Precipitation and coarsening of bismuth plates in Sn–Ag–Cu–Bi and Sn–Cu–Ni–Bi solder joints

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Abstract
In recent years there has been increased interest in Bi-containing solders to improve the reliability of electronics and drive down processing temperatures. When the Bi content is more than ~2 wt% in Sn–Ag–Cu–Bi and Sn–Cu–Ni–Bi solders, (Bi) phase forms by a non-equilibrium eutectic reaction and also precipitates in the solid state. Here, we study the development of bismuth plates during room temperature storage in a range of Bi-containing solders. It is shown that Bi plates precipitate with one of two (Bi)–βSn orientation relationships (ORs). During coarsening the OR with the better lattice match grows at the expense of the other, leading to a single OR. The plate coarsening kinetics scale with the cube root of holding time and are relatively rapid, with plates exceeding 1 µm in length within 1 day at room temperature. Prolonged room temperature storage of more than 1 year resulted in Bi accumulation in 5–20 µm (Bi) particles at βSn grain boundaries.

1 Introduction
Bismuth has been investigated as an addition in Pb-free solders since the beginning of the transition to Pb-free electronics [1–3]. However, after early trials, Bi was abandoned partly because the industry wished to avoid solders with a pasty range, and because residual Pb remained in the supply chain as Sn–Pb surface finishes etc. and the combination of Pb and Bi produced a low temperature eutectic that could lead to early failure [1, 4, 5]. Now that the industry is truly Pb-free, Bi can be used without this risk and, recently, there has been a resurgence of interest in Bi additions mainly for designing the third-generation, high-reliability electronic solders targeting applications in harsher environments [6–13]. Broadly, there are three categories of Bi-containing solders under investigation and entering service: (i) low Bi solders (typically < 2 wt% Bi) strengthened by Bi solid solution strengthening of βSn such as Sn–0.7Cu–0.05Ni–1.5Bi (wt%) [9, 10]; (ii) medium Bi solders (typically 3–7 wt% Bi) strengthened by both Bi solid solution strengthening and (Bi) precipitates such as Sn–3.8Ag–0.7Cu–3Bi–1.5Sb–0.15Ni [14] and Sn–2.25Ag–0.5Cu–6Bi [7]; and (iii) solders based around the Sn–57Bi low melting eutectic for low process temperature electronics such as Sn–57Bi–1Ag, Sn–57.5Bi–0.5Sb and Sn–58Bi [15, 16].

A large amount of experimental data on Bi additions to lead-free solders has been reported. Generally, Bi additions in the range of 1–7 wt% have been demonstrated to generate reliability advantages including increasing solder joint shear strength [17–20], enhancement of joint thermal fatigue resistance [21], enhancement of creep resistance during ageing [22] and improvement of the drop-impact performance [21]. The improved performance of solder joints with Bi additions are commonly explained by solid solution strengthening of the βSn matrix and precipitation strengthening with (Bi) phase [17, 20, 23–25]. Bi additions have been demonstrated to also improve the wetting and spreading performance of lead-free solders [2, 19, 21], to decrease their liquidus temperature [26], to reduce the excessive growth of the Cu₃Sn IMC layer [21, 27, 28] and to prevent Sn-whisker growth [29, 30]. Bi additions have been further demonstrated to retard the rapid degradation of solder joint mechanical response/reliability during ageing, which is typical behaviour for SAC compositions subjected to elevated temperatures [7, 8, 11, 31].

Despite the large amount of research on Bi additions to lead-free solders in the literature, there remain various outstanding questions regarding microstructural stability and (Bi) phase precipitation in service. This work explores the
precipitation and coarsening of (Bi) plates at room temperature in four widely used Pb-free solders each with an addition of 4 wt% Bi: Sn–3Ag–0.5Cu–4Bi (SAC305 + Bi), Sn–1Ag–0.5Cu–4Bi (SAC105 + Bi), Sn–0.7Cu–4Bi, and Sn–0.7Cu–0.05Ni–4Bi (SN100C + Bi). 4 wt% Bi was chosen as it is within the range of typical Bi additions under investigation for ‘medium Bi’ solders [7, 8, 28] and is known to be sufficient to cause the formation of both non-equilibrium eutectic (Bi) particles and the solid-state precipitation of (Bi) plates [10, 32]. Additionally, we study (Bi) precipitation in near-eutectic Sn–57Bi to compare (Bi) precipitation in high-Bi versus medium-Bi solders.

2 Materials and methods

Soldering alloys Sn–3Ag–0.5Cu–4Bi, Sn–1Ag–0.5Cu–4Bi, Sn–0.7Cu–4Bi and Sn–0.7Cu–0.05Ni–4Bi (all additions are in wt%) were prepared from commercial purity (CP) materials by mixing the required amount of Sn–10Ni, Sn–10Cu, 99.9Bi and/or 99.9Ag with ~150 g of 99.9Sn in a graphite crucible and heating in a resistance furnace to 450 °C. After 1-h holding, the melt was stirred with a preheated graphite rod and cast into a stainless steel mould coated in BN. The obtained solder compositions, measured by XRF spectroscopy, are listed in Table 1. Prepared ingots were then rolled to 30 µm foils. 500 ± 20 µm diameter solder balls were prepared by punching 1.6 mm round preforms from the foils and then reflowing them with a ROL1 tacky flux (by IPC J-STD-004) on a hotplate at 280 °C to form spheres by the action of surface tension.

Standard FR4 Cu-OSP test boards were used as Cu substrates with 500 µm circular pads. To produce ball grid array (BGA) solder joints, solder balls were placed on the Cu-OSP pads, fluxed with ROL1 tacky flux, and then reflowed in a LFR400HTX TORNADO reflow oven (Surface Mount Technology, Isle of Wight, UK). The thermal profile involved heating at ~2 K/s to a peak temperature of ~250 °C and cooling at ~3 K/s to room temperature. The time above the eutectic temperature (227 °C for Sn–0.7Cu–0.05Ni) was ~45 s. At least 20 solder joints were soldered and analysed for each composition.

Prepared solder joints were mounted in Struers VersoCit II acrylic cold mounting resin and wet ground to 4000 grit SiC paper followed by polishing with colloidal silica. Analytical scanning electron microscopy (SEM) was conducted on a Zeiss SIGMA field-emission gun-SEM (Carl Zeiss, Oberkochen, Germany) equipped with an Oxford Instruments INCA x-ray dispersive X-ray (EDX) detector (Oxford Instruments, Oxfordshire, UK) and a Bruker electron backscatter diffraction (EBSD) detector (Bruker AXS Inc., Fitchburg, WI, USA). The prepared cross-sections were carbon coated before SEM analysis.

For the quantification of the kinetics of (Bi) precipitate coarsening within the solder matrix, at least ten areas featuring (Bi) plates were analysed for each solder composition at each ageing time using ImageJ processing software [33]. Solder joint ageing was carried out in a laboratory environment at room temperature (RT), which corresponds to 23 ± 2 °C throughout the paper.

For 3-dimensional (3D) characterization of the (Bi) plates, ~20 × 20 × 40 µm volumes containing Bi phase in BGA joints were serially-sliced using a Helios NanoLab dual beam focused ion beam (FIB) microscope and imaged in immersion mode. A milling current of 2.8 nA was used and the slice distance was 40 nm. Raw images were segmented using ImageJ and Matlab, and 3D reconstruction of the (Bi) crystal shape was carried out using Avizo 9.3.0 software.

3 Results and discussion

3.1 Influence of 4 wt% Bi on solder microstructures

Figure 1 shows representative microstructures of Bi-containing BGA joints on Cu substrates: Sn–3Ag–0.5Cu, Sn–1Ag–0.5Cu, Sn–0.7Cu and Sn–0.7Cu–0.05Ni each with 4 wt%Bi. The same cross-sections are shown for joints after 2, 2000 and 10,000 h at room temperature. The precipitation of (Bi) phase, which appears bright in backscattered electron imaging, can be seen clearly after prolonged room temperature holding in all compositions.

Other than the presence of the (Bi) phase, it was found that Bi additions of 4 wt%Bi did not strongly alter the microstructures of these solders. SAC-4Bi joints commonly contained single grain or cyclically twinned beachball morphologies similar to Bi-free SAC joints in [34–37] and

| Nominal composition | Cu (wt%) | Ni (t%) | Bi (wt%) | Ag (wt%) | Sb (wt%) | Fe (wt%) | As (wt%) |
|---------------------|----------|--------|----------|----------|----------|----------|----------|
| Sn–3Ag–0.5Cu–4Bi    | 0.46     | 0.005  | 4.3      | 2.89     | 0.010    | 0.008    | 0.050    |
| Sn–1Ag–0.5Cu–4Bi    | 0.50     | 0.003  | 4.1      | 1.10     | 0.015    | 0.005    | 0.056    |
| Sn–0.7Cu–4Bi       | 0.67     | 0.004  | 4.0      | <0.001   | 0.016    | 0.004    | 0.054    |
| Sn–0.7Cu–0.05Ni–5Bi| 0.71     | 0.039  | 4.2      | <0.001   | 0.011    | 0.002    | 0.051    |

Detected levels of Cd, Co, Al, Zn and Pb were <0.001 wt%
Sn–0.7Cu–4Bi and Sn–0.7Cu–0.05Ni–4Bi joints exhibited columnar βSn growth from the substrate similar to Bi-free Sn–Cu–(Ni) joints in [10, 36, 38–41]. Typical examples of the βSn growth texture are shown in the EBSD IPF maps and pole figures in Fig. 2. The SAC305-4Bi/Cu and SAC105-4Bi/Cu joints each contain 3 cyclic twinned βSn grains, as can be seen from the overlapping {100} planes in the pole figures. The Sn–0.7Cu–4Bi/Cu and Sn–0.7Cu–0.05Ni–4Bi/Cu joints have columnar βSn growth from the substrate, more orientations than the Ag-containing solders and no apparent solidification twinning. Furthermore, similar to past work on Bi-free compositions [10, 42], Sn–3Ag–0.5Cu, Sn–1Ag–0.5Cu, Sn–0.7Cu–0.5Cu, Sn–0.7Cu and Sn–0.7Cu–0.05Ni with 4 wt%Bi solidified with some primary Cu₆Sn₅, βSn dendrites, and interdendritic eutectic particles of Cu₆Sn₅ and, in Ag-containing solders, Ag₃Sn [36]. This is in agreement with our past study that found that Bi additions need to be greater than ~5 wt% Bi to significantly alter the βSn and IMC microstructure of Sn–Cu–Bi and Sn–Cu–Ni–Bi joints on Cu substrates [10].

Figure 3 shows a typical example of the two types of (Bi) phase that existed in all samples: grain boundary blocky particles of (Bi) that initially formed by a non-equilibrium eutectic reaction late during solidification [10], and (Bi) plates that precipitated in the solid state. The precipitation of (Bi) plates mostly occurred from areas of the βSn matrix that were most supersaturated with Bi. For example, (Bi) plates were commonly observed in βSn inter-dendritic regions that formed in the latest solidification stages (i.e. Fig. 3). Figure 1 may seem to indicate different levels of (Bi) coarsening in different alloys. However, comparison of the distribution of Bi-enriched areas in Sn–Ag–Cu–4Bi and Sn–Cu–Ni–4Bi joints showed that all alloys exhibited a similar amount of (Bi) precipitation and similar coarsening kinetics in the βSn matrix. However, there were significant joint-to-joint variations in the amount of non-equilibrium

Fig. 1 Representative microstructures formed in Bi-containing BGA joints on Cu: Sn–3Ag–0.5Cu–4Bi, Sn–1Ag–0.5Cu–4Bi, Sn–0.7Cu–4Bi and Sn–0.7Cu–0.05Ni–4Bi: as-soldered condition (2 h after reflow) and after storage for 2000 h and 10,000 h at 23 ± 2 °C (the same cross-section)
These variations were not found to be alloy specific. According to the analysis shown in Fig. 5b, if present, grain boundary eutectic (Bi) coarsened with a rate almost ten times higher than precipitated (Bi) plates. Analysis of multiple samples and regions showed no significant differences in Bi coarsening between the alloys.

### 3.2 Coarsening kinetics of Bi plates

Figure 4 gives examples of the precipitation of (Bi) in Sn–3Ag–0.5Cu–4Bi and Sn–0.7Cu–0.05Ni–4Bi joints after different holding times (up to 840 h) at room temperature. Note that, for each alloy, the same area is shown at each time. Both the increasing size of (Bi) plates and the decreasing number of plates can be seen clearly. In both alloys, bismuth precipitation in βSn resulted in highly aligned plates which coarsened with time during ageing. Note that, by the time the samples were placed into the SEM chamber (~ 2 h after soldering, Fig. 4), (Bi) precipitates had already nucleated and developed into plates measuring up to 300 nm in length and ~ 25 nm in width. Similar results were observed for all investigated solder compositions.

Figure 5 quantifies the kinetics of (Bi) plate ripening/coarsening. As can be seen from Fig. 5a, the rate at which (Bi) plates increase their mean thickness was proportional to the cube root of ageing time, which corresponds to volume diffusion controlled growth with time constant close to 1/3. It was further found that the results were virtually identical for all investigated solder compositions, i.e. all data collapsed onto almost a single line for Sn–3Ag–0.5Cu–4Bi, Sn–1Ag–0.5Cu–4Bi, Sn–0.7Cu–4Bi and Sn–0.7Cu–0.05Ni–4Bi solders (Fig. 5a) with rate constant, $A$, close to 13 nm$^{1/3}$/h ($w = A^{1/3} + B$). Thus, the precipitation and coarsening of (Bi) plates does not seem to be significantly affected by Ag and Ni additions. Note that the minimum (Bi) plate width detected by SEM in BSE mode was ~ 15 nm and, thus, the data in Fig. 5a are the mean and standard deviation of (Bi) plate widths above this detection limit only.

Figure 5a also shows that the standard deviation in plate width (the error bars) increases with increasing mean plate width. To explore this and build further understanding of the coarsening process, the (Bi) plate size distributions (PSDs) at each aging time were studied. Figure 5c–e are scaled PSDs at four holding times (i.e. the distribution of the plate widths scaled by the mean width, $w/w_\bar{w}$, at each time). Figure 5e plots the scaled PSDs from Fig. 5c, d holding times together with 24 h and 168 h holding time results and shows that the scaled PSDs are approximately self-similar and time independent. Such self-similar scaled PSD coarsening behaviour is common to various mechanisms including Lifshitz-Slyozov-Wagner (LSW) theory [43, 44], Ostwald ripening [45, 46] and coalescence ripening [47]. However, the shape of the PSDs is different to these mechanisms, giving a tail at high $w/w_\bar{w}$ for faceted plate coarsening.
Figure 5b shows that the eutectic (Bi) at βSn grain boundaries also coarsened proportional to the cube root of aging time at room temperature but underwent more rapid growth than the solid-state precipitated (Bi) plates (with rate constant, $A \sim 134 \text{ nm/h}^{1/3}$, i.e. ten times faster). This is likely to be because Bi diffusion along βSn grain boundaries provides a quicker path for Bi atom transport. After 80 days at room temperature the average width of (Bi) particles (precipitated plates + eutectic) present in the solder bulk increased from ~0.25 to up to ~1.6 µm (Fig. 5b), whereas the length of (Bi) plates increased from ~0.5 to up to ~2 µm.

In joints held for much longer than in Fig. 5a, b, it was found that storage times over 1 year resulted in considerable Bi redistribution in the bulk of BGA joints (e.g. Fig. 6). The reduction in number of (Bi) plates due to dissolution during coarsening continued until the majority of Bi accumulated in particles on βSn grain boundaries (i.e. Fig. 6d) leading to further coarsening of the eutectic (Bi) phase. Only trace amounts of aligned (Bi) plates remained in the βSn grains after ageing for 10,000 h ($t^{1/3} = 21.5 \text{ hr}^{1/3}$) (Fig. 6b) leading to large precipitate-free zones and large (Bi) particles at βSn grain boundaries. Note, Fig. 6a–d illustrate prepared (ground and polished) cross-sections after 10,000 h and, therefore, reflect the degree of (Bi) coarsening in the bulk solder.

The relatively rapid (Bi) plate coarsening kinetics at room temperature in Fig. 5a, b is partly because $23 \pm 2 \text{ °C}$ corresponds to a homologous temperature of $T/T_m \sim 0.6$ where there is substantial thermal energy available for diffusion in the matrix. For comparison, typical precipitation heat treatment temperatures in Al-alloys, Mg-alloys and Ni-superalloys are typically $T/T_m \sim 0.5$.

### 3.3 Orientation relationships between βSn matrix and (Bi) plates

Bi precipitates were always found aligned along distinct directions across large areas within one βSn grain. Examples of aligned Bi plates are given in Figs. 3, 4, 6b and 7, and similar examples can be found in the literature [7, 31, 48, 49]. The shape of (Bi) precipitates suggests the existence of preferred interfaces between (Bi) and βSn. Therefore, EBSD was used to study the crystallography of bismuth precipitation.

Figure 7a illustrates a typical region in Sn–0.7Cu–0.05Ni–4 wt%Bi solder featuring horizontally aligned (Bi) plates in a βSn matrix near a (Cu,Ni)$_6$Sn$_5$ particle. Investigation of crystallographic orientation relationships (OR) between (Bi) and βSn was carried out by indexing and analysing pairs of electron backscattered diffraction
patterns (EBSPs) obtained from (Bi) and βSn sharing a common interface (i.e. Fig. 7b, c) similar to [50]. A highly reproducible result was measured: low index planes \{100\} in βSn and \{01-12\} in (Bi) were always parallel in EBSPs (Fig. 7b, c) and were parallel to the interface between Bi and Sn in the BSE images (Fig. 7a) suggesting potential interfacial planes in both phases. Further analysis of zone axes in EBSPs deduced common directions in both crystals. Figure 7b, c illustrates matching zone axes that belong to the established common planes. They are <100> directions in Sn and <2-201> directions in Bi. Therefore, the resulting OR between the βSn matrix and (Bi) precipitates can be summarized as follows:

\{100\}Sn || <01-12>Bi and <100> Sn || <2-201> Bi OR 1

Figure 7d summarizes EBSD data collected from the area in Fig. 7a and expresses it as pole figures for the common planes and directions in both phases. As can be seen from Fig. 7d, the measured OR1 is highly reproducible across all plates in the area of interest, yielding narrow scatter of the data. Various parallel planes and directions associated with OR1 are highlighted: red squares show two parallel planes (010)Sn || (01-12)Bi and (100)Sn || (-1012)Bi; black circles show another parallel plane (001)Sn || (1-102)Bi; and yellow triangles show two common directions [100]Sn || [-2021]Bi and [010]Sn || [02-21] Bi.

More than 200 individual (Bi) plates were analysed in this study and the standard deviation of the scattered data for OR1 for all interfaces was within 1.5°, which confirms the high reproducibility of the measured OR.

Figure 8a is a plot of the arrangement of atoms in the common planes aligned along common directions in βSn and (Bi) according to OR1. Using the ‘planar lattice disregistry’ approach of Bramfitt [51] and crystallographic data in Table 2, the disregistry in the \{100\}Sn and \{01-12\}Bi planes is about 7%, resulting in relatively close atomic matching.
across the interface (Table 3). Given the high reproducibility of OR1, it is most likely the lowest energy interface that can be achieved between βSn and (Bi).

In addition to (Bi) plates with OR1, there were often regions with some (Bi) plates aligned along one or two other directions within the same βSn grain, similar to the regions in Fig. 9a, b. In these cases, it was repeatedly observed that (Bi) plates with OR 1 became increasingly dominant as the microstructure coarsened during ageing whereas the others tended to dissolve. Figure 9c, d demonstrates an example of (Bi) plate evolution in Sn–3Ag–0.5Cu–4Bi after 180 and 230 h at room temperature. It can be seen that (Bi) plates aligned along the major direction coarsen further at the expense of the diminishing (Bi) precipitates having orientations that differ from the main alignment direction. As a consequence of this competition, only one dominant orientation of (Bi) plates remained after 230 h of ageing at RT. Figure 9e

Fig. 6  a, b Sn–3Ag–0.5Cu–4Bi and c, d Sn–0.7Cu–4Bi BGA joints cross-sectioned after ageing for 10,000 h at room temperature (23 ± 2 °C) illustrating Bi redistribution in the solder bulk: majority of Bi is accumulated on grain boundaries (d), however, trace amounts of (Bi) plates still exist (b).

Fig. 7  b, c Representative EBSPs collected from the area marked in a that highlight common planes and directions in βSn matrix and (Bi) precipitates for OR1; d summary of EBSD data expressed as pole figures for the common planes and directions in βSn matrix and (Bi) precipitates.
provides a further example of (Bi) plate evolution in a eutectic region of Sn–3Ag–0.5Cu–4Bi solder after 230 h of ageing at room temperature. In order to understand the nature of this orientation selection, more than 45 individual (Bi) particles with minor orientations were analysed by EBSD. It was found that the dissolving (Bi) plates also had a reproducible orientation relationship (OR2) with the βSn matrix that involves the same planes as in OR1, but the common directions were different. Based on the EBSD data, OR2 can be summarized as follows:

\[ \{100\} \text{Sn} \parallel \{01-12\} \text{Bi} \text{ and } <011> \text{Sn} \parallel <2-201> \text{Bi OR2} \]

Atomic matching in the interfacial planes for OR2 is illustrated in Fig. 8b. The planar lattice disregistry is > 10% for OR2 (Table 2), which is significantly higher (worse) than the interfacial lattice disregistry for OR1 and explains the lower stability of such (Bi)–βSn interfaces during ageing.

Figure 10a, b summarizes the OR1 and OR2 data as inverse pole figures (IPFs) in terms of [001] in βSn, where rhombohedral (Bi) orientations are plotted in the tetragonal IPF of βSn. The average angular misorientation for OR1 is 1.5 ± 0.8° and for OR2 is 1.4 ± 1.3°. This high reproducibility of the angular misorientation measurements for ~ 250 (Bi) plates underlines the strong preference for these ORs and the importance of low energy interfaces in the precipitation and coarsening of (Bi) in βSn.

In contrast to solid-state precipitated (Bi) plates, eutectic (Bi) particles near βSn grain boundaries did not have any special or reproducible ORs with the βSn matrix. More than 50 individual eutectic (Bi) particles were investigated and the EBSD data are summarized in Fig. 10c, which confirms the more random orientation distribution of eutectic (Bi) phase in the βSn matrix than in Fig. 10a, b. Similar results have been previously reported by Vianco and Rejent [17], where TEM investigation did not reveal any coherent interfaces or preferred ORs between the βSn matrix and (Bi) particles found at grain boundaries. Figure 11 is a representative example of such grain boundary eutectic (Bi) phase found next to (Bi) plates aligned in accordance with OR1 after 230 h RT storage.

A further feature of grain boundary (Bi) phase was that, during prolonged ageing times they tended to form hillocks protruding from the polished surface similar to βSn hillock whiskers [54–56]; Fig. 11 contains typical examples.

It can be seen in Figs. 4, 6, 7 and Fig. 12b that (Bi) plates were frequently attached to Ag₃Sn or Cu₆Sn₅ eutectic particles. However, EBSD measurements did not reveal any reproducible ORs between (Bi) and Ag₃Sn or Cu₆Sn₅ IMC phases. The main reason for (Bi) precipitation near...
eutectic IMC particles seems to be that the βSn in these regions is the most Bi-rich since it formed at the end of solidification and, therefore at room temperature, this βSn is the most supersaturated in Bi.

3.4 3D shape of (Bi) crystals precipitating in βSn matrix

The preceding analysis of ORs and coarsening of (Bi) plates (i.e. Figs. 4, 7, 9) was performed on free surfaces created by polishing. In order to understand whether the precipitation of (Bi) plates is different in the bulk volume, specimens were subjected to additional analysis of the subsurface using FIB milling. Figure 12a is a BSE micrograph of a polished area in a Sn–3Ag–0.5Cu–4Bi joint (above the red dashed line) and the corresponding FIB milled slice (below the red dashed line). Further examples of FIB cross-sections are illustrated in Fig. 12b, c. Investigation of FIB slices revealed the presence of sub-surface (Bi) plates (Fig. 12b, d). A combination of EBSD and FIB Slice&View allowed for the determination of the habit planes of the surface and bulk precipitated (Bi) crystals.

The reconstructed 3D shape of typical precipitated bismuth crystals is shown in Fig. 12d. While these crystals usually measured up to 1–3 µm in length, they developed only 0.15–0.35 µm into the bulk producing long prismatic crystals in 3D. The identity and orientation of (Bi) crystals formed on the surface was confirmed by SEM-EDX and EBSD, whereas the subsurface (Bi) plates during FIB experiments were identified only based on their shape and orientation in the βSn matrix. Figure 12d compares (Bi) crystals formed on the surface and in the bulk. It can be seen that the largest facets of the crystals are parallel, which confirms their similar OR with the βSn matrix. Thus, the precipitation OR is the same on the surface and in the bulk.

The crystal habits of (Bi) prisms and plates in Fig. 12 were measured by fitting their terminating planes to the plane equation in MatLab, finding normal vectors to those planes and comparing their projections with stereographic projections of various plane normals in the (Bi) crystal using EBSD data collected for the particular (Bi) plate (Fig. 12e). With this approach, Fig. 12e shows that the habit planes are {01-12}Bi planes. The angular misorientation of ~6° is due to sample alignment deviations during EBSD mapping and FIB milling in separate microscopes.

The habit planes for (Bi) precipitates detected by FIB-tomography are consistent with those identified as OR1 in Fig. 7. Figure 12f shows the atomic arrangement in βSn and

### Table 3

| OR1: {100}Sn || {01-12}Bi and <100> Sn || <2-201> Bi |
|----------------|---------------------------------|-----------------|-----------------|
| [uvw]Sn       | [010]                           | [012]           | [001]           |
| [uvw]Bi       | [2-21]                          | [-1-21]         | [-4-21]         |
| d[uvw]Sn (Å)  | 2.92                            | 4.32            | 3.18            |
| d[uvw]Bi (Å)  | 3.28                            | 4.55            | 3.28            |
| θ (%)         | 12.3                            | 5.3             | 3.1             |
| δ (%)         | 6.9                             |                 |                 |

| OR2: {100}Sn || {01-12}Bi and <011> Sn || <2-201> Bi |
|----------------|---------------------------------|-----------------|-----------------|
| [uvw]Sn       | [011]                           | [02-1]          | [01-3]          |
| [uvw]Bi       | [2-21]                          | [-1-21]         | [-4-3]          |
| d[uvw]Sn (Å)  | 3.22                            | 3.02–9.07       | 2.89–6.29       |
| d[uvw]Bi (Å)  | 3.28                            | 4.75            | 3.28            |
| θ (%)         | 1.8                             | > 15            | > 15            |
| δ (%)         | > 10                            |                 |                 |

Note, for OR2, the linear atomic spacing in (100)Sn plane are stated as a range that brackets min and max atomic distances along chosen directions.
(Bi) phases as a projection view along [001]Sn || [2-201]Bi. βSn–(Bi) interfaces are at ~90° angle and involve the following common planes and directions: (100)Sn || (01-12)Bi, (010)Sn || (-1012)Bi and [001]Sn || [2-201]Bi. As can be seen from Fig. 12f, the elongated (longest) direction of (Bi) plates is parallel with the c-axis in βSn. This is likely to be because [001]Sn is the direction with the smallest (best) disregistry between βSn and (Bi) in OR1 (Fig. 8a). It has been demonstrated that [001] is the fastest diffusion direction in the βSn crystal for some solute elements such as Cu, Ni, Ag and Au [57–59], however, Bi diffusivity in tin has been recently found to have very little effect of Sn grain orientation [60, 61].

3.5 Precipitation of (Bi) in Sn–58Bi/Cu solder joints

In Sn–58Bi/Cu solder joints, solidification occurred mostly by a βSn–(Bi) eutectic reaction after a small fraction of βSn dendrites. (Bi) phase then precipitates in the βSn dendrites in the solid state on further cooling and storage at room temperature. Figure 13 shows a typical example of precipitated (Bi) within βSn dendrites. In Fig. 13b it can be seen that the precipitated (Bi) is not as well aligned as in the solders containing 4 wt% Bi in Figs. 3, 4, 7, 9 and 11 (as mentioned in [62]). However, EBSD analysis in Fig. 13c, d shows that the precipitated (Bi) has OR1 with the surrounding βSn dendrite. This shows that the precipitation ORs measured here are the same in both (i) the ‘medium Bi’ solders under development for high reliability electronics, and (ii) the ‘high Bi’ solders used for low process temperature electronics.

Excessive coarsening of (Bi) that leads to a large bismuth plate size, a large inter-plate distance and large precipitate free zones, followed by the redistribution of (Bi) towards the grain boundaries is highly undesirable, as segregation of (Bi) may degrade the reliability of electronic interconnections [49]. However, for solder joints subjected to thermal-cycling, there may be cyclic (Bi) precipitation and dissolution regimes which needs to be studied in the future. Additionally, as has been demonstrated by Chiu et al. [63], current loading of solder joints increases solubility of Bi in βSn. Nonetheless, if Bi-containing solder joints remain inoperational at room temperature for extended periods, excessive coarsening of (Bi) plates is likely to occur. In future research, it will be important to explore how the changing Bi particle size affects reliability in creep and shock loading.

4 Conclusions

The precipitation and coarsening of bismuth plates during room temperature storage has been studied in Sn–3Ag–0.5Cu–4Bi, Sn–1Ag–0.5Cu–4Bi, Sn–0.7Cu–4Bi, and Sn–0.7Cu–0.05Ni–4Bi (wt%) solders on Cu substrates. The 4 wt% Bi addition is similar to medium-Bi solders strengthened by both Bi solid solution strengthening and (Bi) precipitates, that are under consideration for third-generation, high-reliability electronic solders targeting...
applications in harsher environments. The following conclusions can be drawn:

1. Other than the presence of (Bi) phase, an addition of 4 wt% Bi was not found to significantly alter the typical ‘as-soldered’ microstructures of Sn–3Ag–0.5Cu, Sn–1Ag–0.5Cu, Sn–0.7Cu and Sn–0.7Cu–0.05Ni BGA joints on a Cu substrate.

2. A 4 wt% Bi addition to Sn–3Ag–0.5Cu, Sn–1Ag–0.5Cu, Sn–0.7Cu and Sn–0.7Cu–0.05Ni solders caused rapid precipitation of bismuth plates on the joint polished surface in the form of highly aligned (Bi) plates.

3. For all investigated compositions, the coarsening kinetics of (Bi) plates were diffusion controlled with a time growth constant of 1/3, and the scaled particle width distributions were approximately self-similar and time-independent. Grain boundary eutectic (Bi) coarsened with a rate constant ten times higher than precipitated (Bi) plates. Ni and Ag additions did not affect the (Bi) plate coarsening kinetics significantly.
Two reproducible ORs were detected for precipitated (Bi) plates in the βSn matrix:

\[
\begin{align*}
\text{(OR1)} & : [100]_\text{Sn} \parallel [01-12]_\text{Bi} \quad \text{and} \quad <100> \text{Sn} \parallel <2-201> \text{Bi} \\
\text{(OR2)} & : [100]_\text{Sn} \parallel [01-12]_\text{Bi} \quad \text{and} \quad <011> \text{Sn} \parallel <2-201> \text{Bi}
\end{align*}
\]

OR1 has the better lattice match with planar lattice disregistry of ~7%. During room temperature storage, (Bi) plates with OR1 grew at the expense of those with OR2 (planar lattice disregistry for OR2 > 10%).

The crystal habits of precipitated (Bi) crystals were confirmed by a combination of EBSD and FIB-milling techniques to be \{01-12\}Bi planes.

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