IMC Growth and Shear Strength of Sn-Ag-Bi-In/Au/Ni/Cu BGA Joints During Aging

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The growth kinetics of intermetallic compound (IMC) layers formed between Sn-3Ag-6Bi-2In ball-grid-array (BGA) solder and Au/Ni/Cu substrate by solid-state isothermal aging were examined at temperatures between 343 and 443 K for 0 to 100 days. A quantitative analysis of the IMC layer thickness as a function of time and temperature was performed. The intermetallic layer exhibited a parabolic growth at the given temperature range. Because the values of the time exponent (n) are approximately 0.5, the layer growth of the IMC was primarily controlled by diffusion over the temperature range studied. The apparent activation energy value calculated for the Sn-Ag-Bi-In/Au/Ni/Cu BGA joint was 64.8 kJ/mol. Also, the reliability of the solder ball attachment was characterized by mechanical ball shear tests. The brittleness of the solder joints increased with increasing aging temperature and time, and the fracture occurred within the IMCs and Ni layer. The deterioration of the solder ball shear strength was found to be predominantly caused by the formation of the IMC layer.

1. Introduction

The realization of harmful effects of Pb on the environment and human health, coupled with the threat of legislation, has instigated a search for electronic packaging applications using Pb-free solders.1–4) Many different solder alloys have been proposed as potential Pb-free solder replacements and the most promising of these fall into the general alloy families of Sn-Cu, Sn-Ag and Sn-Ag-Cu.5–10) It has satisfactory wettability, reliability, ductility and strength compared to other Pb-free solders. However, even with these advantages, these alloys have a high melting point. This property can cause some problems such as thermal damage of electronic components due to the high soldering temperature and modification of the soldering equipment.11) In order to overcome the high melting point of Pb-free solders, a Sn-Ag-Bi-In solder alloy has been suggested.11,12) This solder material has a relatively low melting temperature (458–488 K) compared to the Sn-Cu and Sn-Ag solder alloys.

One of the major concerns of BGA technology is the solder joint reliability.12,13,14) An electronic package is generally subjected to different thermal and mechanical loads during manufacturing, storage, transport and operation. High ambient temperatures on the solder joint, for instance, result in the growth of unwanted intermetallic compounds (IMC), which weaken the solder joint strength because of their brittleness and weakness. Therefore, it is necessary to understand and control the factors that govern the kinetics of interfacial reaction.

The Ni coating is commonly used as a protective layer on a Cu conductor in electronic devices.14,15) It has interfaces with the Cu substrate and with the solder. However, there is no chemical reaction at the Cu/Ni interface and the IMC layer is not expected to form at this interface because the Cu-Ni binary system only forms a complete solid solution. Therefore, the existence of this interface is not detrimental to the solder joint.

Some studies on Sn-Ag-Bi-In solder alloy are available in the literature,11,16) but the knowledge of interfacial reaction kinetics and ball shear tests of the solder on Au/Ni metallized Cu substrate is insufficient. Therefore, this study focuses on the growth kinetics of Ni3Sn4 IMC for Sn-3Ag-6Bi-2In solder/Au/Ni metallized Cu BGA substrate system during solid state aging. The growth rate constants of Ni3Sn4 intermetallic were measured as a function of time and temperature, and the activation energies for intermetallic growth were calculated by the Arrhenius equation. In addition, the shear strength of the solder joints was tested as a function of the time and temperature for isothermal aging. The correlation between the shear strength and their corresponding interfacial microstructure on the solder joints are also discussed.

2. Experimental Procedures

2.1 Solder ball attachment

BGA solder used in this study was Sn-3Ag-6Bi-2In (mass%). The size of the solder ball was 500 μm. The substrate was a BT (Bismaleimide Triazine) laminate with subsurface solder bond pads whose nominal size and shape were defined through a circular opening of 460 μm diameter. The pads were composed of electroplated Au/Ni over an underlying Cu pad in thickness of 0.5 and 7.0 μm, respectively. The Sn-Ag-Bi-In solder ball was bonded to the BT substrate in a reflow process employing RMA flux in an IR 4 zone reflow machine (RF-430-N2, Japan Pulse Laboratory Ltd. Co.) with maximum temperatures of 528 K for 60 seconds, respectively.

2.2 Aging treatment and microstructural analysis

Solder joints were cross-sectioned for examination immediately after undergoing the reflow, as well as the aging process, in an oven at temperatures 343, 373, 393, 423 and 443 K for times ranging from 1 to 100 days, respectively. Isothermal aging of solder joints were performed in an oven.
with a temperature stability of ±1 K. The microstructural and chemical analyses of the samples were obtained by using Philips XL 40 FEG scanning electron microscopy (SEM) equipped with energy-dispersive X-ray analysis (EDX). The phases at the interface were identified using X-ray diffraction (XRD) analysis. In all the cases, the quantitative measurements of the IMC layer thickness were done using micrographs taken on the cross-sections of the intermetallic layer. The layer thickness was evaluated using image analysis software to measure the total area of intermetallic layer. The phase areas were divided by the length of boundary shown in the cross-section to yield the average layer thickness.

2.3 Shear strength

The shear test was performed on reflowed and aged samples by using the shear tester (Rhesca Co. Ltd., PTR-1000). The shear tool height of 50 μm and shear speed of 200 μm/s were used. A total of 20 solder ball joints were sheared for each condition. After the ball shear test, the fracture surfaces were investigated thoroughly by SEM in back-scattered electron mode, as well as by EDX.

3. Results and Discussion

Figure 1 shows the SEM micrographs of IMC layers for the interface between Sn-Ag-Bi-In solder and Au/Ni/Cu substrate aged at 423 K for different aging times. During reflow soldering, the topmost Au layer dissolved into the molten solder and formed the randomly distributed AuSn₄ compound within the solder, leaving the Ni layer exposed to the molten solder. The reaction between Ni and molten solder resulted in the formation of a Ni₃Sn₄ layer at the interface. In the as-reflowed joint, the thickness of the IMC was approximately 0.76 μm. According to EDX analysis, the IMC formed on the BGA substrate is composed of Ni-Sn. Ag, Bi and In are not detected in the interfacial layer, indicating

![Fig. 1 SEM micrographs of a Sn-3Ag-6Bi-2In/Au/Ni/Cu interface at 423 K with various aging times; (a) as-reflowed, (b) 1 day, (c) 3 days, (d) 15 days, (e) 35 days and (f) 100 days.](image-url)
that these elements were not directly involved in the interfacial reactions. The $\text{Ni}_3\text{Sn}_4$ IMC thickness increased with aging time, reaching only 3.29 $\mu$m for 100 days of aging at 423 K. Furthermore, $\text{AuSn}_4$ and $\text{Ag}_3\text{Sn}$ particles were found within the solder material. However, reprecipitation of Au as $(\text{Au},\text{Ni})\text{Sn}_4$ at the interface, as shown in the eutectic Sn-Pb solder system,13 was not observed.

Figure 2 shows the SEM micrographs of reaction couples after 50 days aging at different aging temperatures. The aged solder joint consisted of the Ni/Cu substrate, the $\text{Ni}_3\text{Sn}_4$ IMC layer, $\text{Ag}_3\text{Sn}$ particles embedded within the $\text{Ni}_3\text{Sn}_4$ layer, $\text{Ag}_3\text{Sn}$ particles in the solder, Bi phases, and acicular $\text{AuSn}_4$ phases (Fig. 2(c)). With increased aging time and temperature, the $\text{Ag}_3\text{Sn}$ particles became more prevalent in the $\text{Ni}_3\text{Sn}_4$ IMC layer. This observation is consistent with a previous study of IMC growth in a Sn-Ag based solder/substrate diffusion couples.17,18 Also, this is in agreement with the suggestion that Sn diffuses into the IMC layer to react with the Cu substrate. As shown in Figs. 1 and 2, as the aging conditions became more severe, the IMC layer grew.

Figure 3(a) shows the top view of $\text{Ni}_3\text{Sn}_4$ IMC after the sample was aged for 100 days at 343 K. The specimen (coupon type) for XRD analysis was prepared by mechanically removing the solder and etching away the remaining solder part. The IMC found at the interface exhibited a facet structure, and the size of the IMC phase was about 1–3 $\mu$m.

![Fig. 2 SEM micrographs of a Sn-3Ag-6Bi-2In/Au/Ni/Cu interface after aging for 50 days at; (a) 343 K, (b) 373 K, (c) 393 K and (d) 443 K.](image)

![Fig. 3 A top view (a) and X-ray diffraction pattern (b) of the IMC.](image)
The Ni$_3$Sn$_4$ intermetallic surface shown in Fig. 3(a) was then used to obtain the X-ray diffraction pattern of the IMC, shown in Fig. 3(b).

The curve of the average thickness of the Ni$_3$Sn$_4$ IMC versus the square root of aging time at different aging temperatures is given in Fig. 4(a). All the data points fitted well with the following classical theory of diffusion:

$$ W = kt^n $$

where $W$ is the thickness of the IMC layer, $k$ is the growth rate constant, $t$ is the reaction time and $n$ is the time exponent. The IMC layer thickness was found to increase linearly with the square root of aging time and the growth was faster for higher aging temperatures.

The growth rate constant was calculated from a linear regression analysis of $W$ versus $t^{0.5}$, where the slope = $k$. Table 1 lists the growth rate constants calculated for the Ni$_3$Sn$_4$ IMC layer at different aging temperatures. All of the linear correlation coefficient values ($R^2$) for these plots were greater than 0.97. This good linear correlation suggests that the growth of the IMC layer is controlled by diffusion over the temperature range studied. As mentioned above, the growth rate of IMC was faster for higher aging temperature.

<table>
<thead>
<tr>
<th>IMC Temp. (K)</th>
<th>$R^2$</th>
<th>$k^2$ (10$^{-19}$ m$^2$/s)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>343</td>
<td>0.99</td>
<td>0.18</td>
<td>0.44</td>
</tr>
<tr>
<td>373</td>
<td>0.99</td>
<td>0.57</td>
<td>0.53</td>
</tr>
<tr>
<td>Ni$_3$Sn$_4$</td>
<td>0.97</td>
<td>0.93</td>
<td>0.47</td>
</tr>
<tr>
<td>423</td>
<td>0.99</td>
<td>7.50</td>
<td>0.45</td>
</tr>
<tr>
<td>443</td>
<td>0.99</td>
<td>33.48</td>
<td>0.49</td>
</tr>
</tbody>
</table>

If the growth process was controlled by diffusion, the increase of the IMC layer after aging should follow the square root time law, $W = kt^{0.5}$. It is empirically found that the time exponent $(n)$ takes the value of 0.5 when the diffusion reaction is controlled by volume diffusion. The time exponent was evaluated from the equation of the growth kinetics at each aging temperature (Table 1). The diffusion processes appeared to be largely responsible for growth of the IMC layer, although the time exponents were not exactly 0.5.

The following simple Arrhenius relationship was used to determine the activation energy for the Ni$_3$Sn$_4$ IMC growth respectively;

$$ k^2 = k_0^2 \exp(-Q/RT) $$

where $k^2$ is the square of growth rate constant (m$^2$/s), $k_0^2$ is the frequency factor, $Q$ is the activation energy, $R$ is the gas constant (8.314 J/mol-K) and $T$ is the aging temperature (absolute units). The activation energies were calculated from the slope of the Arrhenius plot using a linear regression model. Figure 4(b) shows the Arrhenius plot for the growth of the Ni$_3$Sn$_4$ IMC layers. The apparent activation energy calculated for the growth of the Ni$_3$Sn$_4$ intermetallic was 64.8 kJ/mol.

Table 2 lists the values of the activation energy $(Q)$ obtained from the temperature dependence of $k^2$, with the data from previous works. Although some difference does occur in the data, our result is in good agreement with the results of these previous workers. The discrepancy among the activation energies is due to the differences in the solder alloy, surface finish of substrates and aging temperature range.

Ball shear strength values were measured to evaluate the effect of the interfacial IMC reactions on the mechanical reliability of solder balls as a function of aging conditions. Figure 5 shows the variation of shear strength of the solder balls with respect to aging temperature and time. The average shear strength of the solder joints after reflow was about 14.8 N. As a whole, the shear strength decreased with increasing aging temperature and time. As shown in Fig. 5, it can be clearly seen that initial aging increased the shear strength of solder joint. We also reported a similar result in our previous work. Compared to the IMC thickness data of Fig. 4(a), the IMC thickness has a strong influence on the solder ball shear strength. Increasing the storage temperature and the dwell time leads to increasing the thickness of IMC layers. On the other hand, the ball shear strength was observed to decrease with increasing thickness of the IMC layers. During aging at temperatures of 343, 373 and 393 K, there is relatively little change in the shear strength with
aging time. However, in the case of 423 and 443 K, the shear strength decreased sharply with increasing time. From the shear test result, the shear strengths decreased by 1, 3, 4, 18 and 29% after aging for 100 days at temperatures of 343, 373, 393, 423 and 443 K compared to the strength measured after reflow, respectively. To verify the variation of shear strength, the fracture surfaces were examined by the SEM. After isothermal aging, the fracture surface showed various characteristics depending on aging temperature and time. Figure 6 represents the fracture surfaces after aging for 100 days at various aging temperatures. In the case of as-reflowed sample (Fig. 6(a)), the fracture surface shows ductile and slightly brittle failure. The brittleness of the solder joints increased with increasing aging temperature and time, and the fracture occurred within the IMCs and Ni layer (Fig. 6(f)). According to EDX analysis, the fracture occurred at the interface between the solder and Ni$_3$Sn$_4$ IMC layer and/or Ni$_3$Sn$_4$ IMC layer and Ni layer. As shown in Fig. 6(e), more severe aging resulted in a flat-fracture surface and solder alloy was not present on the fracture surface. From these fractographs, it is clear that these interfaces fail in a very brittle mode. In the ball shear test, fracture occurs at the interface or in the region with the lowest strength. In this study, a fracture analysis indicated that the shear strength could be related to the roughness of the IMC interface. After significant aging, the IMC layer grew and the interface between the IMC layer and bulk solder became smooth (Fig. 1 and 2). Therefore, an adhesive strength came mostly from the bonding strength of the IMC/solder interface. Consequently, IMC thickness and thermal loading history significantly affect the integrity of solder balls in BGA packages.

4. Conclusion

The effects of isothermal aging (343-443 K) on the IMC growth and ball shear strength of Sn-3Ag-6Bi-2In solder/Au/Ni/Cu BGA substrate were presented in this paper. The following conclusions were obtained:

(1) During reflow soldering, the topmost Au layer dissolved into the molten solder and formed the randomly distributed AuSn$_4$ compound within the solder, leaving the Ni layer exposed to the molten solder. The reaction between Ni and molten solder resulted in the formation of a Ni$_3$Sn$_4$ layer at the interface. Ag, Bi and In are not detected in the interfacial layer, indicating that these elements are not directly involved in the interfacial reactions.

(2) The IMC layer thickness was found to increase linearly with the square root of aging time and the growth was observed to be faster for higher aging temperatures. The
Diffusion processes appeared to be largely responsible for growth of the IMC layer, although the time exponents were not exactly 0.5. The apparent activation energy value calculated for the Sn-Ag-Bi-In/Au/Ni/Cu BGA joint was 64.8 kJ/mol.

(3) The shear strength decreased with increasing aging temperature and time. During aging at temperatures of 343, 373 and 393 K, there is relatively little change in the shear strength with aging time. However, in the case of 423 and 443 K, the shear strength decreased sharply with increasing time. The fracture occurred within the IMCs and Ni layer. The deterioration of solder ball shear strength was found to be predominantly caused by the IMC thickness and thermal loading history.

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REFERENCES