thin protective Au layer, which we deposited to ensure wetting by the solder. Once the solder became molten, the Au layer dissolved and slightly increased the Au content in the liquid solder. This process caused the Au–Sn solder to have an off-eutectic composition, and it enabled the proeutectic formation of the ζ-phase. Our results are consistent with the findings of Song et al. The only difference was the UBM structure; that is, in their setup, Song et al. used Cu/electroless Ni/Au.

After we had soldered for 20 s, the protective Au layer had already dissolved into the solder, and the Ni(V) layer had partially dissolved into the solder. Thus, the shape along the interface was rugged. The Al underlayer was sporadically exposed to the solder, and Au–Ni–Sn particles formed at several locations [Fig. 8(a)]. The lamellar microstructure inside the solder was typical of a eutectic alloy. After we had soldered for 1.5 min, the growth of the intermetallic layer was not uniform. Hence, we detected a locally attacked spot in the

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### Table 1 Compositions (in at%) of IMCs after soldering at 400 °C for 32 min.

<table>
<thead>
<tr>
<th>IMC</th>
<th>Au (at%)</th>
<th>Ni (at%)</th>
<th>Sn (at%)</th>
<th>phase formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMC 1</td>
<td>13.6 (±1.1)</td>
<td>47.2 (±1.6)</td>
<td>39.2 (±0.7)</td>
<td>(Au,Ni)5Sn2</td>
</tr>
<tr>
<td>IMC 2</td>
<td>2.9 (±0.1)</td>
<td>72.5 (±0.6)</td>
<td>24.6 (±0.7)</td>
<td>(Au,Ni)3Sn</td>
</tr>
<tr>
<td>bright phase inside the solder</td>
<td>83.1 (±1.0)</td>
<td>16.9 (±1.0)</td>
<td>Au5Sn</td>
<td></td>
</tr>
</tbody>
</table>
Al layer, as marked by an arrow in Fig. 8(b). The spot was probably caused by differences in the Ni content that had dissolved into the molten solder. The eutectic Au–Sn solder that penetrated the Ni(V) layer reached the bottom of the Al layer, and, as shown in Fig. 8(c), some of the Au reacted with Al to form an Au–Al compound. We measured the composition as (70–74)Au(25–29)Al (in atomic percent), and this composition corresponded to the Au$_8$Al$_3$ phase. Moreover, (Au,Ni)$_3$Sn$_2$ formed at the interface of the solder and the Ni(V) layer.

When an Au–Al compound forms at the interface, the volume of the compound expands. The (Au,Ni)$_3$Sn$_2$ layer is lifted up as a result of the compound’s volume expansion and, as shown in Fig. 8(d), the interlocked (Au,Ni)$_3$Sn$_2$ grains are broken and separated at weak points along the interface. Eventually, after we had soldered for 5 min, as shown in Fig. 9, the liquid Au–Sn solder entered through the disconnected (Au,Ni)$_3$Sn$_2$ layer and filled the area below the (Au,Ni)$_3$Sn$_2$ layer and above the Si chip. The arrow shows the presumed direction of the solder flow. By this stage, the entire UBM reacted to form (Au,Ni)$_3$Sn$_2$ or diffused into the solder matrix.

The Au–Al compound forms easily between Au and Al because the activation energy that forms the Au–Al compound is smaller than 1 eV.\textsuperscript{17) To determine the extent to which the formation of the Au–Al compound changes the volume, consideration was given to the densities of Al, Au and the Al–Au compound.\textsuperscript{18) The $\tau$ in eq. (1) expresses the volume ratio of $v_i/v_{Al}$, which is equal to the ratio of the thickness of the Au–Al compound to that of the Al layer, $h_c/h_{Al}$:

$$
\tau = \frac{v_c}{v_{Al}} = \frac{h_c}{h_{Al}} = \rho_{Al} \left(1 + \frac{A_i P_i}{A_{Al} P_{Al}}\right),
$$

where $v$ is the volume, $h$ is the height, $\rho$ is the density, the subscript $c$ stands for the Au–Al compound, $A_i$ is the atomic mass, and $P_i$ is the atomic fraction of $i$ in the Au–Al compound ($i = $ Au, Al). The value of $\rho_{c}$ in Au$_8$Al$_3$ was already calculated using the volume of the unit cell and the number of atoms in the unit cell as given by Range and Buchler.\textsuperscript{19) By using $\rho_{c}$ for Au$_8$Al$_3$ and $\rho_{Al}$, we calculated $A_i$, $P_i$, and $\tau$.\textsuperscript{20)
Table 2 Volume change due to the formation of Au$_8$Al$_3$ IMC between Al and Au.

<table>
<thead>
<tr>
<th>Compound material</th>
<th>unit cell volume (10$^{-24}$ cm$^3$)</th>
<th># of Au atoms in unit cell</th>
<th># of Al atoms in unit cell</th>
<th>density (g/cm$^3$)</th>
<th>$\tau$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_8$Al$_3$</td>
<td>2174.3</td>
<td>96</td>
<td>36</td>
<td>15.19</td>
<td>3.64</td>
</tr>
</tbody>
</table>

$\tau$ in eq. (1)

In Table 2, the value of $\tau$ in Au$_8$Al$_3$ shows that the thickness of the layer increases about 3.6 times more than that of Al. Therefore, when Au$_8$Al$_3$ forms between Au and Al, the volume increases significantly at the joint interface. Because the volume expansion weakens the bond at the joint interface, the joint interface may be separated from the Si chip and a failure may occur in the device. This outcome is of course detrimental, and the Al layer must be protected in a safer way to be used as UBM material. For this purpose, we strongly recommend a Ni(V) layer that is thicker than 0.8 $\mu$m.

4. Summary

We studied the soldering behaviour of the eutectic 80Au–20Sn alloy in two types of metallization with respect to the variables of time and temperature. In the case of the Ni substrate, we observed two IMCs at the joint, namely (Au,Ni)$_2$Sn$_2$ and (Au,Ni)$_3$Sn. The (Au,Ni)$_3$Sn$_2$ phase was initially formed by the reaction between the liquid eutectic Au–Sn solder and the Ni substrate; the (Au,Ni)$_2$Sn phase was formed by the reaction of the preformed (Au,Ni)$_3$Sn$_2$ phase and the Ni substrate. As the soldering temperature increased, the morphology of the (Au,Ni)$_3$Sn$_2$ grains changed from a long, thin, rod-like shape to a short, thick shape. The thickness of the IMC layer was similar up to 32 min, even if the soldering was performed at different temperatures between 300 and 400°C.

We also investigated how the eutectic Au–Sn solder reacted with the sputtered UBM (Al/Ni(V)/Au) at 300°C for 5 min. The protective Au layer dissolved away, and the Ni(V) layer partially dissolved into the solder. Thus, some of the Au reacted with the Al underlayer to form the Au$_8$Al$_3$ compound, and the volume of the compound expanded at the joint. The (Au,Ni)$_3$Sn$_2$ layer at the joint was lifted up and some of the interlocked (Au,Ni)$_3$Sn$_2$ grains were broken and separated at weak points. As a result, the joint interface separated from the Si chip and failure occurred in the device.

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