Effects of Minor Alloy Additions on the Interfacial Reactions with Low Solder Volume for 3D IC Applications

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Chip stacking with low volume solder for 3D IC integration

- 3D IC Micro-bump + Through Silicon Vias (TSV)

### 3D IC integration

![Diagram of 3D IC integration](image)

Advantages:
- Better performance
- Smaller footprint
- Lighter package

![Diagram of 2.5D IC integration](image)

Using a silicon interposer allows for signal remapping from one active chip to another without requiring customized designs.

### 2.5D IC integration

- Micro-bumps with through silicon via (TSV) is an emerging packaging technology, which provides electrical connectivity between different functional dies, high density interconnection with relatively fine pitch, and excellent thermal conductivity in 3D ICs.

- 3D IC technique provides the continuous growth of semiconductor industry, which gives the opportunity to go beyond Moore’s law.

Greatly reduced solder volume in 3D IC solder joints

Ball Grid Arrays

Flip-Chip

Micro-bumps

substrate

Solder

substrate

Wafer level 3-D Ics process technology. A Munding, et al., 2008

Increasing packaging density

To achieve the demands for ultra-fine pitch and higher I/O densities, reduction in solder volume is an inevitable trend for high-end microelectronic applications. Compared with traditional flip chip solder joints, the solder volume of a 3D IC micro-bump shrinks by a factor of 1000.

One well-perceived effect caused by reducing in solder volume is that the solder joint would end in presenting with a relatively large fraction of the intermetallic compounds (IMCs), which inclines to increase the mechanical loadings more than before, and in turn may create some potential reliability challenges. Based on this concern, interfacial reactions between solder and metallization have become one of the imperative issues in evaluating the reliability of 3D IC devices during long-term performance. Accordingly, it is worthwhile to attract more attention and extensive exploration.
**Objective of the present work**

- It is widely known that *minor alloy additions to solder* have pronounced effects on the interfacial reactions between solder and metallization. These alloying elements might substantially change the reaction/growth rate and the morphology of the interfacial reaction products. The objective of this study is mainly focus on investigating the effects of minor alloy additions within limited volume of solder.

- In addition, many studies have been conducted to investigate the effect of minor alloy additions on BGA or Flip-Chip solder joints. However, few literatures or information are reported regarding the role of minor alloying element as well as the subsequent microstructure evolution within the extremely small solder volume.

- In this current study, two extreme types of alloy elements including inert element *Bi*, and a highly reactive element, *Zn* will be added to Sn matrix to study the effects on the interfacial reactions. Furthermore, some potential reliability concerns will be proposed based on ultimate microstructure in a space confined micro-bump during high temperature storage (HTS).

<table>
<thead>
<tr>
<th>Elements</th>
<th>Cu₆Sn₅ growth</th>
<th>Cu₃Sn growth</th>
<th>Thickness of Cu₆Sn₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>Slight increase</td>
<td>Slight decrease</td>
<td>No influence</td>
</tr>
<tr>
<td>Sb</td>
<td>Slight decrease</td>
<td>NA</td>
<td>No influence</td>
</tr>
<tr>
<td>Fe</td>
<td>Slight decrease</td>
<td>Decrease</td>
<td>No influence</td>
</tr>
<tr>
<td>Co</td>
<td>Increase when x₃ &gt; 0.2 at%</td>
<td>Decrease</td>
<td>Decrease</td>
</tr>
<tr>
<td>Mn</td>
<td>NA</td>
<td>Decrease</td>
<td>NA</td>
</tr>
<tr>
<td>Ti</td>
<td>Slight decrease</td>
<td>NA</td>
<td>Increase</td>
</tr>
<tr>
<td>In</td>
<td>Slight increase</td>
<td>NA</td>
<td>No influence</td>
</tr>
<tr>
<td>Ni</td>
<td>Slight decrease</td>
<td>Decrease</td>
<td>Decrease</td>
</tr>
<tr>
<td>Ge</td>
<td>Increase</td>
<td>Increase</td>
<td>Increase</td>
</tr>
</tbody>
</table>

Schematic diagram of the sandwich structure

Chip to Chip bonding

1. Pure Sn
2. Sn10Bi
3. Sn0.4Zn

10um (±1um)

- Aspect ratio of this structure is about 1/100, so the atomic diffusion flux is only along the vertical direction.

Experimental flow chart

1. Bonding sandwich structure
2. Solid / Solid reaction
   isothermal aging @ 120 °C
3. Microstructure observation
Microstructure evolutions of Cu/Sn/Cu @ 120 °C

- Not only IMC but also Kirkendall voids increased at the Cu/Cu₃Sn interface and within the Cu₃Sn layer during aging process.
- Scalloped-like → Planar-like
**Microstructure observation of Cu/Pure Sn/Cu @ 120 °C**

- The followings summarize the interfacial morphology of Cu/Sn/Cu sandwiches structure aged at 120°C for different aging times.

  **As-reflowed**  
  Cu$_6$Sn$_5$ IMC located at the solder/Cu interface was identified by EDX and displayed a scalloped morphology.

  **At 150-1050hr**  
  During solid-state reaction, the morphology of Cu$_6$Sn$_5$ had transformed to a planar-like structure. The thickness of Cu$_6$Sn$_5$ and Cu$_3$Sn increased with aging time. The original Sn layer gradually transformed to Cu$_6$Sn$_5$ and Cu$_3$Sn. In addition, growth of Cu$_3$Sn is much faster than Cu$_6$Sn$_5$, and the ratio of Cu$_3$Sn/Cu$_6$Sn$_5$ had nearly exceed ½. It is believed that Cu$_6$Sn$_5$ growing from the opposite interfaces would eventually impinge on each other during further aging.

**IMC growth kinetics in Cu/Pure Sn/Cu reaction @ 120 °C**

- Based on the above experimental results, the thickness of Cu$_3$Sn was higher than Cu$_6$Sn$_5$, and the IMC growth process remained a diffusion-controlled process.
Microstructure evolutions of Cu/Sn10Bi/Cu @ 120 °C

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Effects of minor Bi addition (Sn10Bi @ 120 °C)

The followings summarize the interfacial morphology of Cu/Sn10Bi/Cu sandwiches structure aged at 120°C for different aging times.

At 150-900hr

The thickness of Cu₆Sn₅ and Cu₃Sn increased with aging time. Compared with the Cu/Sn/Cu case, Cu₃Sn were slightly inhibited. At 750hr, Cu₆Sn₅ growing from the opposite interface started to impinge on each other. In addition, due to the solubility of Bi in Cu₆Sn₅ and Cu₃Sn was extremely low, Bi will be rejected and coarsen together from solder matrix as Sn was consumed by the formation of IMCs. Finally, Bi-rich phase remained in the middle of the interface, which is a typical result of symmetrical interfacial reaction.

At 900-1350hr

Because of lacking residual Sn, Cu₃Sn starts to react with Cu₆Sn₅. The thickness of Cu₃Sn increased with aging time, which leads the reduction in Cu₆Sn₅.

The grain boundary of Cu₆Sn₅ (green dotted circle) was clearly revealed by mechanical polishing. The result showed that Cu₆Sn₅ from opposite side were still two individual grains after long time aging.
**Impurity concentration** rise due to solder consumption

The following schematic drawings show the different stages about impurities that are rejected during the reactions.

Fig.(a) displays the impurities randomly dispersing in the solder joints.

Fig.(b) reveals the impurities rejected from the reaction accumulating at the IMC/solder interface.

Fig.(c) shows all rejected impurities located at the center of the interface, and the IMCs growing from the opposite interfaces started to impinge on each other.

The binding strength of this ultimate microstructure would be a crucial factor mainly affecting the joint reliability in 3D ICs integration, which should be further studied.
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Results & Discussion

IMC growth kinetics in \( \text{Cu/Sn/Cu} \) and \( \text{Cu/Sn10Bi/Cu} \) reaction @ 120 °C

- Compared with \( \text{Cu/Sn/Cu} \) case, it was found that the total IMC in \( \text{Sn10Bi/Cu} \) case increased significantly faster than in pure \( \text{Sn/Cu} \) case during the same solid-state aging condition.

- Bi has been commonly known as an inert element. However, it’s interesting to note that minor Bi additions can slightly retard the growth of Cu3Sn sub-layer during thermal aging at 120°C. This result also implied that Bi in a certain extent participated interfacial reaction, which is worthy of further studying.
Microstructure evolutions of Cu/Sn0.4Zn/Cu @ 120 °C

Effect of Minor Alloy Additions on the Interfacial Reactions with Low Solder Volume for 3D IC Applications | October 5, 2011
**Effects of minor Zn addition (Sn0.4Zn @ 120 °C)**

- The followings summarize the interfacial morphology of Cu/Sn0.4Zn/Cu sandwiches structure aged at 120°C for different aging times.

  **As-reflowed~1050hr**

With increasing time of aging, the morphology of Cu₆Sn₅ became more or less planar. Compared with the Cu/Pure Sn/Cu case, the results indicated that the thickness of Cu₆Sn₅ and Cu₃Sn were markedly retarded by a small amount of Zn addition. In addition, there were no Kirkendall voids within Cu₃Sn even after thermal aging for more than 1050hr, as shown in the enlarged figure of 1050hr.

**IMC growth kinetics in Cu/Sn0.4Zn/Cu reaction @ 120 °C**

- As mentioned earlier, IMCs growing from the opposite interfaces will eventually impinge on each other, which would have the opportunity to become a source of mechanical weakness particular for unanticipated shear strength during long-term performance. In contrast, this circumstance can be effectively prolonged and improved by minor Zn addition.
**Effects of inert and highly reactive elements**

**Sn10Bi V.S. Pure Sn V.S. Sn0.4Zn @ 120°C**

- **Sn10Bi**:
  - 150 hr: Cu layer with Cu$_6$Sn$_5$ and Cu$_3$Sn phases.
  - 600 hr: Cu$_6$Sn$_5$ and Cu$_3$Sn layers form.
  - 1050 hr: Bi-rich layer formed with Cu$_6$Sn$_5$ and Cu$_3$Sn.

- **Pure Sn**:
  - 150 hr: Cu layer with Cu$_6$Sn$_5$ and Cu$_3$Sn phases.
  - 600 hr: Cu$_6$Sn$_5$ and Cu$_3$Sn layers form.
  - 1050 hr: Cu$_6$Sn$_5$ and Cu$_3$Sn layers remain.

- **Sn0.4Zn**:
  - 150 hr: Cu layer with Cu$_6$Sn$_5$ and Cu$_3$Sn phases.
  - 600 hr: Cu$_6$Sn$_5$ and Cu$_3$Sn layers form.
  - 1050 hr: Cu$_6$Sn$_5$ and Cu$_3$Sn layers remain.
The effect on the growth kinetics of the IMC layer in solder/Cu micro-bumps, caused by adding two extreme minor alloy to pure Sn solder alloy, reveals difference in IMC layer growth rate. The growth rate of total IMC layer at the interface of Sn0.4Zn/Cu was much slower than that at the interface of Pure Sn/Cu and Sn10Bi/Cu. Moreover, the above results also indicated that adding minor Zn could extensively decrease the growth rate of Cu₃Sn layer which always accompanied with the formation of micro voids particular in the substrate made by electroplating process.

What’s more, compared with Sn10Bi and Pure Sn, the addition of minor Zn can also effectively suppress the formation of Kirkendall voids at the interface of Cu/Cu₃Sn or within the Cu₃Sn layer even after solid-state aging for 1050hr.
In **Cu/Sn10Bi/Cu** case, Bi atoms would be rejected from the reaction accumulating at the IMC/solder interface during solid/solid isothermal reaction. Finally, Bi located at the center of the interface. IMCs growing from the opposite interfaces started to impinge on each other. The binding strength of this ultimate microstructure should be further studied since it would have the opportunity to become a source of mechanical weakness particular for accidental mechanical shock during long-term performance, which would be a crucial factor mainly affecting the reliability of the diminutive joints in 3D ICs products.

In this study, IMC growth kinetics at the interface of **Cu/Pure Sn/Cu, Cu/Sn10Bi/Cu, and Cu/Sn0.42Zn/Cu** with low solder volume were investigated under high temperature storage duration. Compared with Cu/pure Sn/Cu case, the results showed that the addition of highly reactive element, Zn, can retard the growth rate of total IMCs (including Cu₆Sn₅ and Cu₃Sn) more effectively than the addition of Bi, which can delay the formation of excessive IMC during long-term service. Furthermore, it was found that Zn has prominent effect on inhibiting the formation of micro voids within Cu₃Sn IMC layer and at the interface of Cu/Cu₃Sn. This result will be a helpful reference for ultra-pitch micro-bumps designer to find other choices in inhibiting the formation of excessive IMC in diminutive solder joints.

This effort also indicated that the addition of inert element, Bi, in lead-free solder with 10wt% can significantly enhance the IMC growth in micro-bumps with Cu substrate during thermal aging, and further studies are carried on.
Thanks for your attention