This item was submitted to [Loughborough's Research Repository](#) by the author.
Items in Figshare are protected by copyright, with all rights reserved, unless otherwise indicated.

Perpendicular growth characteristics of Cu-Sn intermetallic compounds at the surface of Sn99Cu1/Cu solder interconnects

PLEASE CITE THE PUBLISHED VERSION

<http://dx.doi.org/10.1007/s11664-015-4043-7>

PUBLISHER

© The Minerals, Metals & Materials Society. Published by Springer.

VERSION

AM (Accepted Manuscript)

PUBLISHER STATEMENT

This work is made available according to the conditions of the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International (CC BY-NC-ND 4.0) licence. Full details of this licence are available at:
<https://creativecommons.org/licenses/by-nc-nd/4.0/>

LICENCE

CC BY-NC-ND 4.0

REPOSITORY RECORD

Chen, Zhiwen, Changqing Liu, Yiping Wu, and Bing An. 2019. "Perpendicular Growth Characteristics of Cu-sn Intermetallic Compounds at the Surface of Sn99cu1/cu Solder Interconnects". figshare.
<https://hdl.handle.net/2134/19455>.

Metadata of the article that will be visualized in OnlineFirst

Please note: Images will appear in color online but will be printed in black and white.

ArticleTitle	Perpendicular Growth Characteristics of Cu-Sn Intermetallic Compounds at the Surface of 99Sn-1Cu/Cu Solder Interconnects	
Article Sub-Title		
Article CopyRight	The Minerals, Metals & Materials Society (This will be the copyright line in the final PDF)	
Journal Name	Journal of Electronic Materials	
Corresponding Author	Family Name	Liu
	Particle	
	Given Name	Changqing
	Suffix	
	Division	
	Organization	Loughborough University
	Address	LE11 3TU, Loughborough, Leicestershire, UK
	Email	C.Liu@lboro.ac.uk
Author	Family Name	Chen
	Particle	
	Given Name	Zhiwen
	Suffix	
	Division	
	Organization	Huazhong University of Science and Technology
	Address	Wuhan, Hubei, People's Republic of China
	Division	
	Organization	Loughborough University
	Address	LE11 3TU, Loughborough, Leicestershire, UK
Author	Family Name	Wu
	Particle	
	Given Name	Yiping
	Suffix	
	Division	
	Organization	Huazhong University of Science and Technology
	Address	Wuhan, Hubei, People's Republic of China
	Email	
Author	Family Name	An
	Particle	
	Given Name	Bing
	Suffix	
	Division	
	Organization	Huazhong University of Science and Technology

Wuhan, Hubei, People's Republic of China

	Received	23 February 2015
Schedule	Revised	
	Accepted	4 September 2015
Abstract	<p>The growth of intermetallic compounds (IMCs) on the free surface of 99Sn-1Cu solder joints perpendicular to the interdiffusion direction has been investigated in this work. The specimens were specifically designed and polished to reveal a flat free surface at the solder/Cu interface for investigation. After aging at 175°C for progressively increased durations, the height of the perpendicular IMCs was examined and found to follow a parabolic law with aging duration that could be expressed as $y = 0.11\sqrt{t}$, where t is the aging duration in hours and y is the height of the perpendicular IMCs in μm. For comparison, the planar growth of IMCs along the interdiffusion direction was also investigated in 99Sn-1Cu/Cu solder joints. After prolonged aging at 175°C, the thickness of the planar interfacial IMC layers also increased parabolically with aging duration and could be expressed as $h_{\text{IMC}} = 0.27\sqrt{t} + 4.6$, where h is the thickness in μm and t is the time in hours. It was found that both the planar and perpendicular growth of the IMCs were diffusion-controlled processes, but the perpendicular growth of the IMCs was much slower than their planar growth due to the longer diffusion distance. It is proposed that Cu_3Sn forms prior to the formation of Cu_6Sn_5 in the perpendicular IMCs, being the reverse order compared with the planar IMC growth.</p>	
Keywords (separated by '-')	Solder joint - planar growth of IMCs - perpendicular growth of IMCs - interdiffusion - growth rate - formation sequence of IMCs	
Footnote Information		

Perpendicular Growth Characteristics of Cu-Sn Intermetallic Compounds at the Surface of 99Sn-1Cu/Cu Solder Interconnects

ZHIWEN CHEN,^{1,2} CHANGQING LIU,^{2,3} YIPING WU,¹ and BING AN¹

1.—Huazhong University of Science and Technology, Wuhan, Hubei, People's Republic of China.
 2.—Loughborough University, Loughborough, Leicestershire LE11 3TU, UK. 3.—e-mail:
 C.Liu@lboro.ac.uk

The growth of intermetallic compounds (IMCs) on the free surface of 99Sn-1Cu solder joints perpendicular to the interdiffusion direction has been investigated in this work. The specimens were specifically designed and polished to reveal a flat free surface at the solder/Cu interface for investigation. After aging at 175°C for progressively increased durations, the height of the perpendicular IMCs was examined and found to follow a parabolic law with aging duration that could be expressed as $y = 0.11\sqrt{t}$, where t is the aging duration in hours and y is the height of the perpendicular IMCs in μm . For comparison, the planar growth of IMCs along the interdiffusion direction was also investigated in 99Sn-1Cu/Cu solder joints. After prolonged aging at 175°C, the thickness of the planar interfacial IMC layers also increased parabolically with aging duration and could be expressed as $h_{\text{IMC}} = 0.27\sqrt{t} + 4.6$, where h is the thickness in μm and t is the time in hours. It was found that both the planar and perpendicular growth of the IMCs were diffusion-controlled processes, but the perpendicular growth of the IMCs was much slower than their planar growth due to the longer diffusion distance. It is proposed that Cu_3Sn forms prior to the formation of Cu_6Sn_5 in the perpendicular IMCs, being the reverse order compared with the planar IMC growth.

Key words: Solder joint, planar growth of IMCs, perpendicular growth of IMCs, interdiffusion, growth rate, formation sequence of IMCs

INTRODUCTION

In electronic devices, the interconnections between components are normally formed by reflowing solder alloys. During such reflow, the reactions between the solder and substrate are essential to the formation of reliable solder interconnects. However, the interfacial intermetallic compound (IMC) layers produced during reflow can grow continuously during subsequent service due to interdiffusion and solid-state reactions, particularly when devices are exposed to elevated temperature. Excessive growth of interfacial IMC layers can significantly deteriorate the mechanical integrity of

the entire solder joint because of the incompatible mechanical properties of the interfacial IMC layers in comparison with the solder alloy and substrate.^{1–3} Hence, growth of IMCs at the solder/substrate interface has received continuous attention from researchers.^{4–8}

The interfacial IMC layers extensively investigated in literature normally cover the entire solder/substrate interface and grow along the direction of interdiffusion between the solder and substrate.^{4–8} Therefore, this type of interfacial IMC layer is termed the planar IMC layer in this work, as illustrated in Fig. 1. Moreover, IMCs (i.e., Cu-Sn IMCs) can also protrude out of the free surface of solder joints, perpendicular to the diffusion direction within the solder joint,⁹ as illustrated in Fig. 1. This is termed the perpendicular IMC in this work.

(Received February 23, 2015; accepted September 4, 2015)

Journal : 11664_JEM

Article No.: 4043

Dispatch : 18-9-2015

☐ LE
☒ CP

Pages : 10

☐ TYPESET
☒ DISK

Fig. 1. Planar and perpendicular growth of IMCs at the 99Sn-1Cu/Cu interface in solder joints.

Fig. 2. Schematics of (a) specimen for characterizing perpendicular growth of IMCs and (b) perpendicular growth of IMCs (the red region) on the top surface of the specimen after aging.

In contrast to the numerous works reported on characterization of planar IMCs in solder joints, the perpendicular growth of IMCs has seldom been investigated. The mechanism of the perpendicular growth of IMCs also remains unclear. In electromigration tests, it was suggested that such perpendicular IMCs were “squeezed out” by compressive stress induced by current stressing at the interface in the solder joint.^{9,10} However, study on the spreading of IMCs implied that interdiffusion of atoms on the free surface can also result in growth of IMCs on the free surface.¹¹

In this study, the perpendicular growth of IMCs was investigated in specifically designed 99Sn-1Cu/Cu solder joints. The top surface of the solder joints was polished and profiled using a white-light interferometer after gradually prolonged aging at 175°C to measure the height of the perpendicular IMCs. Scanning electron microscopy (SEM) was employed to examine the morphology of the perpendicular IMCs from the top, and cross-sectional views were prepared by focused ion beam (FIB). In comparison, the ordinary planar growth of interfacial IMC layers at the 99Sn-1Cu/Cu interface was also characterized by grinding and polishing to reveal the cross-section of the solder joints after aging at the same temperature for increasing periods. Correlations and differences between the IMC growth along these two directions are also presented.

EXPERIMENTAL PROCEDURES

Perpendicular Growth of IMCs

To investigate the perpendicular growth of IMCs, a pocket with dimensions of 15 mm × 15 mm × 2.5 mm was machined within a Cu (purity 99.9%) specimen. A proper amount of 99Sn-1Cu solder was placed in the pocket and reflowed in an oven. During reflow, a thermocouple was attached to the specimen to monitor its temperature. After reflow, the specimens were ground and polished to ensure that the top surface across the solder/Cu interface was smooth in one plane. The specimen after polishing is shown schematically in Fig. 2a.

The four specimens were then stored in an oven at temperature of 175°C to facilitate the perpendicular

growth of IMCs at the solder/Cu interface (as illustrated by the red region in Fig. 2b). After aging for every 168 h until 1132.5 h, the specimens were removed from the oven after cooling. The height of the perpendicular IMCs on the polished top surface was then measured using a white-light interferometer (Zygo NewView 5000) at the same location for a given specimen. The areas of the scanned regions were no smaller than 1.5 mm × 1.0 mm to ensure reliability of the obtained morphology of the specimens. The obtained surface morphology data were then converted into a series of profiles to calculate the average height of the perpendicular IMCs on the specimen.

After these measurements, SEM was used to examine the perpendicular IMCs from the top. FIB was also utilized to mill the specimen across the 99Sn-1Cu/Cu interface to reveal the cross-section of the perpendicular IMCs after aging. However, milling the samples with FIB should be carefully planned as it could potentially introduce several types of artificial damage in the specimens: (1) the polished sample surface could be seriously damaged in a wide range during the milling and imaging with the ion beam in FIB; (2) the reliability of the measured heights of the perpendicular IMCs could be affected due to damage of the IMCs on the top surface; (3) the large hole in the sample and the fresh surface left by milling could lead to significant oxi-

136 dation of the sample in subsequent aging. Hence,
137 cross-sectioning with FIB was implemented only
138 after finishing all the aging and measurements, to
139 minimize its potential influence on the reliability of
140 the measured heights of the perpendicular IMCs.

141 Planar Growth of IMCs

142 For comparison with the perpendicular growth of
143 IMCs on solder joints after aging, another set of
144 99Sn-1Cu solder was reflowed on polished Cu (pu-
145 rity 99.9%) substrate using the same reflow condi-
146 tions as in “Perpendicular Growth of IMCs” section,
147 to investigate the planar growth of IMCs within
148 solder joints. The six specimens were then stored in
149 an oven at 175°C to promote the planar growth of
150 IMCs after reflow. After aging for every 168 h, the
151 specimens were ground and polished to reveal the
152 cross-section of the solder joint, as illustrated in
153 Fig. 3. The interfacial Cu_6Sn_5 and Cu_3Sn layers
154 which grew along the interdiffusion direction were
155 then revealed by etching with ethanol (80 vol.%)
156 and hydrochloric acid (20 vol.%) solution. An
157 Olympus BX60 M microscope was utilized for
158 observation of the planar interfacial IMC layers.
159 The interfaces between the solder, Cu_6Sn_5 , Cu_3Sn ,
160 and Cu in the microscope images were fit with trac-
161 ces using Image-Pro image analysis software.
162 Hence, the average thickness of a specific IMC layer
163 could be derived by calculating the mean distance
164 between two adjacent traces.

165 RESULTS

166 Perpendicular Growth of IMCs

167 The perpendicular IMCs on the 99Sn-1Cu/Cu
168 samples were examined by SEM and profiled with
169 the Zygo NewView 5000 after aging for every 168 h.
170 Figure 4a, c and e illustrates the morphological
171 evolution of the perpendicular IMCs on the top
172 surface of 99Sn-1Cu solder joints after progressively
173 prolonged aging. Examples of surface profiles from
174 the corresponding specimens are shown in Fig. 4b, d
175 and f, leveled with the Cu part in the profile to re-
176 move the effect of the angle between the specimen
177 and the instrument during scanning. Before aging,

Fig. 3. Schematic of the specimen for investigating the planar growth of IMCs within 99Sn-1Cu/Cu solder joints after aging at 175°C

the surface of the 99Sn-1Cu solder joints was
smooth across the solder/Cu interface after polish-
ing, as illustrated in Fig. 4a. No perpendicular
IMCs could be identified. Correspondingly, there is
no notable peak at the solder/Cu interface in the
surface profile in Fig. 4b. The height difference be-
tween the solder part and Cu surface was probably
due to the higher polishing rate on the softer solder
in comparison with the polishing rate on the Cu
during sample preparation.

After aging at 175°C for 168 h, a line of IMCs was
observed to protrude out of the surface at the solder/
Cu interface, as shown in Fig. 4c. The spikes of the
perpendicular IMCs can also be identified in the
corresponding surface profile in Fig. 4d. The aver-
age height of the perpendicular IMCs can be esti-
mated to be about 0.5 μm , with the Cu surface as
reference. When the aging was extended to
1132.5 h, the perpendicular IMCs grew significantly
in both height and width, as illustrated in Fig. 4e,
and the height of the perpendicular IMCs increased
to approximately 1.5 μm (Fig. 4f).

FIB was then utilized to reveal a cross-sectional
view of the perpendicular IMCs at the solder/Cu
interface after aging for 1132.5 h (Fig. 5). It is evi-
dent that the perpendicular IMCs on the sample
surface were dendritic along several specific direc-
tions, which is different from the layer-type inter-
facial IMC layers within solder joints. Both Cu_6Sn_5
and Cu_3Sn phases can be found in the perpendicular
IMCs, with the Cu_3Sn at the bottom of the dendrites
close to the Cu/ Cu_3Sn interface. The “root” of the
perpendicular IMCs was a Cu-rich region, so the
 Cu_3Sn phase was probably produced before the
formation of Cu_6Sn_5 in the initial perpendicular
growth of IMCs,^{12–14} as discussed further in “Com-
parison of Growth Mechanisms” section below.
Furthermore, it can also be observed that the Cu/
 Cu_3Sn interface and $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ interface in the
planar IMCs shifted towards the Cu side near the
sample surface. In contrast, the Cu_6Sn_5 /solder
interface remained at a similar position within the
same region.

The perpendicular IMCs on the sample surface
were profiled using the Zygo NewView 5000 after
aging. A series of surface profiles (grey region in
Fig. 6a) could then be extracted from the obtained
surface morphology across the solder/Cu interface,
from which an average surface profile of the region
could be derived (red profile in Fig. 6b). The height
of the perpendicular IMCs was then evaluated by
calculating the height difference between the peak
and the Cu surface in the average profile of the
scanned region. The relation between the heights of
the perpendicular IMCs and the aging duration is
plotted in Fig. 6b. Each data point in the figure
represents the average height of the perpendicular
IMCs from four specimens. It can be seen that the
height of the perpendicular IMCs generally in-
creased linearly with the square root of the aging
duration, which can be expressed as

Fig. 4. Top views showing evolution of perpendicular IMCs after aging at 175°C for (a) 0 h, (c) 168 h, and (e) 1132.5 h, and (b, d, f) example surface profiles from corresponding specimens.

$$y = 0.11\sqrt{t}, \quad (1)$$

where t is the aging duration in hours and y is the height of the perpendicular IMCs in μm . The parabolic correlation between the height of the perpendicular IMCs and the aging duration indicates that the perpendicular growth of the IMCs on the free surface of the solder joints is a diffusion-controlled process.^{15,16}

Planar Growth of IMCs

For comparison, the planar growth of IMCs along the interdiffusion direction between the solder and Cu was also studied by aging and etching. Figure 7

shows a comparison of the planar IMCs in a 99Sn-1Cu/Cu solder joint before aging and after aging at 175°C for 1006.5 h. It can be observed that the interfacial IMC layers grew significantly, from about 5 μm before aging to approximately 15 μm after aging for 1006.5 h. The morphology of the planar IMC layers also transformed from dendritic to layer type after aging.

Furthermore, only an interfacial Cu_6Sn_5 layer can be identified at the solder/Cu interface in Fig. 7a. The absence of a Cu_3Sn layer can be attributed to the insufficient reflow time for formation of an interfacial Cu_3Sn layer before cooling^{17–19} or the low magnification of the microscope. After aging, the Cu_6Sn_5 layer thickened notably and a

Fig. 5. Cross-sectional view of perpendicular IMCs at 99Sn-1Cu solder/Cu interface after aging at 175°C for 1132.5 h. The platinum (Pt) on the top was used to protect the materials beneath from damage by the ion beam during FIB milling.

Fig. 6. Perpendicular growth of IMCs versus aging duration: (a) example series of surface profiles derived from the scanned region of a specimen, with the solid highlighted line as the mean value of the multiple measurements represented in the grey region; (b) average height of perpendicular IMCs versus the square root of aging duration.

layer of Cu_3Sn was produced between the Cu_6Sn_5 layer and Cu substrate, as illustrated in Fig. 7b.

The thicknesses of the interfacial Cu_6Sn_5 , Cu_3Sn , and entire IMC layers were measured using the method explained in “Planar Growth of IMCs” section and are plotted as a function of aging duration in Fig. 8. Each data point in the figure is the average thickness of six specimens, and the error bar

Fig. 7. Observation of planar IMC layers at the 99Sn-1Cu solder/Cu interface (a) before aging and (b) after aging at 175°C for 1006.5 h.

indicates the standard deviation of the measurements. The linear fitting was based on the understanding that the planar growth of interfacial IMC layers is primarily dominated by the opposing diffusion of Sn and Cu atoms during aging, following a parabolic law with aging duration.²⁰ Figure 8 shows that the curve fitting result is a close approximation to the measured thickness of the interfacial IMC layers after increasing aging durations, and the relation can be expressed as

$$h_{\text{IMC}} = 0.27\sqrt{t} + 4.6, \\ h_{\text{Cu}_6\text{Sn}_5} = 0.16\sqrt{t} + 4.1 \quad \text{and} \quad h_{\text{Cu}_3\text{Sn}} = 0.17\sqrt{t}, \quad (2)$$

where t is the aging duration in hours and h is the thickness of each layer in μm . In comparison with the diffusion coefficients reported in Ref. 20, the value obtained in this work is within a reasonable range. Equation 2 also implies that the planar growth of IMCs is governed by the interdiffusion between the solder and Cu during aging.^{15,16} The constants in this equation, 4.6 and 4.1, indicate the initial thickness of the IMC layer before aging. They are supposed to be the same, since only a Cu_6Sn_5 layer can be observed before aging (Fig. 7a)). The minor variation between them could be due to error

Fig. 8. Correlation between growth of interfacial IMC layers and aging duration at 175°C.

in the measurements and curve fitting. From Fig. 8, it can also be found that the thickness of the interfacial Cu_3Sn and Cu_6Sn_5 layers did not follow a strict linear relation with the aging duration. This can be ascribed to the deviation in the measurement and the different initial states of the sites randomly chosen for measurement.

DISCUSSION

As presented in “Results” section, both perpendicular and planar growth of IMCs occurred at the solder/Cu interface, depending on the opposing interdiffusion of Sn and Cu atoms during aging. However, there are several differences between the growth of the IMCs in these two directions.

Movement of $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ and $\text{Cu}_3\text{Sn}/\text{Cu}$ Interfaces

The cross-section of the 99Sn-1Cu/Cu solder joint revealed by FIB illustrates that the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ and $\text{Cu}/\text{Cu}_3\text{Sn}$ interfaces moved towards the Cu side near the surface of the 99Sn-1Cu/Cu solder joint, as shown in Fig. 5. In contrast, the $\text{Cu}_6\text{Sn}_5/\text{solder}$ interface remained relatively more consistently within the same region. This shift of the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ and $\text{Cu}/\text{Cu}_3\text{Sn}$ interfaces leads to significant expansion of the Cu_6Sn_5 layer and a decrease in the thickness of the Cu_3Sn layer. Given the compositions of the Sn and Cu elements in these two types of IMC, it can be deduced that the concentration of Sn grows remarkably near the free surface of the solder joint.

In the region close to the sample surface, both bulk and surface diffusion of Sn atoms can contribute to the movement of Sn atoms during aging. However, for the region farther from the surface, Sn atoms can only move by bulk diffusion. Therefore, the increase in the Sn concentration near the sample surface indicates that the surface diffusion of Sn

atoms is much faster than their bulk diffusion in solder joints, which obeys the general observation that surface diffusion is faster than bulk diffusion.^{21,22}

Furthermore, this increase of the concentration of Sn also indicates a drop in the fraction of Cu atoms near the surface of the solder joints. Because the major diffusion mechanism for both Cu and Sn atoms is surface diffusion in this region, it is reasonable to conclude that the surface diffusion of Sn atoms is much faster than the surface diffusion of Cu atoms. Otherwise, the Cu-rich Cu_3Sn phase would expand instead of the Sn-rich Cu_6Sn_5 phase and the $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ interface and $\text{Cu}_6\text{Sn}_5/\text{solder}$ interface would move towards the solder side near the sample surface.

Comparison of Growth Mechanisms

For the planar growth of IMCs in solder joints, the IMC layers at the solder/Cu interface are normally formed during reflow. Although the existence of a Cu_3Sn layer in Sn-based solder/Cu solder joints after reflow remains controversial, it is generally accepted that the formation of Cu_6Sn_5 and Cu_3Sn is not simultaneous, with the former being prior to the latter.^{23–26} In contrast, in perpendicular IMCs, the Cu_3Sn is produced first, followed by the formation of Cu_6Sn_5 . These opposite formation sequences of Cu_6Sn_5 and Cu_3Sn in the perpendicular and planar IMCs can be primarily attributed to the different proportions of Sn and Cu atoms in the corresponding regions.

The initial formation of a planar Cu_6Sn_5 layer in a solder joint (i.e., a 99Sn-1Cu/Cu solder joint in this work) relies on the reaction between liquid solder and Cu during reflow. When the liquid solder is in contact with solid Cu, Cu_6Sn_5 is generated quickly due to the comparable concentration of Sn and Cu atoms in a localized region until the Cu_6Sn_5 layer covers the entire solder/Cu interface²⁷ (Fig. 9a). The growth of Cu_6Sn_5 in subsequent aging is primarily based on the reaction $6\text{Cu} + 5\text{Sn} \rightarrow \text{Cu}_6\text{Sn}_5$.²⁸

The growth of Cu_3Sn in planar IMCs during aging can be attributed to two possible mechanisms: the reaction between Sn and Cu ($3\text{Cu} + \text{Sn} \rightarrow \text{Cu}_3\text{Sn}$) and the transformation of Cu_6Sn_5 ($\text{Cu}_6\text{Sn}_5 + 9\text{Cu} \rightarrow 5\text{Cu}_3\text{Sn}$).²⁹ Both mechanisms suggest that the formation of a Cu_3Sn layer requires a Cu-enriched region.³⁰ Therefore, a Cu_3Sn layer can only be produced when the concentration of Sn is low enough at the $\text{Cu}_6\text{Sn}_5/\text{Cu}$ interface. This can happen only after the thickness of the interfacial Cu_6Sn_5 layer exceeds a certain threshold and the number of free Sn atoms near the Cu side is sufficiently reduced by the increasing diffusion distance (Fig. 9b). Therefore, the formation of Cu_3Sn is always after the formation of Cu_6Sn_5 in planar growth of IMCs (Fig. 9c). The subsequent growth of Cu_3Sn can be attributed to the decomposition of Cu_6Sn_5 due to the

Fig. 9. Schematic of growth characteristics of planar IMCs: (a) formation of initial Cu_6Sn_5 phase; (b) distribution of free Sn and Cu atoms at the interface due to diffusion process; (c) formation of Cu_3Sn at the $\text{Cu}_6\text{Sn}_5/\text{Cu}$ interface due to higher concentration of Cu.

Fig. 10. Formation of Cu_3Sn and Cu_6Sn_5 in perpendicular IMCs: (a) formation of Cu_3Sn and diffusion at the beginning of aging; (b) schematic illustration of the number of free Sn and Cu atoms within perpendicular IMCs from the bottom to top; (c) formation of Cu_6Sn_5 after Cu_3Sn grows to a certain height and movement of $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ and $\text{Cu}_3\text{Sn}/\text{Cu}$ interfaces towards the Cu side. (SD: surface diffusion, BD: bulk diffusion).

lack of Sn atoms at the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ interface and the possible reaction between Sn and Cu atoms at the $\text{Cu}/\text{Cu}_3\text{Sn}$ interface.²⁹

In contrast, the perpendicular growth of IMCs starts at the Cu side in the 99Sn-1Cu/Cu solder joint during aging (as shown in Figs. 4c and 5), which is probably due to the faster surface diffusion of Sn atoms as suggested in “Movement of $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ and $\text{Cu}_3\text{Sn}/\text{Cu}$ Interfaces” section. At the beginning of the perpendicular growth of the IMCs, the distance for diffusion of Cu atoms is negligible. However, Sn atoms need to diffuse through the entire planar Cu_6Sn_5 layer and a part of the planar Cu_3Sn layer to react with Cu atoms. Therefore, the proportion of Cu atoms is much higher than the proportion of Sn atoms in the region where perpendicular IMCs start growing. This Cu-rich region can lead to the formation and growth of

Cu_3Sn ($\text{Cu} + 3\text{Sn} \rightarrow \text{Cu}_3\text{Sn}$) before production of any Cu_6Sn_5 (Fig. 10a) during aging, as reported by other researchers.^{12–14}

After the initial formation of Cu_3Sn , the subsequent perpendicular growth of IMCs can be divided into two directions: the height direction and the width direction. For the height direction, when the Sn atoms reach the root of the perpendicular IMCs by diffusion, a part of the Sn can react with Cu atoms ($\text{Cu} + \text{Sn} \rightarrow \text{Cu}_3\text{Sn}$) to contribute to the perpendicular growth of the Cu_3Sn phase. However, the Sn and Cu atoms are not necessarily completely consumed by this reaction, because of the high activation energy required for formation of Cu_3Sn .^{31,32} Hence, the rest of the Sn and Cu atoms, possibly the majority of them, are able to move further to the frontier of the perpendicular Cu_3Sn by surface diffusion (and possibly a minor part of

Fig. 11. Comparison of perpendicular and planar growth of IMCs at the solder/Cu interface during aging at 175°C.

of Cu and Sn that contributes to the perpendicular growth of IMCs is believed to be much faster than their bulk diffusion in the planar growth.

For the perpendicular growth of IMCs, the sum diffusion distance of both Sn and Cu atoms generally consist of the thickness of the planar IMC layers and the height of the perpendicular IMCs, $D_{\text{perpendicular}} = H_{\text{planar IMCs}} + H_{\text{perpendicular IMCs}}$, where $D_{\text{perpendicular}}$ is the sum diffusion distance of both Sn and Cu for the perpendicular growth of IMCs, $H_{\text{planar IMCs}}$ is the thickness of the planar IMC layers, and $H_{\text{perpendicular IMCs}}$ is the height of the perpendicular IMCs. However, for the planar growth of IMCs within the solder joint, the total diffusion distance for both Sn and Cu atoms is the thickness of the planar IMC layers, $D_{\text{planar}} = H_{\text{planar IMCs}}$, where D_{planar} is the sum diffusion distance of both Sn and Cu atoms for planar growth of IMCs. Due to the additional height of the perpendicular IMCs ($H_{\text{perpendicular IMCs}}$) in the diffusion path, it is reasonable to conclude that the diffusion distance for perpendicular growth of IMCs is always longer than the diffusion path for planar growth of IMCs, $D_{\text{perpendicular}} > D_{\text{planar}}$.

The available free Sn and Cu atoms for producing the two types of IMCs can also significantly affect the growth rates along the two directions. The supply of Sn and Cu atoms in the planar growth of IMCs basically relies on the opposing diffusion from the adjacent solder and Cu substrate at the two sides of the IMC layers (as illustrated in Fig. 9c), which can be regarded as infinite. However, for the perpendicular growth of IMCs, the Sn and Cu atoms need to pass the planar IMC layers by surface diffusion and bulk diffusion before they can reach the root of the perpendicular IMCs (Fig. 10a). During diffusion, both Sn and Cu atoms can possibly be captured by the reactions that contribute to the planar growth of IMCs, particularly the Sn atoms from the solder side. The significant expansion of

bulk diffusion because of the small volume of Cu_3Sn present). The distance for diffusion of free Sn and Cu atoms along the height direction increases with the perpendicular growth of the Cu_3Sn present. As discussed in "Movement of $\text{Cu}_3\text{Sn}/\text{Cu}_6\text{Sn}_5$ and $\text{Cu}_3\text{Sn}/\text{Cu}$ Interfaces" section, the surface diffusion of Cu atoms is much slower in comparison with the surface diffusion of Sn atoms. Hence, with the perpendicular growth of the IMCs, the number of free Cu atoms in the perpendicular IMCs decreases much faster than the number of Sn atoms (as illustrated in Fig. 10b). This can result in a drop in the concentration of free Cu atoms at the frontier of the perpendicular Cu_3Sn . When the perpendicular Cu_3Sn is high enough and the diffusion distance for Sn and Cu atoms reaches a certain value, the fractions of Cu and Sn atoms become comparable. This can then lead to the formation and growth of Cu_6Sn_5 at the top of the perpendicular IMCs ($6\text{Cu} + 5\text{Sn} \rightarrow \text{Cu}_6\text{Sn}_5$) (Fig. 10c). Hence, the formation of Cu_6Sn_5 can only happen after the formation and growth of Cu_3Sn in the perpendicular IMCs in the height direction.

In the width direction, the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ interface in the planar IMCs moves towards the Cu_3Sn side (Figs. 5 and 10c) near the sample surface due to the much faster surface diffusion of Sn atoms during aging. Because of the greater supply of Sn atoms in comparison with the supply of Cu, a part of or even the entire Cu-rich Cu_3Sn phase present could be gradually transformed to Sn-rich Cu_6Sn_5 phase ($2\text{Cu}_3\text{Sn} + 3\text{Sn} \rightarrow \text{Cu}_6\text{Sn}_5$)³³ in both perpendicular IMCs (illustrated by the Cu_3Sn phase in dashed lines in Fig. 10c) and the planar IMCs near the sample surface. This decomposition of the Cu_3Sn phase could also happen at the $\text{Cu}_6\text{Sn}_5/\text{Cu}_3\text{Sn}$ interface in the perpendicular IMCs to facilitate growth of Cu_6Sn_5 along the height direction. On the other hand, the $\text{Cu}_3\text{Sn}/\text{Cu}$ interface in the planar IMCs also moves towards the Cu side near the sample surface because of the faster surface diffusion of Sn atoms. New Cu_3Sn can also be produced near the new $\text{Cu}_3\text{Sn}/\text{Cu}$ interface by the reaction $3\text{Cu} + \text{Sn} \rightarrow \text{Cu}_3\text{Sn}$ in both the planar and perpendicular IMCs (Fig. 10c), since this is a Cu-rich region.

Comparison of Growth Rates

A comparison of the growth rates of the perpendicular and planar IMCs is illustrated in Fig. 11. It is evident that the perpendicular growth of IMCs is much slower than the planar growth of interfacial IMC layers. Consequently, the thickness of the planar IMCs after aging is several times greater than the height of the perpendicular IMCs after aging for similar periods.

The lower growth rate of the perpendicular IMCs can be primarily ascribed to the longer diffusion distance of Sn and Cu atoms and the limited and decreasing supply of both Sn and Cu atoms in the perpendicular growth, though the surface diffusion

the planar Cu_6Sn_5 layer near the sample surface in Fig. 5 can be attributed to Sn atoms captured during surface diffusion from the solder to the bottom of the perpendicular IMCs. Hence, unlike the infinite supply of Sn and Cu atoms in the planar growth of IMCs, the supply of free atoms to the perpendicular growth of IMCs is limited.

After the Sn and Cu atoms reach the root of the perpendicular IMCs, they need to diffuse further from the bottom to the top (Fig. 10c), so that the height of the perpendicular IMCs can grow during aging. Because of the increasing diffusion distance due to the perpendicular growth of the IMCs, the numbers of free Sn and Cu atoms that can contribute to the perpendicular growth drop continuously during aging, as illustrated in Fig. 10b. Consequently, the limited and decreasing number of available Sn and Cu atoms can significantly retard the perpendicular growth of IMCs during aging, which is different from the planar growth of IMCs.

Potential Effects of Perpendicular Growth of IMCs

It has been reported that the growth of Cu_6Sn_5 and Cu_3Sn during aging can induce stress evolution within interfacial IMC layers due to volume shrinkage resulting from the density increase in solid-state reactions.³⁴ It is reasonable to assume that the growth of planar IMC layers in this work can also induce build-up of residual stress during aging. Similar to the effect of the growth of Sn whiskers,³⁵ perpendicular growth of IMCs may partly release this residual stress at the solder/Cu interface.³⁵ On the other hand, the residual stress in solder joints may also facilitate the perpendicular growth of IMCs, based on the suggestion that the perpendicular IMCs in solder joints after electromigration tests were “squeezed out” by compressive stress.^{9,10} However, the effect of the stress on the planar growth of IMCs remains uncertain, deserving further study.

Similar to the effect of Sn whiskers, perpendicular growth of IMCs can also possibly lead to failure of fine-pitch packages. In electronic packages, though there is no specifically prepared free surface, the perpendicular IMCs can still grow into the gap between two adjacent solder joints, which is perpendicular to the diffusion direction. When the pitch is reduced below 50 μm (as in three-dimensional packages), the gap between two adjacent microbumps is only 10 μm to 20 μm .^{36,37} In this case, perpendicular growth of IMCs is very likely to lead to shorts, which could be worse if the packaging density increases further in the future. Furthermore, protruding IMCs could be fractured into particles under vibration or mechanical loads. These loose IMC particles are also harmful to device reliability.

The risk of shorts due to perpendicular IMCs can be minimized by underfilling. It has been suggested that void-free encapsulation, such as conventional flip-chip

underfill, can well suppress growth of Sn whiskers to prevent electrical shorts.³⁸ This means that good encapsulation can also retard perpendicular growth of IMCs to prevent the resulting shorts. However, if the packaging density increases further, the decreasing gap between two adjacent microbumps could possibly bring significant challenges in achieving void-free encapsulation³⁹ and promote the possibility of electrical shorts. Hence, the perpendicular growth of IMCs should be further investigated in the future.

CONCLUSIONS

Planar and perpendicular growth of Cu-Sn IMCs in 99Sn-1Cu/Cu solder joints were studied after aging. From the cross-sectional views of perpendicular IMCs revealed by FIB, it was found that the morphology of the perpendicular IMCs was dendritic, which is different from the layer-type planar IMCs. Furthermore, the Cu/Cu₃Sn and Cu₃Sn/ Cu_6Sn_5 interfaces within the solder joint moved towards the Cu side near the sample surface, which can be ascribed to faster surface diffusion of Sn atoms within this region.

The formation sequence of Cu_6Sn_5 and Cu_3Sn in the perpendicular IMCs was also found to be opposite to that in planar IMC layers within solder joints. In perpendicular IMCs, the formation of Cu_3Sn is prior to the formation of Cu_6Sn_5 , because of the high concentration of Cu atoms where the perpendicular growth of IMCs starts. However, the Cu_6Sn_5 is believed to form before the Cu_3Sn in planar interfacial IMC layers, since a Cu-rich region is required to produce Cu_3Sn in planar IMC layers.

Both the planar and perpendicular growth of IMCs follow a parabolic law with aging duration, indicating that the growth was dominated by interdiffusion of Sn and Cu atoms during aging. However, the perpendicular growth of IMCs was much slower than the planar growth of IMCs. This can be attributed to the longer diffusion distance and the limited supply of Sn and Cu atoms in the perpendicular growth of IMCs during aging.

ACKNOWLEDGEMENTS

Z.C. would like to acknowledge the joint PhD programme between Loughborough University (UK) and Huazhong University of Science and Technology (China). This research was also supported by a Marie Curie International Research Staff Exchange Scheme Project within the 7th European Community Framework Programme, No. PIRSES-GA-2010-269113, entitled “Micro-Multi-Material Manufacture to Enable Multifunctional Miniaturised Devices (M6),” as well as the National Natural Science Foundation of China (No. 60976076).

REFERENCES

1. Y. Ping-Feng, L. Yi-Shao, S.-R. Jian, and C. Jiunn, *8th International Conference on Electronic Packaging Technology*, Shanghai, 14–17 August, 2007, pp. 1–5.

2. L. Jiang, H. Jiang, and N. Chawla, *J. Electron. Mater.* 41, 2089 (2012).
3. Q.K. Zhang, J. Tan, and Z.F. Zhang, *J. Appl. Phys.* 110, 014502 (2011).
4. S.W.R. Lee and S. Fubin, *International Microsystems, Packaging, Assembly Conference Taiwan 2006*, Taipei, 18–20 October, 2006, pp. 105–108.
5. J.H.L. Pang, T.H. Low, B.S. Xiong, X. Luhua, and C.C. Neo, *Thin Solid Films* 462–463, 370 (2004).
6. J.-W. Yoon, S.-W. Kim, and S.-B. Jung, *Mater. Trans.* 45, 727 (2004).
7. Y. Liu and F. Sun, *J. Mater. Sci. Mater. Electron.* 24 (2013).
8. C. Chen, H.-Y. Hsiao, Y.-W. Chang, F. Ouyang, and K.N. Tu, *Mater. Sci. Eng. R.* 73, 85 (2012).
9. T.Y. Lee, K.N. Tu, and D.R. Frear, *J. Appl. Phys.* 90, 4502 (2001).
10. C.-M. Chen and C.-H. Chen, *J. Electron. Mater.* 36, 1363 (2007).
11. Y.S. Kaganovskii, L.N. Paritskaya, V.V. Bogdanov, and A.O. Grengo, *Acta Mater.* 45, 3927 (1997).
12. J. Gong, C. Liu, P.P. Conway, and V.V. Silberschmidt, *Scripta Mater.* 60, 333 (2009).
13. C.Y. Liu and K.N. Tu, *J. Mater. Res.* 13, 37 (1998).
14. Y.S. Kaganovskii, L.N. Paritskaya, and V.V. Bogdanov, *Powder Metall. Met. C+* 47, 652 (2008).
15. Y.C. Chan, A.C.K. So, and J.K.L. Lai, *Mater. Sci. Eng. B* 55, 5 (1998).
16. W. Peng, E. Monlevade, and M.E. Marques, *Microelectron. Reliab.* 47, 2161 (2007).
17. X. Li, F. Li, F. Guo, and Y. Shi, *J. Electron. Mater.* 40, 5221 (2011).
18. Z. Huijing, Q. Lin, L. Hua, Z. Ning, and M. HaiTao, *14th International Conference on Electronic Packaging Technology*, Dalian, 11–14 August, 2013, pp. 372–376.
19. H. Xiao, X.Y. Li, Y.X. Zhu, J.L. Yang, J. Chen, and F. Guo, *J. Mater. Sci. Mater. Electron.* 24, 2527 (2013).
20. T.-T. Luu, A. Duan, K. Aasmundtveit, and N. Hoivik, *J. Electron. Mater.* 42, 3582 (2013).
21. H.K. Kim, H.K. Liou, and K.N. Tu, *J. Mater. Res.* 10, 497 (1995).
22. X. Chen, Z. Yun, F. Chonglun, and J.A. Abys, *IEEE Trans. Electron. Packag. Manuf.* 28 (2005).
23. M.Y. Tsai, S.C. Yang, Y.W. Wang, and C.R. Kao, *J. Alloys Compd.* 494, 123 (2010).
24. T. Laurila, V. Vuorinen, and J.K. Kivilahti, *Mater. Sci. Eng. R.* 49, 1 (2005).
25. K.N. Tu and R.D. Thompson, *Acta Metall. Mater.* 30, 947 (1982).
26. B.-J. Lee, N.M. Hwang, and H.M. Lee, *Acta Mater.* 45, 1867 (1997).
27. R.A. Gagliano, G. Ghosh, and M.E. Fine, *J. Electron. Mater.* 31, 1195 (2002).
28. X. Deng, G. Piotrowski, J.J. Williams, and N. Chawla, *J. Electron. Mater.* 32, 1403 (2003).
29. Z. Kejun, R. Stierman, C. Tz-Cheng, D. Edwards, K. Ano, and K.N. Tu, *J. Appl. Phys.* 97, 024508 (2005).
30. C.-C. Pan, C.-H. Yu, and K.-L. Lin, *Appl. Phys. Lett.* 93 (2008).
31. Y. Wu, J. Sees, C. Pouraghabagher, L.A. Foster, J. Marshall, E. Jacobs, and R. Pinizzotto, *J. Electron. Mater.* 22, 769 (1993).
32. H.L.J. Pang, K.H. Tan, X.Q. Shi, and Z.P. Wang, *Mater. Sci. Eng. A* 307, 42 (2001).
33. C. Yu, Y. Yang, J. Chen, J. Xu, J. Chen, and H. Lu, *Mater. Lett.* 128 (2014).
34. J.Y. Song, J. Yu, and T.Y. Lee, *Scripta Mater.* 51, 167 (2004).
35. K.N. Tu, C. Chen, and A. Wu, *J. Mater. Sci. Mater. Electron.* 18, 269 (2007).
36. M. Kawano, S. Uchiyama, Y. Egawa, N. Takahashi, Y. Kurita, K. Soejima, M. Komuro, S. Matsui, K. Shibata, J. Yamada, M. Ishino, H. Ikeda, Y. Saeki, O. Kato, H. Kikuchi, and T. Mitsuhashi, *International Electron Devices Meeting 2006*, San Francisco, 11–13 December, 2006, pp. 1–4.
37. Y. Seung Wook, K. Jae Hoon, N. Suthiwongsunthorn, P.C. Marimuthu, and F. Carson, *IEEE International Conference on 3D System Integration 2009*, San Francisco, 28–30 September, 2009, pp. 1–5.
38. J. Brusse, G. Ewell, and J. Siplon, *22nd Capacitor and Resistor Technology Symposium*, New Orleans, 25–29 March, 2002, pp. 67–80.
39. C.Y. Khor, M.Z. Abdullah, Z.M. Ariff, and W.C. Leong, *Int. Commun. Heat Mass.* 39, 670 (2012).

Journal : 11664
Article : 4043

Author Query Form

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your article, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query	Details Required	Author's Response
AQ1	Kindly check the term 'Sn99Cu1/Cu' has been changed throughout as '99Sn-1Cu/Cu'.	
AQ2	As per the information provided by the publisher, Fig. 2 will be black and white in print; hence, please confirm whether we can add "colour figure online" to the caption.	
AQ3	Kindly confirm "linear" here.	
AQ4	Kindly confirm this edit from "until" to "when".	
AQ5	Kindly confirm the stoichiometry of this equation.	
AQ6	Please provide page number for Refs. 7, 22, and 30.	
AQ7	Kindly check and confirm all the references identified correctly.	