Metadata of the article that will be visualized in OnlineFirst

ArticleTitle	Perpendicular Growth Characteristics of Cu-Sn Intermetallic Compounds at the Surface of 99Sn-1 Solder Interconnects	
Article Sub-Title		
Article CopyRight	The Minerals, Metals & (This will be the copyr	& Materials Society ight line in the final PDF)
Journal Name	Journal of Electronic N	Iaterials
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
	Email	
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

	Address	Wuhan, Hubei, People's Republic of China
	Email	
	Received	23 February 2015
Schedule	Revised	
	Accepted	4 September 2015
Abstract	perpendicular to the specifically design. After aging at 175° examined and four where <i>t</i> is the aging the planar growth of joints. After prolor parabolically with thickness in μ m an the IMCs were diffi- than their planar gr formation of Cu ₆ Sn growth.	rmetallic compounds (IMCs) on the free surface of 99Sn-1Cu solder joints e interdiffusion direction has been investigated in this work. The specimens were ed and polished to reveal a flat free surface at the solder/Cu interface for investigation. ² C for progressively increased durations, the height of the perpendicular IMCs was ad to follow a parabolic law with aging duration that could be expressed as $y = 0.11\sqrt{t}$, g duration in hours and y is the height of the perpendicular IMCs in μ m. For comparison, of IMCs along the interdiffusion direction was also investigated in 99Sn-1Cu/Cu solder need aging at 175°C, the thickness of the planar interfacial IMC layers also increased aging duration and could be expressed as $h_{IMC} = 0.27\sqrt{t} + 4.6$, where h is the d t is the time in hours. It was found that both the planar and perpendicular growth of fusion-controlled processes, but the perpendicular growth of the IMCs was much slower rowth due to the longer diffusion distance. It is proposed that Cu ₃ Sn forms prior to the n ₅ in the perpendicular IMCs, being the reverse order compared with the planar IMC
Keywords (separated by '-')	Solder joint - plana formation sequence	ar growth of IMCs - perpendicular growth of IMCs - interdiffusion - growth rate - e 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 μ m. 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 $h_{\rm IMC} = 0.27\sqrt{t} + 4.6$, where h is the thickness in μ m 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

32

INTRODUCTION

33 In electronic devices, the interconnections be-34 tween components are normally formed by reflow-35 ing solder alloys. During such reflow, the reactions 36 between the solder and substrate are essential to 37 the formation of reliable solder interconnects. 38 However, the interfacial intermetallic compound 39 (IMC) layers produced during reflow can grow con-40 tinuously during subsequent service due to inter-41 diffusion and solid-state reactions, particularly 42 when devices are exposed to elevated temperature. 43 Excessive growth of interfacial IMC layers can sig-44 nificantly deteriorate the mechanical integrity of

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

the entire solder joint because of the incompatible 45 mechanical properties of the interfacial IMC layers 46 in comparison with the solder alloy and substrate. $^{1-3}$ Hence, growth of IMCs at the solder/substrate interface has received continuous attention 49 from researchers. 50

The interfacial IMC layers extensively investi-51 gated in literature normally cover the entire sol-52 der/substrate interface and grow along the direction 53 54 of interdiffusion between the solder and substrate.^{4–8} Therefore, this type of interfacial IMC 55 layer is termed the planar IMC layer in this work, 56 as illustrated in Fig. 1. Moreover, IMCs (i.e., Cu-Sn 57 IMCs) can also protrude out of the free surface of 58 solder joints, perpendicular to the diffusion direc-59 tion within the solder joint,⁹ as illustrated in Fig. 1. 60 This is termed the perpendicular IMC in this work. 61

1 2

6

7

10

11

12

13

14

15

16 17

18

19 20

21

22

23

24

25

26

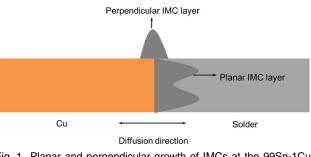
27

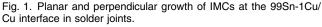
28

29

30

Journal : 11664_JEM	Dispatch : 18-9-2015	Pages : 10
Article No.: 4043	□ LE IZ CP	□ TYPESET Ø DISK





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 per-IMCs "squeezed pendicular were out" bv 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

62

63

64

65

66

67

68

69 70

71

72

73

92

Author Proo

74 In this study, the perpendicular growth of IMCs 75 was investigated in specifically designed 99Sn-1Cu/ 76 Cu solder joints. The top surface of the solder joints 77 was polished and profiled using a white-light interferometer after gradually prolonged aging at 78 79 175°C to measure the height of the perpendicular 80 IMCs. Scanning electron microscopy (SEM) was 81 employed to examine the morphology of the per-82 pendicular IMCs from the top, and cross-sectional 83 views were prepared by focused ion beam (FIB). In 84 comparison, the ordinary planar growth of interfa-85 cial IMC layers at the 99Sn-1Cu/Cu interface was 86 also characterized by grinding and polishing to re-87 veal the cross-section of the solder joints after aging 88 at the same temperature for increasing periods. 89 Correlations and differences between the IMC 90 growth along these two directions are also pre-91 sented.

EXPERIMENTAL PROCEDURES

93 Perpendicular Growth of IMCs

94 To investigate the perpendicular growth of IMCs, a pocket with dimensions of 15 mm imes 15 mm imes 15 mm imes95 96 2.5 mm was machined within a Cu (purity 99.9%) 97 specimen. A proper amount of 99Sn-1Cu solder was 98 placed in the pocket and reflowed in an oven. During 99 reflow, a thermocouple was attached to the specimen 100 to monitor its temperature. After reflow, the speci-101 mens were ground and polished to ensure that the top 102 surface across the solder/Cu interface was smooth in 103 one plane. The specimen after polishing is shown 104 schematically in Fig. 2a.

105 The four specimens were then stored in an oven at 106 temperature of 175°C to facilitate the perpendicular

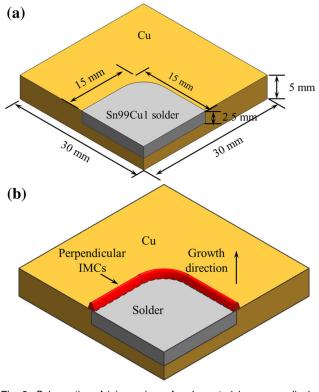


Fig. 2. Schematics of (a) specimen for characterizing perpendicular growth of IMCs and (b) perpendicular growth of IMCs (the red region) on the top surface of the specimen after aging.

growth of IMCs at the solder/Cu interface (as illus-107 trated by the red region in Fig. 2b). After aging for 108 every 168 h until 1132.5 h, the specimens were re-109 moved from the oven after cooling. The height of the 110 perpendicular IMCs on the polished top surface was 111 then measured using a white-light interferometer 112 (Zygo NewView 5000) at the same location for a gi-113 ven specimen. The areas of the scanned regions 114 were no smaller than $1.5 \text{ mm} \times 1.0 \text{ mm}$ to ensure 115 reliability of the obtained morphology of the speci-116 mens. The obtained surface morphology data were 117 then converted into a series of profiles to calculate 118 the average height of the perpendicular IMCs on the 119 specimen. 120

After these measurements, SEM was used to 121 122 examine the perpendicular IMCs from the top. FIB was also utilized to mill the specimen across the 123 99Sn-1Cu/Cu interface to reveal the cross-section of 124 the perpendicular IMCs after aging. However, mil-125 126 ling the samples with FIB should be carefully planned as it could potentially introduce several 127 types of artificial damage in the specimens: (1) the 128 polished sample surface could be seriously damaged 129 in a wide range during the milling and imaging with 130 the ion beam in FIB; (2) the reliability of the mea-131 sured heights of the perpendicular IMCs could be 132 affected due to damage of the IMCs on the top sur-133 face; (3) the large hole in the sample and the fresh 134 135 surface left by milling could lead to significant oxi-



Journal : 11664_JEM	Dispatch : 18-9-2015	Pages : 10
Article No.: 4043	□ LE IZ CP	□ TYPESET ✓ DISK

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

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 minimize its potential influence on the reliability of 139

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.%) and hydrochloric acid (20 vol.%) solution. An 156 157 Olympus BX60 M microscope was utilized for observation of the planar interfacial IMC layers. 158 159 The interfaces between the solder, Cu₆Sn₅, Cu₃Sn, 160 and Cu in the microscope images were fit with traces 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.

RESULTS

Perpendicular Growth of IMCs 166

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 remove the effect of the angle between the specimen 176 177 and the instrument during scanning. Before aging,

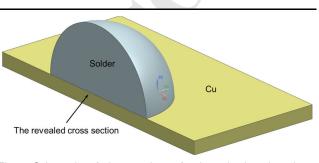


Fig. 3. Schematic of the specimen for investigating the planar growth of IMCs within 99Sn-1Cu/Cu solder joints after aging at 175°C

the surface of the 99Sn-1Cu solder joints was 178 179 smooth across the solder/Cu interface after polishing, as illustrated in Fig. 4a. No perpendicular 180 IMCs could be identified. Correspondingly, there is 181 no notable peak at the solder/Cu interface in the 182 surface profile in Fig. 4b. The height difference be-183 184 tween the solder part and Cu surface was probably due to the higher polishing rate on the softer solder 185 in comparison with the polishing rate on the Cu 186 during sample preparation. 187

After aging at 175°C for 168 h, a line of IMCs was 188 observed to protrude out of the surface at the solder/ 189 Cu interface, as shown in Fig. 4c. The spikes of the 190 perpendicular IMCs can also be identified in the 191 corresponding surface profile in Fig. 4d. The aver-192 age height of the perpendicular IMCs can be esti-193 mated to be about 0.5 μ m, with the Cu surface as 194 195 reference. When the aging was extended to 1132.5 h, the perpendicular IMCs grew significantly 196 197 in both height and width, as illustrated in Fig. 4e, 198 and the height of the perpendicular IMCs increased 199 to approximately 1.5 μ m (Fig. 4f).

FIB was then utilized to reveal a cross-sectional 200 view of the perpendicular IMCs at the solder/Cu 201 interface after aging for 1132.5 h (Fig. 5). It is evi-202 dent that the perpendicular IMCs on the sample 203 surface were dendritic along several specific direc-204 tions, which is different from the layer-type inter-205 facial IMC layers within solder joints. Both Cu₆Sn₅ 206 and Cu₃Sn phases can be found in the perpendicular 207 IMCs, with the Cu_3Sn at the bottom of the dendrites 208 close to the Cu/Cu₃Sn interface. The "root" of the 209 210 perpendicular IMCs was a Cu-rich region, so the 211 Cu₃Sn phase was probably produced before the formation of Cu₆Sn₅ in the initial perpendicular 212 growth of IMCs,^{12–14} as discussed further in "Com-213 parison of Growth Mechanisms" section below. 214 Furthermore, it can also be observed that the Cu/ 215 Cu₃Sn interface and Cu₃Sn/Cu₆Sn₅ interface in the 216 planar IMCs shifted towards the Cu side near the 217 sample surface. In contrast, the Cu₆Sn₅/solder 218 interface remained at a similar position within the 219 same region. 220

The perpendicular IMCs on the sample surface 221 were profiled using the Zygo NewView 5000 after 222 223 aging. A series of surface profiles (grey region in Fig. 6a) could then be extracted from the obtained 224 225 surface morphology across the solder/Cu interface, from which an average surface profile of the region 226 could be derived (red profile in Fig. 6b). The height 227 of the perpendicular IMCs was then evaluated by 228 calculating the height difference between the peak 229 230 and the Cu surface in the average profile of the scanned region. The relation between the heights of 231 232 the perpendicular IMCs and the aging duration is plotted in Fig. 6b. Each data point in the figure 233 234 represents the average height of the perpendicular IMCs from four specimens. It can be seen that the 235 height of the perpendicular IMCs generally in-236 creased linearly with the square root of the aging 237 238 duration, which can be expressed as



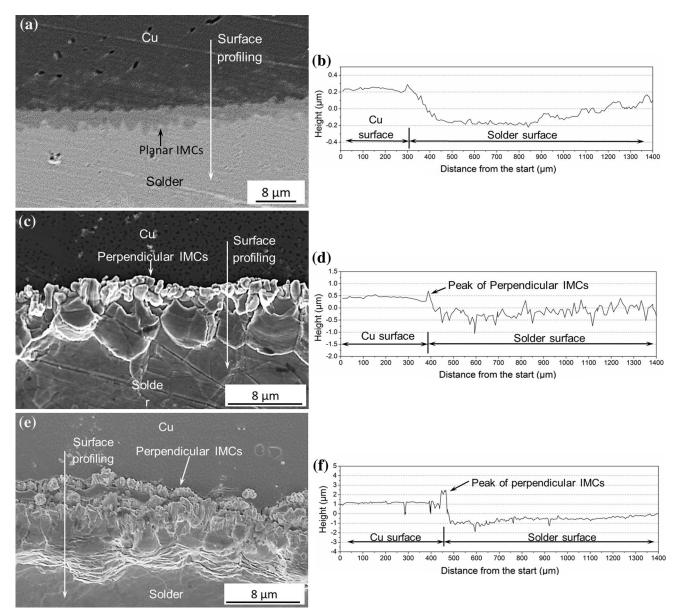


Fig. 4. Top views showing evolution of perpendicular IMCs after aging at 175°C for (a) 0 h, (c) 168 h, and (e) 1132.5 h, and (b, d, f) example surface profiles from corresponding specimens.

$$y = 0.11\sqrt{t},\tag{1}$$

where *t* is the aging duration in hours and *y* is the height of the perpendicular IMCs in μ m. 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}

248 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-252 1Cu/Cu solder joint before aging and after aging at 253 175°C for 1006.5 h. It can be observed that the 254 interfacial IMC layers grew significantly, from 255 about 5 μ m before aging to approximately 15 μ m 256 after aging for 1006.5 h. The morphology of the 257 planar IMC layers also transformed from dendritic 258 259 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



Journal : 11664_JEM	Dispatch : 18-9-2015	Pages : 10
Article No.: 4043	□ LE IZ CP	□ TYPESET ✔ DISK

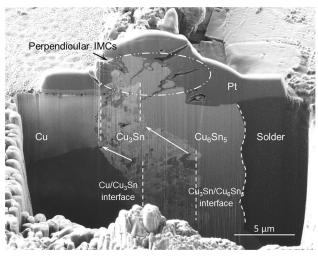


Fig. 5. Cross-sectional view of perpendicular IMCs at 99Sn-1Cu solder/Cu interface after aging at 175° C for 1132.5 h. The platinum (Pt) on the top was used to protect the materials beneath from damage by the ion beam during FIB milling.

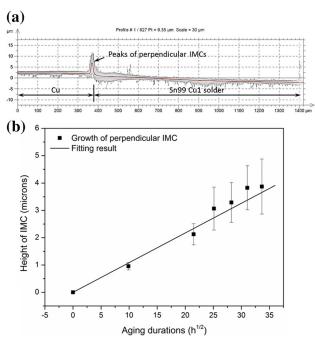


Fig. 6. Perpendicular growth of IMCs versus aging duration: (a) example series of surface profiles derived from the scanned region of a specimen, with the solid highlighted line as the mean value of the multiple measurements represented in the grey region; (b) average height of perpendicular IMCs versus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

267 layer of Cu_3Sn was produced between the Cu_6Sn_5 268 layer and Cu substrate, as illustrated in Fig. 7b. 269 The thicknesses of the interfacial Cu_6Sn_5 , Cu_2Sn_5

269 The thicknesses of the interfacial Cu_6Sn_5 , Cu_3Sn , 270 and entire IMC layers were measured using the 271 method explained in "Planar Growth of IMCs" sec-272 tion and are plotted as a function of aging duration 273 in Fig. 8. Each data point in the figure is the aver-274 age thickness of six specimens, and the error bar

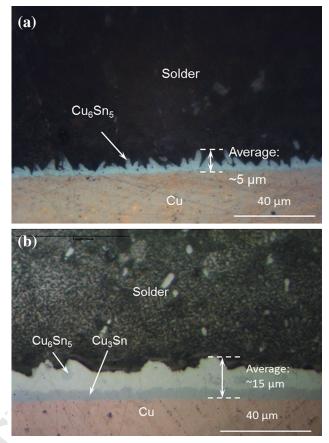


Fig. 7. Observation of planar IMC layers at the 99Sn-1Cu solder/Cu interface (a) before aging and (b) after aging at 175°C for 1006.5 h.

275 indicates the standard deviation of the measure-276 ments. The linear fitting was based on the understanding that the planar growth of interfacial IMC 277 layers is primarily dominated by the opposing dif-278 fusion of Sn and Cu atoms during aging, following a 279 parabolic law with aging duration.²⁰ Figure 8 shows 280 that the curve fitting result is a close approximation 281 to the measured thickness of the interfacial IMC 282 layers after increasing aging durations, and the 283 relation can be expressed as 284

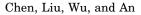
$$egin{aligned} h_{ ext{IMC}} &= 0.27 \sqrt{t} + 4.6, \ h_{ ext{Cu6Sn5}} &= 0.16 \sqrt{t + 4.1} & ext{and} & h_{ ext{Cu3Sn}} = 0.17 \sqrt{t}, \end{aligned}$$

<u>ن</u>

289 where t is the aging duration in hours and h is the thickness of each layer in μ m. In comparison with 288 the diffusion coefficients reported in Ref. 20, the 289 value obtained in this work is within a reasonable 290 range. Equation 2 also implies that the planar 291 growth of IMCs is governed by the interdiffusion 292 between the solder and Cu during aging.^{15,16} The 293 constants in this equation, 4.6 and 4.1, indicate the 294 initial thickness of the IMC layer before aging. They 295 296 are supposed to be the same, since only a Cu_6Sn_5 297 layer can be observed before aging (Fig. 7a)). The minor variation between them could be due to error 298



	Journal : 11664_JEM	Dispatch : 18-9-2015	Pages : 10
			TYPESET
\sim	Article No.: 4043	CP	V DISK



352

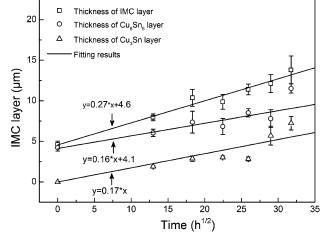


Fig. 8. Correlation between growth of interfacial IMC layers and aging duration at 175°C.

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 Cu₃Sn/Cu₆Sn₅ and Cu₃Sn/Cu Interfaces

315 The cross-section of the 99Sn-1Cu/Cu solder joint 316 revealed by FIB illustrates that the Cu₆Sn₅/Cu₃Sn 317 and Cu/Cu₃Sn interfaces moved towards the Cu side 318 near the surface of the 99Sn-1Cu/Cu solder joint, as 319 shown in Fig. 5. In contrast, the Cu₆Sn₅/solder 320 interface remained relatively more consistently 321 within the same region. This shift of the $Cu_6Sn_5/$ 322 Cu₃Sn and Cu/Cu₃Sn interfaces leads to significant 323 expansion of the Cu₆Sn₅ layer and a decrease in the 324 thickness of the Cu₃Sn layer. Given the composi-325 tions of the Sn and Cu elements in these two types 326 of IMC, it can be deduced that the concentration of 327 Sn grows remarkably near the free surface of the 328 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 336 solder joints, which obeys the general observation 337 that surface diffusion is faster than bulk diffusion.^{21,22} 338 339

Furthermore, this increase of the concentration of 340 Sn also indicates a drop in the fraction of Cu atoms 341 near the surface of the solder joints. Because the 342 major diffusion mechanism for both Cu and Sn 343 atoms is surface diffusion in this region, it is rea-344 sonable to conclude that the surface diffusion of Sn 345 atoms is much faster than the surface diffusion of 346 Cu atoms. Otherwise, the Cu-rich Cu₃Sn phase 347 would expand instead of the Sn-rich Cu_6Sn_5 phase 348 and the Cu₃Sn/Cu₆Sn₅ interface and Cu₆Sn₅/solder 349 interface would move towards the solder side near 350 the sample surface. 351

Comparison of Growth Mechanisms

For the planar growth of IMCs in solder joints, 353 the IMC layers at the solder/Cu interface are nor-354 355 mally formed during reflow. Although the existence of a Cu₃Sn layer in Sn-based solder/Cu solder joints 356 after reflow remains controversial, it is generally 357 accepted that the formation of Cu₆Sn₅ and Cu₃Sn is 358 not simultaneous, with the former being prior to the 359 ²⁶ In contrast, in perpendicular IMCs, the latter.²³ 360 Cu₃Sn is produced first, followed by the formation of 361 Cu₆Sn₅. These opposite formation sequences of 362 Cu₆Sn₅ and Cu₃Sn in the perpendicular and planar 363 IMCs can be primarily attributed to the different 364 365 proportions of Sn and Cu atoms in the corresponding regions. 366

The initial formation of a planar Cu₆Sn₅ layer in a 367 solder joint (i.e., a 99Sn-1Cu/Cu solder joint in this 368 work) relies on the reaction between liquid solder 369 and Cu during reflow. When the liquid solder is in 370 contact with solid Cu, Cu₆Sn₅ is generated quickly 371 due to the comparable concentration of Sn and Cu 372 atoms in a localized region until the Cu₆Sn₅ layer 373 covers the entire solder/Cu interface²⁷ (Fig. 9a). The 374 growth of Cu₆Sn₅ in subsequent aging is primarily 375 based on the reaction 6Cu + 5Sn \rightarrow Cu₆Sn₅.² 376

The growth of Cu₃Sn in planar IMCs during aging 377 378 can be attributed to two possible mechanisms: the reaction between Sn and Cu $(3Cu + Sn \rightarrow Cu_3Sn)$ 379 and the transformation of Cu_6Sn_5 (Cu_6Sn_5 + 380 $9Cu \rightarrow 5Cu_3Sn$).²⁹ Both mechanisms suggest that 381 the formation of a Cu₃Sn layer requires a Cu-en-382 riched region.³⁰ Therefore, a Cu₃Sn layer can only 383 be produced when the concentration of Sn is low 384 enough at the Cu₆Sn₅/Cu interface. This can happen 385 only after the thickness of the interfacial Cu_6Sn_5 386 layer exceeds a certain threshold and the number of 387 free Sn atoms near the Cu side is sufficiently re-388 duced by the increasing diffusion distance (Fig. 9b). 389 390 Therefore, the formation of Cu₃Sn is always after 391 the formation of Cu₆Sn₅ in planar growth of IMCs 392 (Fig. 9c). The subsequent growth of Cu_3Sn can be attributed to the decomposition of Cu₆Sn₅ due to the 393



Journal : 11664_JEM	Dispatch : 18-9-2015	Pages : 10
Article No.: 4043	□ LE IV CP	□ TYPESET ✔ DISK
		DISK

Perpendicular Growth Characteristics of Cu-Sn Intermetallic Compounds at the Surface of $99\mathrm{Sn-1Cu/Cu}$ Solder Interconnects

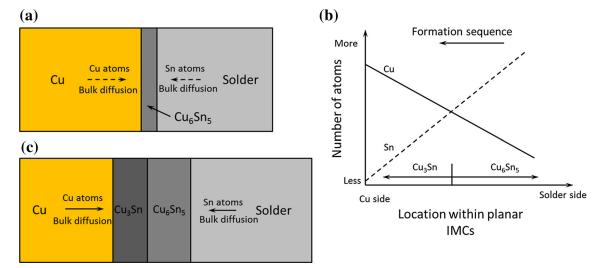


Fig. 9. Schematic of growth characteristics of planar IMCs: (a) formation of initial Cu_6Sn_5 phase; (b) distribution of free Sn and Cu atoms at the interface due to diffusion process; (c) formation of Cu_3Sn at the Cu_6Sn_5/Cu interface due to higher concentration of Cu.

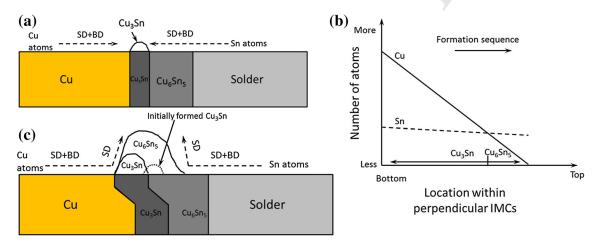


Fig. 10. Formation of Cu_3Sn and Cu_6Sn_5 in perpendicular IMCs: (a) formation of Cu_3Sn and diffusion at the beginning of aging; (b) schematic illustration of the number of free Sn and Cu atoms within perpendicular IMCs from the bottom to top; (c) formation of Cu_6Sn_5 after Cu_3Sn grows to a certain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

lack of Sn atoms at the Cu₆Sn₅/Cu₃Sn interface and
the possible reaction between Sn and Cu atoms at
the Cu/Cu₃Sn interface.²⁹

397 In contrast, the perpendicular growth of IMCs 398 starts at the Cu side in the 99Sn-1Cu/Cu solder joint 399 during aging (as shown in Figs. 4c and 5), which is probably due to the faster surface diffusion of Sn 400 401 atoms as suggested in "Movement of Cu₃Sn/Cu₆Sn₅ 402 and Cu₃Sn/Cu Interfaces" section. At the beginning 403 of the perpendicular growth of the IMCs, the dis-404 tance for diffusion of Cu atoms is negligible. How-405 ever, Sn atoms need to diffuse through the entire planar Cu₆Sn₅ layer and a part of the planar Cu₃Sn 406 layer to react with Cu atoms. Therefore, the pro-407 408 portion of Cu atoms is much higher than the proportion of Sn atoms in the region where 409 perpendicular IMCs start growing. This Cu-rich 410 411 region can lead to the formation and growth of $Cu_3Sn~(Cu + 3Sn \rightarrow Cu_3Sn)$ before production of any $Cu_6Sn_5~(Fig.~10a)$ during aging, as reported by other researchers. $^{12-14}$

After the initial formation of Cu₃Sn, the subsequent perpendicular growth of IMCs can be divided 416 into two directions: the height direction and the 417 width direction. For the height direction, when the 418 Sn atoms reach the root of the perpendicular IMCs 419 by diffusion, a part of the Sn can react with Cu 420 atoms $(Cu + Sn \rightarrow Cu_3Sn)$ to contribute to the 421 perpendicular growth of the Cu₃Sn phase. However, 422 the Sn and Cu atoms are not necessarily completely 423 consumed by this reaction, because of the high 424 activation energy required for formation of $Cu_3Sn.^{31,32}$ Hence, the rest of the Sn and Cu atoms, 425 426 possibly the majority of them, are able to move 427 further to the frontier of the perpendicular Cu₃Sn 428 by surface diffusion (and possibly a minor part of 429



413 414 415

430 bulk diffusion because of the small volume of Cu₃Sn 431 present). The distance for diffusion of free Sn and 432 Cu atoms along the height direction increases with 433 the perpendicular growth of the Cu₃Sn present. As 434 discussed in "Movement of Cu₃Sn/Cu₆Sn₅ and 435 Cu₃Sn/Cu Interfaces" section, the surface diffusion 436 of Cu atoms is much slower in comparison with the 437 surface diffusion of Sn atoms. Hence, with the per-438 pendicular growth of the IMCs, the number of free 439 Cu atoms in the perpendicular IMCs decreases 440 much faster than the number of Sn atoms (as 441 illustrated in Fig. 10b). This can result in a drop in 442 the concentration of free Cu atoms at the frontier of 443 the perpendicular Cu_3Sn . When the perpendicular 44 Cu₃Sn is high enough and the diffusion distance for 45 Sn and Cu atoms reaches a certain value, the frac-46 tions of Cu and Sn atoms become comparable. This 47 48 49 50 can then lead to the formation and growth of Cu₆Sn₅ of the at the top perpendicular IMCs $(6Cu + 5Sn \rightarrow Cu_6Sn_5)$ (Fig. 10c). Hence, the formation of Cu₆Sn₅ can only happen after the forma-451 tion and growth of Cu₃Sn in the perpendicular IMCs 452 in the height direction.

Proof

453 In the width direction, the Cu₆Sn₅/Cu₃Sn interface 454 in the planar IMCs moves towards the Cu₃Sn side 455 (Figs. 5 and 10c) near the sample surface due to the 456 much faster surface diffusion of Sn atoms during 457 aging. Because of the greater supply of Sn atoms in 458 comparison with the supply of Cu, a part of or even 459 the entire Cu-rich Cu₃Sn phase present could be 460 gradually transformed to Sn-rich Cu₆Sn₅ phase $(2Cu_3Sn + 3Sn \rightarrow Cu_6Sn_5)^{33}$ in both perpendicular 461 IMCs (illustrated by the Cu₃Sn phase in dashed lines 462 in Fig. 10c) and the planar IMCs near the sample 463 surface. This decomposition of the Cu₃Sn phase could 464 465 also happen at the Cu_6Sn_5/Cu_3Sn interface in the perpendicular IMCs to facilitate growth of Cu₆Sn₅ 466 467 along the height direction. On the other hand, the 468 Cu₃Sn/Cu interface in the planar IMCs also moves 469 towards the Cu side near the sample surface because 470 of the faster surface diffusion of Sn atoms. New 471 Cu₃Sn can also be produced near the new Cu₃Sn/Cu 472 interface by the reaction $3Cu + Sn \rightarrow Cu_3Sn$ in 473 both the planar and perpendicular IMCs (Fig. 10c), 474 since this is a Cu-rich region.

475 **Comparison of Growth Rates**

476 A comparison of the growth rates of the perpen-477 dicular and planar IMCs is illustrated in Fig. 11. It 478 is evident that the perpendicular growth of IMCs is 479 much slower than the planar growth of interfacial 480 IMC layers. Consequently, the thickness of the 481 planar IMCs after aging is several times greater 482 than the height of the perpendicular IMCs after 483 aging for similar periods.

484 The lower growth rate of the perpendicular IMCs 485 can be primarily ascribed to the longer diffusion 486 distance of Sn and Cu atoms and the limited and 487 decreasing supply of both Sn and Cu atoms in the 488 perpendicular growth, though the surface diffusion

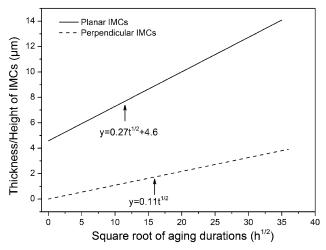


Fig. 11. Comparison of perpendicular and planar growth of IMCs at the solder/Cu interface during aging at 175°C.

489 of Cu and Sn that contributes to the perpendicular 490 growth of IMCs is believed to be much faster than their bulk diffusion in the planar growth. 491

For the perpendicular growth of IMCs, the sum 492 diffusion distance of both Sn and Cu atoms gener-493 ally consist of the thickness of the planar IMC lay-494 ers and the height of the perpendicular IMCs, 495 $D_{\text{perpendicular}} = H_{\text{planar}}$ IMCs + $H_{\text{perpendicular}}$ IMCs, where $D_{\text{perpendicular}}$ is the sum diffusion distance of 496 497 both Sn and Cu for the perpendicular growth of 498 IMCs, $H_{\text{planar IMCs}}$ is the thickness of the planar 499 IMC layers, and $H_{\text{perpendicular IMCs}}$ is the height of the perpendicular IMCs. However, for the planar 500 501 growth of IMCs within the solder joint, the total 502 diffusion distance for both Sn and Cu atoms is the 503 thickness of the planar IMC layers, $D_{\text{planar}} = H_{\text{planar IMCs}}$, where D_{planar} is the sum diffusion dis-504 505 tance of both Sn and Cu atoms for planar growth of 506 IMCs. Due to the additional height of the perpen-507 508 dicular IMCs $(H_{\text{perpendicular IMCs}})$ in the diffusion 509 path, it is reasonable to conclude that the diffusion 510 distance for perpendicular growth of IMCs is always longer than the diffusion path for planar growth of 511 IMCs, $D_{\text{perpendicular}} > D_{\text{planar}}$. The available free Sn and Cu atoms for producing 512

513 514 the two types of IMCs can also significantly affect the growth rates along the two directions. The 515 supply of Sn and Cu atoms in the planar growth of 516 IMCs basically relies on the opposing diffusion from 517 the adjacent solder and Cu substrate at the two 518 sides of the IMC layers (as illustrated in Fig. 9c), 519 which can be regarded as infinite. However, for the 520 perpendicular growth of IMCs, the Sn and Cu atoms 521 522 need to pass the planar IMC layers by surface dif-523 fusion and bulk diffusion before they can reach the root of the perpendicular IMCs (Fig. 10a). During 524 diffusion, both Sn and Cu atoms can possibly be 525 captured by the reactions that contribute to the 526 planar growth of IMCs, particularly the Sn atoms 527 from the solder side. The significant expansion of 528



eatch : 18-9-2015 Pag	ges: 10
	TYPESET DISK
	LE 🗆

529 the planar Cu₆Sn₅ layer near the sample surface in 530 Fig. 5 can be attributed to Sn atoms captured dur-531 ing surface diffusion from the solder to the bottom of 532 the perpendicular IMCs. Hence, unlike the infinite 533 supply of Sn and Cu atoms in the planar growth of 534 IMCs, the supply of free atoms to the perpendicular 535 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.

549 **Potential Effects of Perpendicular Growth of** 550 **IMCs**

551 It has been reported that the growth of Cu_6Sn_5 552 and Cu₃Sn during aging can induce stress evolution 553 within interfacial IMC layers due to volume shrinkage resulting from the density increase in 554 solid-state reactions.³⁴ It is reasonable to assume 555 that the growth of planar IMC layers in this work 556 can also induce build-up of residual stress during 557 558 aging. Similar to the effect of the growth of Sn whiskers,35 perpendicular growth of IMCs may 559 560 partly release this residual stress at the solder/Cu 561 interface.³⁵ On the other hand, the residual stress in 562 solder joints may also facilitate the perpendicular 563 growth of IMCs, based on the suggestion that the 564 perpendicular IMCs in solder joints after electromigration tests were "squeezed out" by compressive 565 stress.^{9,10} However, the effect of the stress on the 566 567 planar growth of IMCs remains uncertain, deserv-568 ing further study.

569 Similar to the effect of Sn whiskers, perpendicular 570 growth of IMCs can also possibly lead to failure of 571 fine-pitch packages. In electronic packages, though 572 there is no specifically prepared free surface, the 573 perpendicular IMCs can still grow into the gap be-574 tween two adjacent solder joints, which is perpen-575 dicular to the diffusion direction. When the pitch is 576 reduced below 50 μ m (as in three-dimensional pack-577 ages), the gap between two adjacent microbumps is only 10 μ m to 20 μ m.^{36,37} In this case, perpendicular 578 579 growth of IMCs is very likely to lead to shorts, which 580 could be worse if the packaging density increases 581 further in the future. Furthermore, protruding IMCs 582 could be fractured into particles under vibration or 583 mechanical loads. These loose IMC particles are also 584 harmful to device reliability.

The risk of shorts due to perpendicular IMCs can be 585 586 minimized by underfilling. It has been suggested that 587 void-free encapsulation, such as conventional flip-chip

underfill, can well suppress growth of Sn whiskers to 588 prevent electrical shorts.³⁸ This means that good 589 encapsulation can also retard perpendicular growth of 590 IMCs to prevent the resulting shorts. However, if the 591 packaging density increases further, the decreasing 592 gap between two adjacent microbumps could possibly 593 594 bring significant challenges in achieving void-free encapsulation³⁹ and promote the possibility of elec-trical shorts. Hence, the perpendicular growth of 595 596 IMCs should be further investigated in the future. 597

CONCLUSIONS

599 Planar and perpendicular growth of Cu-Sn IMCs in 99Sn-1Cu/Cu solder joints were studied after 600 aging. From the cross-sectional views of perpendic-601 ular IMCs revealed by FIB, it was found that the 602 morphology of the perpendicular IMCs was den-603 dritic, which is different from the layer-type planar 604 IMCs. Furthermore, the Cu/Cu₃Sn and Cu₃Sn/ 605 Cu₆Sn₅ interfaces within the solder joint moved to-606 wards the Cu side near the sample surface, which 607 can be ascribed to faster surface diffusion of Sn 608 atoms within this region. 609

The formation sequence of Cu₆Sn₅ and Cu₃Sn in 610 the perpendicular IMCs was also found to be oppo-611 site to that in planar IMC layers within solder 612 joints. In perpendicular IMCs, the formation of 613 Cu_3Sn is prior to the formation of Cu_6Sn_5 , because 614 of the high concentration of Cu atoms where the 615 perpendicular growth of IMCs starts. However, the Cu₆Sn₅ is believed to form before the Cu₃Sn in planar interfacial IMC layers, since a Cu-rich region is required to produce Cu₃Sn in planar IMC layers.

Both the planar and perpendicular growth of 620 IMCs follow a parabolic law with aging duration, 621 indicating that the growth was dominated by 622 interdiffusion of Sn and Cu atoms during aging. However, the perpendicular growth of IMCs was much slower than the planar growth of IMCs. This 625 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. 628

ACKNOWLEDGEMENTS

Z.C. would like to acknowledge the joint PhD pro-630 gramme between Loughborough University (UK) and Huazhong University of Science and Technology 632 (China). This research was also supported by a Marie Curie International Research Staff Exchange 634 Scheme Project within the 7th European Community Framework Programme, No. PIRSES-GA-2010-636 269113, entitled "Micro-Multi-Material Manufac-637 ture to Enable Multifunctional Miniaturised Devices 638 (M6)," as well as the National Natural Science Foundation of China (No. 60976076).

REFERENCES

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	Journal : 11664_JEM	Dispatch : 18-9-2015	Pages : 10
	Article No.: 4043	□ LE ☑ CP	□ TYPESET ☑ DISK
		± •.	± 5.6.0

536

537

538

539

540

541

542

543

544

545

546

547

548

598

623 624

626 627

631

629

633

635

639 640

641

642

- 645 2. L. Jiang, H. Jiang, and N. Chawla, J. Electron. Mater. 41, 646 2089 (2012). 647
 - Q.K. Zhang, J. Tan, and Z.F. Zhang, J. Appl. Phys. 110, 3. 014502 (2011).

648

649 650

651 652 653

654

- S.W.R. Lee and S. Fubin, International Microsystems, 4. Packaging, Assembly Conference Taiwan 2006, Taipei, 18-20 October, 2006, pp. 105-108.
- J.H.L. Pang, T.H. Low, B.S. Xiong, X. Luhua, and C.C. Neo, 5 Thin Solid Films 462-463, 370 (2004).
- J.-W. Yoon, S.-W. Kim, and S.-B. Jung, Mater. Trans. 45, 6. 727 (2004)
- 655 656 657 7. Y. Liu and F. Sun, J. Mater. Sci. Mater. Electron. 24 (2013).
 - C. Chen, H.-Y. Hsiao, Y.-W. Chang, F. Ouyang, and K.N. Tu, 8. Mater. Sci. Eng. R. 73, 85 (2012).
- 658 659 660 T.Y. Lee, K.N. Tu, and D.R. Frear, J. Appl. Phys. 90, 4502 9. (2001)
- 661 661 662 663 664 664 664 10. C.-M. Chen and C.-H. Chen, J. Electron. Mater. 36, 1363 (2007).
 - Y.S. Kaganovskii, L.N. Paritskaya, V.V. Bogdanov, and A.O. 11. Grengo, Acta Mater. 45, 3927 (1997). J. Gong, C. Liu, P.P. Conway, and V.V. Silberschmidt,
 - 12. Scripta Mater. 60, 333 (2009).
 - C.Y. Liu and K.N. Tu, J. Mater. Res. 13, 37 (1998). 13.
 - Y.S. Kaganovskii, L.N. Paritskaya, and V.V. Bogdanov, 14. Powder Metall. Met. C+ 47, 652 (2008).
 - 63 64 65 66 67 68 69 70 15.Y.C. Chan, A.C.K. So, and J.K.L. Lai, Mater. Sci. Eng. B 55, 5 (1998).
 - 671 672 673 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)
 - 674 675 676 677 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.
 - 678 679 680 H. Xiao, X.Y. Li, Y.X. Zhu, J.L. Yang, J. Chen, and F. Guo, 19. J. Mater. Sci. Mater. Electron. 24, 2527 (2013). 681
 - 20.T.-T. Luu, A. Duan, K. Aasmundtveit, and N. Hoivik, J. Electron. Mater. 42, 3582 (2013).
 - 682 683 21.H.K. Kim, H.K. Liou, and K.N. Tu, J. Mater. Res. 10, 497 684 (1995).

- 22 X. Chen, Z. Yun, F. Chonglun, and J.A. Abys, IEEE Trans. Electron. Packag. Manuf. 28 (2005).
- M.Y. Tsai, S.C. Yang, Y.W. Wang, and C.R. Kao, J. Alloys 23.Compd. 494, 123 (2010).
- T. Laurila, V. Vuorinen, and J.K. Kivilahti, Mater. Sci. Eng. 24.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).
- Z. Kejun, R. Stierman, C. Tz-Cheng, D. Edwards, K. Ano, 29.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). K.N. Tu, C. Chen, and A. Wu, J. Mater. Sci. Mater. Electron. 35. 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.
- J. Brusse, G. Ewell, and J. Siplon, 22nd Capacitor and 38. 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_JEM	Dispatch : 18-9-2015	Pages : 10
Article No.: 4043	CP	🗹 DISK

685

686

687

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.	