Dissolution and reaction between Au and molten eutectic PbSn solder

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Abstract

Dissolution and reaction both play important roles in the interaction between Au studs and PbSn solders. The kinetics of interfacial reaction in this system has been studied by measuring the rate of Au consumption and growth rate of the AuSn intermetallic compound (IMC) layer at temperatures from 190 °C through 260 °C. Different AuSn compounds are identified at different isothermal bonding temperatures in accordance with the Au/Pb/Sn ternary phase diagram. The rates of Au consumption and AuSn layer growth can be shown to obey a time-based power-law relationship. The rate of Au consumption into molten eutectic PbSn solder is non-parabolic with a time exponent varying from 0.276 to 0.575. The Au consumption is faster than the growth of the AuSn layers because Au dissolves rapidly into molten solder even with the formation of intermetallic layers.

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1. Introduction

Soldering is one of the oldest metallurgical processes for joining metal parts. The use of solder in modern microelectronic technology is ubiquitous due to its indispensable role in stencil printing, good thermal performance, reliable joints, and robust assembly processes [1,2]. Au is commonly used with solder in a flip chip interconnection system [3,4]. This is driven by Austud bumping technology, which motivates a fine-pitch, low-cost solution using existing wirebond infrastructures and removing underbump metallization for flip chip bonding [5]. The Au and solder interconnect enables a fluxless interconnect system [6]. However, being a tin-based solder, poor reliability with Au may be a result of rapid kinetics in forming a brittle intermetallic compound (IMC). Formation of IMC gives rise to a decrease in both peel strength and shear strength [7–9], dampening the prospect of Au and solder in flip chip solutions. Thus, the interface kinetics of Au with solder is studied to enhance joint reliability of fluxless thermo-mechanical bonding with joint-in-via architecture in an ambient atmosphere [6]. Both dissolution and reaction play important roles in interfacial interaction [10]. The total chemical driving force arises from the dissolution of substrate in molten solder and from the interfacial reaction in forming intermetallic compounds [11]. As Au comes into contact with molten solder, Au first dissolves and diffuses throughout the solder [12]. This is due to the high solubility of Au in molten eutectic PbSn solder, about 7.8% at 220 °C [12]. At the interface, the molten solder reaches the solubility limit of Au, and IMC starts to form. IMC nucleates heterogeneously and eventually grows into a layer. This produces the IMC AuSn4 and AuSn2 at the interface. Similar phases are observed for eutectic solder with AuNi/Cu metallization during reflow at 225 °C [10]. The formation of AuSn4 occurs at 177 °C; AuSn2 forms between the Au and AuSn4 once a layer of AuSn4 is formed, Au dissolution is significantly reduced [13]. Besides the continued dissolution of Au, the IMC layer is also consumed in the molten solder through spalling of AuSn4 intermetallics from the interface [10,12]. During cooling, the saturated Au solution precipitates as AuSn4 intermetallics. The morphologies and kinetics at the interface have a profound effect on assembly and joint reliability. According to

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past literature, a thin intermetallic layer is desirable for forming joints with metallurgical bonds; however, excessive intermetallic growth is deleterious to joint reliability. As Au diffuses rapidly in solder [13–15], formation of brittle Au-containing IMC is a serious concern. According to Kim and Tu [13], Au has an interdiffusion coefficient of $6 \times 10^{-7}$ cm$^2$ s$^{-1}$ in molten solder at 240 $^\circ$C. The dissolution rate of Au wire in eutectic solder at 209 $^\circ$C is estimated to be 1.33 $\mu$m s$^{-1}$ [16–18]. Due to the fast dissolution of Au in molten solder, a coarse, anisotropic, brittle AuSn compound forms, which results in a weak interface between the AuSn compound and the solder matrix [7].

2. Experimental procedure

Gold studs with a tip diameter of 25 $\mu$m were mechanically bumped on an aluminium-metallized die using a thermosonic wire bonder. The Au-bumped die was then bonded into a corresponding via containing eutectic PbSn solder [4]. The height of the Au studs was measured using a high-magnification 2D microscope. A total of 50 bumps were measured, and the average height of the studs was used for analysis. The interaction of Au with molten eutectic PbSn was investigated at temperatures of 190, 230, and 260 $^\circ$C for durations of 0.3, 1, and 3 s. The bonded Au-solder samples were directly encapsulated in epoxy and sectioned for analysis using a diamond cut-off wheel. The cross-sections of the joints were prepared for metallography. The phase characterization was carried out using a scanning electron microscope (SEM) with an energy-dispersive X-ray detector (EDX). For better phase contrast, the SEM images were captured in back-scattering mode; each intermetallic layer was identified by EDX, and the layer thickness was measured at different locations across the interface using a digitized SEM micrograph. After bonding, the remaining height of the Au stud was measured using a high-magnification microscope. That measurement was then subtracted from the average height of the stud to estimate the thickness of the Au consumed. The number of moles of Au in each intermetallic layer and Au consumed was estimated by subtracting the initial conical volume of the bumps from the remaining conical bumps after bonding and dividing by the molar volume of the intermetallic phases and Au, respectively. The molar volume of AuSn$_2$, AuSn$_4$, and Au were taken as 42.8, 75.0, 10.2 cm$^3$ mol$^{-1}$, respectively [19].

3. Result and discussion

3.1. Phase morphologies under different bonding conditions

Fig. 1 is the SEM image of the solid-liquid interface after bonding at 190 $^\circ$C for 0.3 s. A thin layer of AuSn$_4$ was formed at the interface during solidification. The needle-like AuSn$_4$ phase radiated from the interface. The sequence of the IMC formation can be traced using the concept of local equilibrium [20] and the binary section of the ternary phase diagram [9,21]. As such, AuSn$_4$ appeared to be the first phase at 190 $^\circ$C as estimated by the isothermal line in Fig. 2. This phase eventually formed a continuous AuSn$_4$ intermetallic layer as seen at the interface in Fig. 1. During cooling, the saturated Au solution precipitated as AuSn$_4$ according to the Au/PbSn phase diagram. This resulted in needle-like AuSn$_4$ formation throughout the solder due to its orthorhombic crystal structure. At the interface, the intermetallic broke off and fell into the molten solder, brittle and further stressed by the precipitation cooling. As such, it appeared as though it had spilled off from the interface. Ho et al. [10] observed similar results for Au with PbSn. Fig. 3 shows precipitation of AuSn$_4$ phases at the base of the joint. The AuSn$_4$ phases were ascertainment to be from the dissolved Au as there was no sign of AuSn$_4$ phases forming with eutectic PbSn in the via architecture. This suggested a high diffusivity of Au in molten solder. The drive of these AuSn$_4$ phases may be a concentration gradient of Au or the lowering of the free energy through the formation of ternary thermodynamic phases Au$_{0.5}$Ni$_{0.5}$Sn$_4$ [22,23]. For samples at 190 $^\circ$C for 1 and 3 s, similar AuSn$_4$ phases were observed with thickening in the IMC layer and with more rod-like AuSn$_4$ phases spalling off the interface into the solder (Fig. 4). Identical phases were observed
Fig. 3. Interfacial microstructures showing AuSn$_4$ phases at the base of the Au–PbSn joint after bonding.

Fig. 4. Thickening of AuSn$_4$ layer and rod-like AuSn$_4$ phases spalling off the interface at 190$^\circ$C for 3 s. This was the result of more Au dissolving into molten PbSn over a longer bonding time.

Fig. 5 is the SEM back-scattered images for bonding at 230$^\circ$C for 1 s. EDX analysis identified that a thin layer of about 1 $\mu$m of the AuSn$_2$ phase formed at the interface followed by AuSn$_4$ layer of about 5 $\mu$m at 0.3 s. A large rod-like AuSn$_4$ phase appeared as dendrites encroaching into the bulk solder. The formation of the AuSn$_2$ layer is thermodynamically favored at 230$^\circ$C (Fig. 2). This suggests that AuSn$_2$ forms at the bonding interface while Au dissolves into molten PbSn. Due to the higher bonding temperature, the diffusivity of Au increases and more Au diffuses into the solder. During cooling, the saturated solution precipitates as AuSn$_4$ with Pb-rich phases around the vicinity. At higher bonding temperatures, the amount of AuSn$_2$ phase at the base increases. Similarly, the thickening intermetallic layer and growth of AuSn$_4$ formations were observed at longer bonding times.

At a bonding temperature of 260$^\circ$C, AuSn$_2$ and AuSn$_4$ layers were detected and the AuSn$_2$ layer thickened. Larger chunks of rod-like AuSn$_4$ phases were observed to spall off the interface as shown in Fig. 6. Table 1 summarizes the IMC morphologies at the solid–liquid interface. Similarly, the thickening phenomenon and rod-like AuSn$_4$ phases were seen to extend into the bulk solder as bonding time increased.

3.2. Kinetics at the solid–liquid interface

Following Ghosh [24], a generic power law in Eq. (1) was used to establish the relationship between the Au consumed and its IMC growth in the Au-eutectic PbSn solder system. In Eq. (1), $x$ is the intermetallic thickness, $k$ the rate constant at temperature $T$, $t$ the time of bonding, and $n$ is the time exponent. This equation has similar empirical expressions as one set forth by Ghosh [24] for kinetic growth since the rate of Au diffusion in molten solder dominates the reaction. Time-dependent diffusivity is indicated by $n$ (that is, $n < 0.5$ diffusivity increase with time, and vice

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>0.3</th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>AuSn$_2$</td>
<td>AuSn$_4$</td>
<td>AuSn$_4$</td>
</tr>
<tr>
<td>230</td>
<td>AuSn$_4$ and AuSn$_2$</td>
<td>AuSn$_4$ and AuSn$_2$</td>
<td>AuSn$_4$ and AuSn$_2$</td>
</tr>
<tr>
<td>260</td>
<td>AuSn$_4$ and AuSn$_2$</td>
<td>AuSn$_4$ and AuSn$_2$</td>
<td>AuSn$_4$ and AuSn$_2$</td>
</tr>
</tbody>
</table>

Table 1. Summary of morphologies present with different TM bonding temperatures
versa), while \( k \) is the rate constant with temperature (that is, diffusivity is higher with an increase in temperature).

By applying a natural logarithm in Eq. (1), a regression line can be plotted over the growth of individual AuSn intermetallic layers and over the rate of Au thickness consumed over time, as shown in Fig. 7 to estimate \( n \) and \( k \) using Eq. (2).

\[ x = k t^n \]  
\[ \ln x = n \ln t + \ln k \]  

Fig. 7 shows the growth of AuSn\(_4\) layers and the consumption of Au at 190\(^\circ\) C. The Au thickness was consumed at a constant rate of 3.27 \( \times 10^{-4} \) cm s\(^{-1}\) with a time exponent of 0.575\(^{[1]}\). The rate of Au thickness consumption appears to retard with time. This is likely due to the formation and growth of the AuSn\(_4\) layer, which acts as the diffusion barrier for Au to dissolve into molten solder. As the diffusion barrier’s thickness increases with time, the rate of Au dissolved into molten solder decreases. The AuSn\(_4\) thickness seen at 190\(^\circ\) C, which may include thickness gained from precipitation during cooling, was closed to the Au thickness consumed. Positive IMC growths were also observed for AuSn\(_2\) and AuSn\(_4\) intermetallic layers at a bonding temperature of 230\(^\circ\) C, as shown in Fig. 8. It was difficult to quantify the growth of the AuSn IMC layers in solid-liquid interdiffusion by examining the growth of an individual IMC layer. The individual IMC layers grew at different rates with time due to changes in the atomic volume of diffusing species\(^{[11]}\), different IMC layer formations\(^{[11]}\), different layers formed by precipitation, etc. The sum of all the IMC layers’ thickness does not equal the thickness of the Au consumption. This is because a significant amount of Au is dissolved into the molten solder during solid-liquid interdiffusion. The next section will quantify the amount of Au dissolved in molten solder.

IMC growth is a complex process, which is difficult to describe mathematically. The rate of gold consumption appears to be a better representation in solid-liquid interdiffusion than does a direct description of IMC growth. The \( k \) and \( n \) of the consumed thickness of Au for bonding temperatures of 190, 230, and 260\(^\circ\) C are computed and summarized in Table 2. The rate constant \( k \) increased with bonding the temperature as the diffusivity increased. This behavior is similar to the Arrhenius relationship\(^{[25,26]}\), where the rate constant is exponentially proportional to an inverted absolute temperature in Kelvin.

The coefficient of the time exponent \( n \) varies for 0.575 for 190\(^\circ\) C and 0.28 for bonding temperatures from 230\(^\circ\) C through 260\(^\circ\) C with \( n \) for temperatures from 230\(^\circ\) C through 260\(^\circ\) C being almost similar. A non-parabolic Au-consumption rate was observed for the solid-liquid interdiffusion for Au with molten eutectic solder. This differed from Au with SnAgCu where a parabolic Au consumption rate was observed\(^{[27]}\). Thus, the interdiffusion coefficient of Au into molten solder cannot be computed and compared. The differences in the relationship were accounted for by the different intermetallic diffusion barriers and thickness formed at the bonding temperature. This generated a different atomic mechanism with a different diffusivity rate for Au diffusing through the barrier into molten solder. The rate of Au consumption varied with time and dissolution rate in the same order of magnitude as given by Bader\(^{[18]}\).

### 3.3. Dissolving of Au in solid-liquid interface

During bonding, the dissolution and reaction mechanisms compete with each other to reduce the free energy of the sys-

![Fig. 7. Growth of AuSn\(_4\) layers and Au thickness consumed at 190\(^\circ\) C.](image)

![Fig. 8. Growth of AuSn\(_2\), AuSn\(_4\), total IMC layer, and Au consumed at 230\(^\circ\) C.](image)

\[ y = 0.575x + 1.18 \]  
\[ y = 0.500x + 1.15 \]  

Table 2: Summary of the rate constant \( k \) and the coefficient of the time component

<table>
<thead>
<tr>
<th>Temperature</th>
<th>190(^\circ) C</th>
<th>230(^\circ) C</th>
<th>260(^\circ) C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant ( k ) (( \mu )m s(^{-1}))</td>
<td>3.27</td>
<td>9.79</td>
<td>15.36</td>
</tr>
<tr>
<td>Time exponent ( n )</td>
<td>0.575</td>
<td>0.276</td>
<td>0.287</td>
</tr>
</tbody>
</table>
tem. As solid–liquid interdiffusion is three to four orders of magnitude faster than solid interdiffusion \cite{12} and Au has high diffusivity in molten solder, the movement of Au was used to estimate the amount of Au dissolving into molten solder. The Au consumed interacted with Sn in molten PbSn solder to form \begin{equation}
\text{AuSn}_4 \text{ and } \text{AuSn}_2. \end{equation}
Simultaneously, the Au dissolves into the molten solder. Thus, the difference between the amount of Au consumed and the amount of Au in the diffusion barrier layers can be used to estimate the amount of Au dissolved in molten solder. Assuming that the intermetallic layers are the diffusion barriers for ease of analysis, the number of moles of Au atoms was computed for 190, 230, and 260 °C as shown in Fig. 9(a–c), respectively. In Fig. 9, the amount of Au consumed was found to be much higher than the growth of the AuSn layers. A significant amount of Au dissolves into molten solder during solid–liquid interdiffusion, even in the presence of IMC diffusion barrier layers. Fig. 10 summarizes the percentage of Au dissolved into molten solder with time. A high percentage (about 50%) of the Au consumed was estimated to have dissolved in the molten solder. The increase in bonding temperatures increased the amount of Au dissolving into the molten solder. Once the diffusion barrier was formed, it retarded the rate of Au dissolving into molten solder.

4. Conclusion

Study of the interface reaction between Au and molten eutectic PbSn reveals four main things:

(1) The AuSn intermetallic layer at different bonding temperatures can be determined through the concept of local equilibrium with the binary section of the ternary phase diagram.

(2) When bonding at 190 °C, a continuous AuSn\textsubscript{4} intermetallic layer forms. At the same time, needle-like AuSn\textsubscript{4} precipitates in bulk solder. At 230 and 260 °C, a new intermetallic layer of AuSn\textsubscript{2} is observed. At these temperatures, rod-like AuSn\textsubscript{4} precipitates. AuSn\textsubscript{4} phases are found to be thermodynamically stable at the base of the joint.

(3) A time-based power-law relationship estimates well the rates of gold consumption and AuSn layer growth: \( x = k t^n \).
The rate of Au consumption into molten eutectic PbSn solder is found to be non-parabolic with time exponent $n$ varying from 0.276 to 0.575.

At initial bonding, a significant amount of Au dissolved into the molten solder while Au reacted with Sn. The rate of Au retarded as the diffusion barrier was formed, while the Au continued to dissolve into the molten solder. The amount of Au dissolving into molten solder is significant and needs to be accounted for in solid–liquid interdiffusion.

References