Size effect model on kinetics of interfacial reaction between Sn-xAg-yCu solders and Cu substrate

M. L. Huang & F. Yang

Electronic Packaging Materials Laboratory, School of Materials Science & Engineering, Dalian University of Technology, Dalian, 116024, China.

Nowadays, the state-of-art soldering technologies are facing new challenges of modern microelectronic manufacturing, e.g., greater functionality and higher density circuit interconnections between Si chips and the substrates. The essential process in solder joining is the chemical reaction between Cu and Sn to form intermetallic compounds with a strong metallic bonding. With the trend from two-dimensional to three dimensional integrated circuits (3D IC), the diameter of solder bumps on stack chips is downsizing from the current 100 μm to expected 1 μm in future.

Since the solder volume will be reduced by a factor of 8 when the diameter is reduced by a factor of 2, the composition of the downsizing solder joints will be significantly affected. This is because of the dissolution of under bump metallizations (UBMs) or constituent element consumption by interfacial IMC formation, and in turn the interfacial reaction will be affected. Therefore, size reduction of solder bumps is an additional detrimental factor for the reliability of solder joints. This is the focus of our modeling study.

Moreover, due to environmental concern of lead toxicity, lead-free solders are used to replace the traditional Sn-Pb solders. The most popular lead-free substitutes in industry are Sn-rich solder alloys such as Sn-Cu, Sn-Ag and Sn-Ag-Cu systems. Because of the higher soldering temperatures and higher Sn contents of these lead-free solders comparing to the eutectic Sn-37Pb solder, severe interfacial reaction occurs. This imposes a general reliability concern to lead-free soldering.

Many studies have already been carried out to investigate the size effect on the interfacial reaction in solder/Cu joints. Choi et al. found that a thicker interfacial IMC layer formed if a thinner Sn layer was used. Chan et al. compared the interfacial reactions of Sn-37Pb and Sn-3.5Ag-0.5Cu solder balls of 500 and 760 μm in diameter, and found that the Cu consumption in the larger solder balls was much higher than that in the smaller ones, whereas the mean thickness of the interfacial IMC was smaller for the larger solder balls. They concluded that, with a higher ratio of substrate area to solder volume, the IMC formation at the interface was dominant; otherwise IMC formation within the solder was dominant. Park et al. reported that the thickness of interfacial Cu₆Sn₅ layer increased as the size of solder balls decreased. They deduced that the dissolution rate of Cu in smaller solder balls was higher than that in larger solder balls. This is because it is easier for smaller solder balls to reach the solution saturation limit by interfacial reaction, and consequently no more Cu will be dissolved from the substrate, as shown by Chang et al.
Although the size effect on the interfacial reaction between lead-free solder and Cu substrate was experimentally investigated, the mechanism has not been fully understood. Previously, Tu et al.\textsuperscript{11,12} proposed a ripening theory to describe the growth of scallop-type Cu$_6$Sn$_5$ grains during soldering. In that study, however, the size effect of solder joint was not considered. In the ripening theory, the interfacial scallop-type Cu$_6$Sn$_5$ grains on a constant interfacial area were idealized as hemispheres, thereby causing the total interfacial grains to have a constant surface while their volumes increase during the ripening reaction. It is a non-conservative ripening. The growth or the increase in the total volume of the scallops requires the simultaneous dissolution of Cu from the substrate into the molten solder via the channels between the scallops. On the other hand, the dissolution of some small scallops into the molten solder occurs due to ripening, yet it is with respect to the mean-field concentration, not to the concentration in the bulk of the molten solder which is far away from the scallops. So, a mean-field concentration liquid (i.e., negligible outflux of Cu) around the scallops is a necessary condition for the flux driven ripening (FDR) theory, where the increase of average concentration in the bulk of the molten solder which is far away from the solution saturation after the initial reflow (45 s) for both Sn-3.0Ag-0.5Cu and Sn-3.5Ag solders. This is due to the fact that smaller solder balls dissolve significantly less Cu than larger solder balls, since the volume of a ball is third power of its diameter. Although the total amount of dissolved Cu, i.e., the consumption of the Cu substrate, is higher for larger solder balls, the average Cu concentration in those balls is still smaller. The experimental Cu concentration distributions in different diameter Sn-3.5Ag solder balls are listed in Table 1, which are consistent with the simulated results. Fig. 4 shows the average Cu concentrations in different diameter solder balls as a function of time. In general, larger solder balls have a lower average Cu concentration, and the difference in the average Cu concentration is significant at the early stage of reaction. Consequently, the absolute value of Cu concentration gradient $dc/dx$ at the interface is also higher for larger solder balls, as shown in Fig. 5. The Cu concentration gradient is considered as the driving force of dissolution of Cu atoms. The dissolution kinetics of Cu substrate is related to the size of interfacial Cu$_6$Sn$_5$ grains because grain boundary diffusion (in fact liquid channel diffusion\textsuperscript{14}) is the controlling mechanism of Cu atoms through the interfacial IMC layer. Larger Cu concentration gradient at the interface results in larger Cu flux from the interface zone into the liquid solder and thus smaller size of interfacial Cu$_6$Sn$_5$ grains, i.e., larger grain boundary (channel) areas are available to facilitate rapid diffusion of Cu atoms through the interfacial IMC layer and in turn accelerate the dissolution rate of Cu atoms from the substrate into the liquid solder. Therefore, the interfacial reaction in solder joints is a dynamic response to a combination of effects of IMC growth, consumption of Cu substrate and composition variation at the interface.

Based on these analyses, a model was established to describe the kinetics of the interfacial reaction in Sn-xAg-yCu/Cu solder joints. Fig. 6(a) shows the schematic of Cu influx $J_{\text{in}}$ and Cu outflux $J_{\text{out}}$. $J_{\text{in}}$ represents the flux of Cu atoms into the Cu$_6$Sn$_5$/solder interface zone, which is the sum of three fluxes ($J_1$, $J_2$ and $J_3$), as shown in Fig. 6(b). $J_1$ represents the Cu flux diffusion along the boundary from the Cu substrate into the Cu$_6$Sn$_5$/solder interface zone; $J_2$ represents the Cu flux diffusing from the Cu substrate to the Cu$_6$Sn$_5$/solder interface zone via bulk diffusion through the IMC grains; $J_3$ represents the direct dissolution of Cu$_6$Sn$_5$ into the molten solder at the Cu$_6$Sn$_5$/solder interface zone. The first term, $J_{\text{in}}$, is considered to be dominant, since it is known that the consumption of the Cu substrate is grain boundary diffusion (channel diffusion) controlled during reflow-soldering process\textsuperscript{11,12,15}. Therefore, for simplicity, it is assumed that the flux $J_1$ equals $J_{\text{in}}$. $J_{\text{out}}$ represents the Cu flux diffusing from the Cu$_6$Sn$_5$/solder interface zone into the molten solder. It is considered that some Cu atoms supplied by $J_{\text{in}}$ feed the growth of interfacial Cu$_6$Sn$_5$ and the other Cu atoms

**Results**

The size effect and the corresponding model. Fig. 1 shows the schematic of solder balls with four different diameters on Cu substrates before reflow. Fig. 2 shows the top-view SEM images of Cu$_6$Sn$_5$ grains for Sn-3.0Ag-0.5Cu and Sn-3.5Ag solder balls with different diameters after the initial reflow at 250°C. The common scallop-type Cu$_6$Sn$_5$ grains formed at the interfaces during the wetting reactions. However, the size of Cu$_6$Sn$_5$ grains decreases remarkably as the diameter of solder balls increases from 200 μm to 500 μm. The average diameter of the Cu$_6$Sn$_5$ grains for 200 μm Sn-3.0Ag-0.5Cu solder balls was 5.2 μm, while that for 500 μm solder balls was 2.44 μm. Similarly, for Sn-3.5Ag solder balls, the average diameter of the Cu$_6$Sn$_5$ grains decreased from 4.7 μm to 1.76 μm when the diameter of the solder balls increased from 200 μm to 500 μm. It is noted that the size of Cu$_6$Sn$_5$ grains for 200 μm solder balls was more than twice of that for 300 μm solder balls. The experimental results further demonstrated that this difference in the grain size still existed even after 5 reflows, which clearly demonstrates the size effect.

Fig. 3 shows the 2D slices of the simulated concentration distributions of Cu in Sn-3.0Ag-0.5Cu and Sn-3.5Ag solder balls with different diameters after the initial reflow. Smaller solder balls (200 and 300 μm in diameter) are almost saturated while larger ones are far from the solution saturation after the initial reflow (45 s) for both Sn-3.0Ag-0.5Cu and Sn-3.5Ag solders. This is due to the fact that smaller solder balls dissolve significantly less Cu than larger solder balls, since the volume of a ball is third power of its diameter. Although the total amount of dissolved Cu, i.e., the consumption of the Cu substrate, is higher for larger solder balls, the average Cu concentration in those balls is still smaller. The experimental Cu concentration distributions in different diameter Sn-3.5Ag solder balls are listed in Table 1, which are consistent with the simulated results. Fig. 4 shows the average Cu concentrations in different diameter solder balls as a function of time. In general, larger solder balls have a lower average Cu concentration, and the difference in the average Cu concentration is significant at the early stage of reaction. Consequently, the absolute value of Cu concentration gradient $dc/dx$ at the interface is also higher for larger solder balls, as shown in Fig. 5. The Cu concentration gradient is considered as the driving force of dissolution of Cu atoms. The dissolution kinetics of Cu substrate is related to the size of interfacial Cu$_6$Sn$_5$ grains because grain boundary diffusion (in fact liquid channel diffusion\textsuperscript{14}) is the controlling mechanism of Cu atoms through the interfacial IMC layer. Larger Cu concentration gradient at the interface results in larger Cu flux from the interface zone into the liquid solder and thus smaller size of interfacial Cu$_6$Sn$_5$ grains, i.e., larger grain boundary (channel) areas are available to facilitate rapid diffusion of Cu atoms through the interfacial IMC layer and in turn accelerate the dissolution rate of Cu atoms from the substrate into the liquid solder. Therefore, the interfacial reaction in solder joints is a dynamic response to a combination of effects of IMC growth, consumption of Cu substrate and composition variation at the interface.

Based on these analyses, a model was established to describe the kinetics of the interfacial reaction in Sn-xAg-yCu/Cu solder joints. Fig. 6(a) shows the schematic of Cu influx $J_{\text{in}}$ and Cu outflux $J_{\text{out}}$. $J_{\text{in}}$ represents the flux of Cu atoms into the Cu$_6$Sn$_5$/solder interface zone, which is the sum of three fluxes ($J_1$, $J_2$ and $J_3$), as shown in Fig. 6(b). $J_1$ represents the Cu flux diffusion along the boundary from the Cu substrate into the Cu$_6$Sn$_5$/solder interface zone; $J_2$ represents the Cu flux diffusing from the Cu substrate to the Cu$_6$Sn$_5$/solder interface zone via bulk diffusion through the IMC grains; $J_3$ represents the direct dissolution of Cu$_6$Sn$_5$ into the molten solder at the Cu$_6$Sn$_5$/solder interface zone. The first term, $J_{\text{in}}$, is considered to be dominant, since it is known that the consumption of the Cu substrate is grain boundary diffusion (channel diffusion) controlled during reflow-soldering process\textsuperscript{11,12,15}. Therefore, for simplicity, it is assumed that the flux $J_1$ equals $J_{\text{in}}$. $J_{\text{out}}$ represents the Cu flux diffusing from the Cu$_6$Sn$_5$/solder interface zone into the molten solder. It is considered that some Cu atoms supplied by $J_{\text{in}}$ feed the growth of interfacial Cu$_6$Sn$_5$ and the other Cu atoms

Figure 1 | Schematic of Cu/solder joints before reflow.
dissolve into the molten solder. As a result, the Cu consumption is dominantly contributed by Jin; the IMC growth is contributed by the difference between Jin and Jout. Consequently, a mathematical model on the kinetics of the interfacial reaction can be established based on the mass fluxes of Jin and Jout. 

The existence of thin Cu3Sn layer is ignored in this model, since it is not a diffusion barrier and has little effect on Cu diffusion. Meanwhile, the morphology of interfacial Cu6Sn5 grains is assumed to have a scallop top and a hexagonal pillar structure, as shown in Fig. 6(c). The grains are densely packed over the whole interface, as shown in Fig. 6(d). Fig. 6(e) shows the schematic of Cu6Sn5 grains that have an average side length of l and a channel width of δ. To reduce the unknown parameter, it is reasonable to assume that l equals the average thickness of interfacial Cu6Sn5 layer, since an approximately linear relationship between the average diameter of scallop Cu6Sn5 grains and the thickness of interfacial IMC layer was exhibited.

The mass influx of Cu atoms is approximately expressed as

\[ J_{in} = DS_{gb} \frac{C_b - C_e}{l}, \]

where D is the diffusivity of Cu atoms at grain boundary (liquid channel between neighboring grains, and it is assumed to equal the diffusivity of Cu atoms in the liquid solder), S_{gb} is the ratio of grain boundary (channel) area to the whole area, C_e is the equilibrium concentration of Cu (in wt.%) in solder at the planar interface between Cu6Sn5 and molten solder, and C_b is the equilibrium concentration of Cu (in wt.%) in solder at the interface between substrate and solder at the bottom of grain boundary.

Considering that A_a and A_b represents the interfacial areas occupied by grains and grain boundaries, respectively, the total area A is expressed as

\[ A = A_a + A_b \]

If N is the number of grains in the total area, then

\[ A_a = N \times \frac{3\sqrt{3}}{2} l^2, \]

and

\[ A_b = N \times \frac{6}{l} l \times δ = 3lNδ, \]

so that

\[ S_{gb} = \frac{A_b}{A_a + A_b} = \frac{1}{\sqrt{3l/2δ + 1}}. \]

From Fick’s first law, the mass outflux of Cu atoms is expressed as

\[ J_{out} = -D \frac{dC}{dx}, \]

where \( dC/dx \) represents the Cu concentration gradient at the solder/Cu6Sn5 interface in the direction normal to the interface, which can be obtained in the simulation process.

The growth rate of interfacial Cu6Sn5 and the consumption rate of Cu substrate are described as

\[ \frac{dl}{dt} = \rho_{solder} (J_{in} - J_{out}) \]

\[ = \rho_{solder} \left[ S_{gb} (C_b - C_e) / l + dC/dx \right], \]

and

Figure 2 | Top-view images of Cu6Sn5 grains for Sn-3.0Ag-0.5Cu solder balls with diameters of (a) 200, (b) 300, (c) 400 and (d) 500 μm; and those for Sn-3.5Ag solder balls with diameters of (e) 200, (f) 300, (g) 400 and (h) 500 μm after the initial reflow.

Figure 3 | Simulated Cu concentration distributions in different diameter (a) Sn-3.0Ag-0.5Cu and (b) Sn-3.5Ag solder balls after one reflow (45 s).
where $w$ is the weight fraction of Cu in Cu$_6$Sn$_5$, $\rho_{solder}$ is the mass density of solder (the density variation subject to the change of Cu concentration is ignored), $\rho_{IMC}$ is the mass density of Cu$_6$Sn$_5$, and $\rho_{Cu}$ is the mass density of Cu.

Substituting $S_{gb}$ in equation (6) and equation (7) with equation (4), the final formats can be derived:

$$\frac{dT_{Cu}}{dt} = \frac{I_{in}}{\rho_{Cu}} = \frac{D\rho_{solder}S_{gb}(C_b - C_e)}{\rho_{Cu}^l},$$

(7)

$$\frac{dt}{dt} = \frac{D\rho_{solder}(C_b - C_e)}{w\rho_{IMC}(\sqrt{3}l^2/2\delta + l)} + dC/dx,$$

(8)

$$\frac{dT_{Cu}}{dt} = \frac{D\rho_{solder}(C_b - C_e)}{\rho_{Cu}(\sqrt{3}l^2/2\delta + l)}.$$

(9)

Comparison of calculated and experimental results. In the calculation, a fourth/fifth-order Runge-Kutta-Fehlberg algorithm was applied to numerically integrate equations (8) and (9). Assuming $\delta = 0.05$ $\mu$m$^2$, $C_b - C_e \approx 0.001$ $\mu$m, $\rho_{Cu} = 8.96$ g/cm$^3$, $\rho_{solder} = 7.4$ g/cm$^3$, $\rho_{IMC} = 8.28$ g/cm$^3$, and $w = 0.39$, the thickness of interfacial Cu$_6$Sn$_5$ and the consumption of Cu substrate as a function of reaction time for different diameter solder balls were finally obtained. To make equation (8) meaningful, an initial IMC thickness, which can be obtained by setting equation (8) to be zero, was set to conduct the calculation.

This treatment is of physical meaning since there should be a critical grain size that the IMC grains can grow if larger than it. The calculated value of initial IMC thickness ranged from 0.1 to 0.5 $\mu$m, which is similar to the experimental value in the literature.

Figs. 7 and 8 show the simulated thicknesses of interfacial Cu$_6$Sn$_5$ and the consumptions of Cu substrates as a function of reaction time for the four different diameter Sn-3.0Ag-0.5Cu and Sn-3.5Ag solder balls, respectively. For comparison, the experimental results are displayed by solid symbols while the simulated results are displayed by empty symbols. It is shown that the calculated data are in good agreements with the experimental results. The size effect that smaller solder balls have thicker interfacial Cu$_6$Sn$_5$ layers and less consumptions of Cu is clearly demonstrated by both the calculated and experimental results. The thickness of interfacial Cu$_6$Sn$_5$ layer has an abrupt rise at the early beginning, even though the dissolution of Cu substrate into the molten solder is large at this time. However, the growth rate of the interfacial Cu$_6$Sn$_5$ slows down after the initial ramp, which is due to the fact that the Cu$_6$Sn$_5$ grains formed at the early beginning constrain $J_{in}$, while $J_{out}$ remains large since the solder balls are still unsaturated and thus a large Cu concentration gradient still exists, especially for larger solder balls. After prolonged reaction time, though $J_{out}$ goes down, $J_{in}$ decreases faster than $J_{out}$ due to the continuously thickening of interfacial Cu$_6$Sn$_5$ layer, resulting in a smaller difference between $J_{in}$ and $J_{out}$ and thus a smaller growth rate.

The consumption rate of Cu substrate is significantly high at the early beginning and then gradually decreases, which is in accordance with the above explanation of the growth behavior of interfacial IMC. The fast growth of interfacial Cu$_6$Sn$_5$ layer and the rapid dissolution of Cu substrate at the beginning were both substantially slowed down after the initial reaction.

Table 1 | Cu concentration distribution in different diameter Sn-3.5Ag solder balls after the initial reflow (water cooled)

| Ball diameter | Distance from the interface (μm) | Cu concentration (wt. %) | Average Cu concentration of the whole cross-section (wt. %) |
|---------------|---------------------------------|--------------------------|----------------------------------------------------------|
| 200 μm        | 22                              | 1.52                     | 1.81                                                      |
|               | 63                              | 1.82                     |                                                           |
| 300 μm        | 20                              | 1.82                     | 1.75                                                      |
|               | 65                              | 1.83                     |                                                           |
|               | 115                             | 1.73                     |                                                           |
|               | 184                             | 1.72                     |                                                           |
| 400 μm        | 31                              | 1.76                     | 1.36                                                      |
|               | 112                             | 1.24                     |                                                           |
|               | 200                             | 1.01                     |                                                           |
|               | 312                             | 0.71                     |                                                           |
| 500 μm        | 43                              | 1.46                     | 1.01                                                      |
|               | 128                             | 1.39                     |                                                           |
|               | 257                             | 0.56                     |                                                           |
|               | 369                             | 0.62                     |                                                           |

Figure 4 | Simulated average Cu concentrations as a function of time in different diameter (a) Sn-3.0Ag-0.5Cu and (b) Sn-3.5Ag solder balls.
of Cu into the molten solder results in the high consumption rate of Cu substrate at the early beginning stage\(^13\). The continuously thickening of IMC layer and reducing of grain boundary areas decrease the consumption rate of Cu substrate.

To verify the model, the experimental data on the thickness of interfacial IMC and the consumption of Cu in the literature\(^10\) were compared with the calculated data using the present model. Since the reflow-soldering temperature varied and the peak temperature was 235°C, an appropriate \(D\) value of \(2.2 \times 10^{-9}\) m\(^2\)/s was chosen in the calculation. The solubility of Cu is set to be 1.2 wt.% at 235°C\(^14\). The calculated values of interfacial IMC thicknesses are shown in Fig. 9(a), and the corresponding experimental results are shown in Fig. 9(b). The calculated values are in good agreements with the experimental results, despite that the calculated values are about 1 μm smaller than the experimental ones after the first reflow and 1 μm larger after the fifth reflow. The deviation arises probably because the physical parameters chosen in the present work might slightly deviate from the real values. In addition, the average thickness of Cu\(_6\)Sn\(_5\) lacked a clear dependency on the initial Cu concentration in the solder in that experimental result, as shown in Fig. 9(b)\(^10\), while the calculated results using the present model can precisely reveal the small difference in the thickness of interfacial Cu\(_6\)Sn\(_5\) IMC layer that was caused by the difference in the initial Cu concentration, as shown in Fig. 9(a). The higher the initial Cu concentration in the solder was, the thicker the interfacial IMC layer would be. Fig. 10(a) shows the calculated values of Cu consumptions using the present model. These calculated values are in good agreements with the experimental results presented in the literature\(^10\), as shown in Fig. 10(b).

**Concept of Cu concentration gradient.** Size Effect on Interfacial Reaction. The size effect on interfacial reaction is explained based on the Cu concentration gradient at the interface. As shown in Fig. 6, larger solder balls have a higher Cu concentration gradient at the interface, resulting in larger outflux of Cu, and consequently resulting in smaller interfacial Cu\(_6\)Sn\(_5\) grains and more consumption of Cu substrate. Furthermore, the Cu concentration gradient at the interface of larger solder balls affects the interfacial reaction for a longer period of time, since larger molten solders approach the solution saturation slowly. This enhances the differences in the thickness of interfacial IMC and the consumption of Cu substrate. The size effect that smaller interfacial Cu\(_6\)Sn\(_5\) grains formed in larger solder balls can be understood on the basis of these mutually reinforcing effects. It is the difference in the Cu concentration gradient at the interface that eventually accounts for the size effect.

Affected by the Cu concentration gradient, larger solder balls had a larger difference in IMC thickness. As shown in Fig. 7(a) and Fig. 8(a), although the volume ratio of 300 μm balls to 200 μm balls is 1.95, the interfacial Cu\(_6\)Sn\(_5\) of 200 μm solder balls exceeded that of 300 μm balls by around 0.2 μm in thickness, but in contrast the difference in the interfacial IMC thickness is 1 μm between 400 μm and 500 μm solder balls, where the volume ratio of 500 μm balls to 400 μm balls is 1.95. This is due to the fact that for smaller solder balls, a shorter time is needed to reach the solution saturation of Cu, which significantly reduces the effective time for the Cu concentration gradient to affect the interfacial IMC growth.

**Effect of initial Cu concentration.** The calculated data showed that the growth kinetics of interfacial IMC in Sn-3.0Ag-0.5Cu solder balls was...
higher than those in Sn-3.5Ag solder balls, as shown in Fig. 7(a) and Fig. 8(a). It is concluded that 0.5 wt. % Cu addition had an effect on the growth of interfacial IMC, which agrees with the experimental results. The measured thicknesses of interfacial Cu$_6$Sn$_5$ IMC layers after the initial reflow ranged from 2.6 µm (500 µm) to 3.6 µm (200 µm) for Sn-3.0Ag-0.5Cu solder balls, and from 1.9 µm (500 µm) to 2.9 µm (200 µm) for Sn-3.5Ag solder balls, respectively. A difference of around 0.7 µm in the interfacial IMC thickness was revealed after the initial reflow. The reason for this phenomenon is attributed to the different Cu concentration gradients normal to the interfaces, as shown in Fig. 5(a) and (b). Smaller initial Cu concentration results in higher interfacial Cu concentration gradient and thus smaller interfacial Cu$_6$Sn$_5$ grains.

An additional experiment was conducted to further verify this concept, and the detailed information was described in the Methods section. As shown in Fig. 11(a), larger Cu$_6$Sn$_5$ grains formed during the first interfacial reaction between the Sn-3.5Ag-0.75Cu solder ball and Cu pad, while after the further reaction with the Sn-3.5Ag solder ball, as shown in Fig. 11(b), the size of Cu$_6$Sn$_5$ grains became smaller, indicating that a larger interfacial Cu concentration gradient resulted in smaller interfacial Cu$_6$Sn$_5$ grains.

It was reported that the Cu concentration had a strong effect on the Cu consumption, but this effect also depends on the size of the solder joints. As shown in Fig. 7(b) and Fig. 8(b), the initial Cu concentration has a significant effect on the Cu consumption for larger solder joints. As to the 500 µm solder balls, the measured consumptions of Cu substrates after the initial reflow were 7.16 µm for Sn-3.0Ag-0.5Cu/Cu joints and 9.87 µm for Sn-3.5Ag/Cu joints, i.e., the Cu consumption is higher in solder joints with a smaller initial Cu concentration. The role of initial Cu concentration on the Cu consumption in smaller solder balls (for the 200 µm case) is weakened. The measured consumptions of Cu substrates after the initial reflow were 1.99 µm for Sn-3.0Ag-0.5Cu/Cu joints and 2.17 µm for Sn-3.5Ag/Cu joints. This is because smaller solder balls would quickly reach the solution saturation of Cu within 45 s for both Sn-3.0Ag-0.5Cu/Cu and Sn-3.5Ag/Cu joints, as shown in Fig. 3 and Fig. 4. As a result, the effective time of the Cu concentration gradient was greatly reduced.

As the consumed Cu either transformed into interfacial IMCs or dissolved into the molten solder, the consumption of Cu was the sum of the consumption by interfacial IMC formation and the outflux of Cu $J_{out}$. Although the interfacial Cu$_6$Sn$_5$ IMC layers for Sn-3.5Ag solder balls were about 0.7 µm less than those for Sn-3.0Ag-0.5Cu solder balls (Fig. 8(a) and 9(a)), the consumptions of Cu for Sn-3.5Ag solder balls were obviously higher than those for Sn-3.0Ag-0.5Cu solder balls (Fig. 8(b) and 9(b)). This is because that $J_{out}$ is proportional to the Cu concentration gradient, and solder balls with a smaller initial Cu concentration (Sn-3.5Ag) have a higher Cu concentration.
Concentration gradient at the interface and consequently a higher $J_{out}$, and further results in a higher Cu consumption after a same period of soldering time, compared with solder balls with a higher initial Cu concentration (Sn-3.0Ag-0.5Cu).

Discussion

It has been reported that the growth kinetics of interfacial Cu$_6$Sn$_5$ follows a $t^{1/3}$ law in the Cu saturated molten solder, where the diffusion is grain boundary diffusion (channel diffusion) controlled$^{5,11,12,15}$. When the molten solder reaches the solution saturation of Cu, $J_{out}$ will become zero and $J_{in}$ will fully supply the growth of interfacial IMC. Thus, the growth rate can be expressed as

$$\frac{dl}{dt} \sim D_{solder} \left( \frac{C_{\text{Cu}} - C_{\text{eq}}}{\sqrt{3}l^2/2\delta + l} \right) \rho_{\text{IMC}}, \quad (10)$$

As the value of $l$ is usually tens or hundreds times larger than that of $\delta$, $l$ is negligible comparing to $\sqrt{3}l^2/2\delta$, therefore $dl/dt \propto 1/l$, which indicates a $t^{1/3}$ dependence of interfacial IMC growth. The model proposed in the present work is also applicable to the $t^{1/3}$ case.

When the solder is unsaturated, the growth kinetics of interfacial IMC is expected to deviate from the $t^{1/3}$ law due to the $J_{out}$ term in equation (8). This term restricts the fast growth of IMC at the early stage of reaction, which results in the slower growth kinetics than that of $t^{1/3}$. When the solution saturation is reached, the growth kinetics approaches $t^{1/3}$ growth rate. Thus, for smaller solder joints, the growth kinetics of interfacial Cu$_6$Sn$_5$ is closer to a $t^{1/3}$ law since the molten solder rapidly reaches the solution saturation, as shown in Figs. 7(a) and 8(a).

It is emphasized that the growth kinetics of interfacial Cu$_6$Sn$_5$ is the result of the interaction of the two fluxes, i.e., the difference between $J_{in}$ and $J_{out}$. Whether the growth of IMC is enhanced or restrained is determined by the two fluxes.

Previously, Dybkov$^{13}$ proposed an IMC growth and dissolution mechanism where the dissolution is related to the solder volume. The growth kinetics of interfacial IMC is expressed as

$$\frac{dl}{dt} = \frac{k_{0B1}B_{1}}{1 + k_{0B1}/k_{1B1}} + \frac{k_{0A2}}{1 + k_{0A2}/k_{1A2}} - b \exp(-at), \quad (11)$$

where $k_{0B1}$ and $k_{0A2}$ are chemical constants, $k_{1B1}$ and $k_{1A2}$ are diffusion constants, $a = kS/V$ and $b = c_k/\rho_\phi$, $c_k$ is the saturation concentration of Cu in the solder, $\rho$ is the density of Cu$_6$Sn$_5$, $S$ is the surface area of the dissolving solid, $V$ is the volume of the liquid phase and $\phi$ is the mass fraction of Cu in the dissolved Cu$_6$Sn$_5$. The dissolution rate constant $k$ is expressed as $k = D/\delta'$, where $\delta'$ represents the thickness of the diffusion boundary layer.

Figure 9 | Interfacial Cu$_6$Sn$_5$ thicknesses in solder/Cu joints with different initial Cu concentrations: (a) calculated and (b) experimental$^{10}$, one reflow cycle is 90 s.

Figure 10 | Consumptions of Cu substrates in solder/Cu joints with different initial Cu concentrations: (a) calculated and (b) experimental$^{10}$, one reflow cycle is 90 s.
The third term on the right side of equation (11) is deduced from the following equation:

\[
\frac{dc}{dt} = \frac{kS}{V}(C_s - C) \tag{12}
\]

where \( C \) is the concentration of the dissolved substance in anywhere of the liquid phase (solder) outside of the diffusion boundary layer at time \( t \). In equation (12), it is assumed that the volume of liquid solder outside the diffusion boundary layer equals the volume of the total liquid (\( V \)), which means that the volume of the diffusion boundary layer is neglected. Thus, in Dybkov’s model, \( \delta' \) must be much smaller than the height of the liquid phase (solder).

Dybkov’s model is successful in describing the IMC growth in the bulk liquid solder, however, it yields no satisfactory fit for small volume solder joints such as BGA solder balls and flip chip bumps, i.e., the size effect on the interfacial reaction cannot be described using that model. One reason is that the thickness of the hypothetical diffusion boundary layer \( \delta' \), which is usually in the magnitude of 100 \( \mu \)m, is very small compared to the dimension of the bulk liquid solder in that model. However, since small solder joint has a diameter comparable to the dimension of \( \delta' \), the model cannot describe the growth behavior of interfacial IMC in this case. The second reason is that the effect of grain boundary on the growth of interfacial IMC is not considered in that model. The grain boundary diffusion has a significant effect on the growth of interfacial IMC grains, due to the interfering dissolution mechanism of Cu into the solder 8.

In summary, the size effect on the kinetics of interfacial reaction between the lead-free solder balls (Sn-3.0Ag-0.5Cu and Sn-3.5Ag) and Cu substrates was experimentally demonstrated. The downsizing of solder balls resulted in larger interfacial Cu6Sn5 grains, thicker interfacial IMC layer, less consumption of Cu substrate and higher average Cu concentration in the molten solder in lead-free soldering on Cu substrate. Theoretically, a CGC model on the kinetics of interfacial reaction is proposed, which is based on grain boundary diffusion (channel diffusion) controlled mass transport, interrelationship and mutual acting mechanism of these factors in wetting reaction process. The Cu concentration gradient at the interface, which is a function of solder volume, initial Cu concentration and soldering time, is the root cause of the size effect. The growth kinetics of interfacial Cu6Sn5 obeys a \( t^{1/3} \) law when the molten solder has approached the solution saturation, and is slower otherwise due to the interfering dissolution mechanism. The size effect introduced in this model is also applicable to the previously reported work.

**Methods**

Sn-3.0Ag-0.5Cu and Sn-3.5Ag solder balls with four different diameters (200, 300, 400 and 500 \( \mu \)m) were reflow-soldered on Cu substrates with an opening diameter of 250 \( \mu \)m. The samples were subjected to one single reflow or multiple refows for up to 5 times with a peak temperature of 250°C and a total duration of 45 s above the melting point.

An additional experiment was conducted. A Sn-3.5Ag-0.75Cu solder ball of 400 \( \mu \)m in diameter was first reflow-soldered on a Cu pad at 250°C for 45 s, and then the bulk solder bump was etched away to expose the interfacial Cu6Sn5 grains on the Cu pad. Subsequently, a Sn-3.5Ag solder ball of 400 \( \mu \)m in diameter was placed and then reflow soldered on the exposed interfacial Cu6Sn5 grains on Cu pad with the same soldering condition, in order to observe the size change of the interfacial Cu6Sn5 grains.

The as-reflowed samples were cleaned in an ultrasonic bath using ethanol to remove the remaining flux. They were subsequently embedded into epoxy resin, mechanically ground and polished for microstructural observation. Finally, the samples were carefully etched to enhance topography and contrast of the cross-sectional microstructure. For top-view images of the solder/Cu interfaces, the samples were etched in a 10 vol. % HNO3 aqueous solution to remove the bulk solders in order to expose the interfacial IMC grains.

The microstructure in cross-section and top-view perspectives were examined using a scanning electron microscope (SEM), combined with an energy dispersive X-ray spectrometer (EDX). The average thicknesses of both IMC layer and consumption of Cu substrate were determined by dividing their areas by the linear lengths of the interfaces measured using an imaging processing software from the cross-sectional images.

1. Tu, K. N. Solder joint technology. Materials, properties, and reliability Vol. 92 Springer Series in Materials Science [Hull, R., Jagdish, C., Osgood, R. M., Parist, J., Wang, Z. M., Uchida, S.-i. & Seong, T.-Y. (eds.)] (Springer-Verlag, New York, 2007).
2. Hsiao, H. Y. et al. Unidirectional growth of microbumps on (111)-oriented and nanotwinned copper. Science 336, 1007–1010 (2012).
3. Li, Y., Moon, K. S. & Wong, C. P. Electronics without lead. Science 308, 1419–1420 (2005).
4. Laurila, T., Vuorinen, V. & Kivilahti, J. K. Interfacial reactions between lead-free solders and common base materials. Mater. Sci. Eng. R 49, 1–60 (2005).
5. Huang, M. L., Loehrer, T., Ostmann, A. & Reichl, H. Role of Cu in dissolution kinetics of Cu metallization in molten Sn-based solders. Appl. Phys. Lett. 86, 181908 (2005).
6. Choi, W. K., Kang, S. K. & Shih, D. Y. A study of the effects of solder volume on the interfacial reactions in solder joints using the differential scanning calorimetry technique. J. Electron. Mater. 31, 1283–1291 (2002).
7. Sharif, A., Chan, Y. C. & Islam, R. A. Effect of volume in interfacial reaction between eutectic Sn–Pb solder and Cu metallization in microelectronic packaging. Mater. Sci. Eng. B 106, 120–125 (2004).
8. Islam, M. N., Sharif, A. & Chan, Y. C. Effect of volume in interfacial reaction between eutectic Sn–3.5% Ag–0.5% Cu solder and Cu metallization in microelectronic packaging. J. Electron. Mater. 34, 143–149 (2005).
9. Park, Y. S. et al. Effects of fine size lead-free solder ball on the interfacial reactions and joint reliability. Proceedings of the 60th IEEE Electronic Components and Technology Conference, Las Vegas, NV, USA: New York: IEEE (2010, June 1–4).
10. Chang, C. C., Lin, Y. W., Wang, Y. W. & Kao, C. R. The effects of solder volume and Cu concentration on the consumption rate of Cu pad during reflow soldering. J. Alloys Compd. 492, 99–104 (2010).
11. Kim, H. K. & Tu, K. N. Kinetic analysis of the soldering reaction between eutectic SnPb alloy and Cu accompanied by ripening. Phys. Rev. B 53, 16027–16034 (1996).
12. Gusak, A. M. & Tu, K. N. Kinetic theory of flux-driven ripening. Phys. Rev. B 66, 115403 (2002).
13. Dybkov, V. I. Growth kinetics of chemical compound layers (Cambridge International Science Publishing, Cambridge, 1998).
14. Moon, K. W., Boettiger, W. J., Kattner, U. R., Biancianni, F. S. & Handwerker, C. A. Experimental and thermodynamic assessment of Sn–Ag–Cu solder alloys. J. Electron. Mater. 29, 1122–1136 (2000).
Acknowledgments
This work is supported by the National Natural Science Foundation of China under Grant Nos. 51475072 and 51171036. The authors thank Prof. K.N. Tu at UCLA for valuable comments and discussion. One of the authors (M.L. Huang) thanks the Alexander von Humboldt Foundation for the award of a research fellowship.

Author contributions
M.L.H. designed the experiments and proposed the mechanism. F.Y. carried out the experiments and performed simulations.

Additional information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Huang, M.L. & Yang, F. Size effect model on kinetics of interfacial reaction between Sn-xAg-yCu solders and Cu substrate. Sci. Rep. 4, 7117; DOI:10.1038/srep07117 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/4.0/