Harnessing heterogeneous nucleation to control tin orientations in electronic interconnections

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While many aspects of electronics manufacturing are controlled with great precision, the nucleation of tin in solder joints is currently left to chance. This leads to a widely varying melt undercooling and different crystal orientations in each joint, which results in a different resistance to electromigration, thermomechanical fatigue, and other failure modes in each joint. Here we identify a family of nucleants for tin, prove their effectiveness using a novel droplet solidification technique, and demonstrate an approach to incorporate the nucleants into solder joints to control the orientation of the tin nucleation event. With this approach, it is possible to change tin nucleation from a stochastic to a deterministic process, and to generate single-crystal joints with their c-axis orientation tailored to best combat a selected failure mode.

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The nucleation of crystals is a key step in numerous processes in biology, earth science, materials engineering, and beyond. Substantial research has focused on understanding and controlling crystal nucleation, for example: to trigger the nucleation of ice crystals in clouds and cause rain\(^1\); to prevent the freezing of water in the cells of plants and animals\(^2,3\); to produce high-quality protein crystals and other biomolecules\(^3\); to prevent crystallization and promote glass formation\(^4\); and to minimize the grain size in metal castings and improve mechanical properties\(^5,6\). Nucleation is also central to the microstructures of electronic solder joints and plays an important role in determining the reliability of electronic systems\(^7\).

When electronics fail, the culprit is often the solder joints that interconnect the components. Most electronic solder joints contain at least 95% \(\beta\)Sn phase to enable soldering at a temperature tolerable to the electronic components, but the \(\beta\)Sn must then operate at up to 80% of its melting point while enduring a high current density, mechanical loading, and thermal cycling. Thus, solder joints are often the weakest link in an electronic system and, with the continuous miniaturization of electronics, the challenges of electromigration, thermomigration, thermomechanical fatigue, and mechanical fatigue are becoming ever more crucial\(^8,9\). Each of these failure modes is a strong function of the crystallographic orientation of \(\beta\)Sn in a solder joint because tetragonal \(\beta\)Sn has highly anisotropic properties. For example, the diffusivities of common solutes (e.g., Cu\(^10\), Ni\(^11\), Ag\(^12\)) are up to four orders of magnitude faster along the \(c\)-axis than along the \(a\)-axis; the coefficient of thermal expansion (CTE)\(^13\)–\(^16\) is approximately two times higher along \(c\) than \(a\); \(\beta\)Sn has its highest stiffness along its direction of maximum CTE (the \(c\)-axis)\(^13\); and \(\beta\)Sn also has strong plastic anisotropy\(^17\). There is a consistent agreement that solder joints with the \(\beta\)Sn \(c\)-axis parallel with the \\

![Fig. 1](https://example.com/fig1.png)  
**Fig. 1** Typical \(\beta\)Sn microstructures and orientations in Cu/Sn-3Ag-0.5Cu/Cu joints.  
**a** EBSD inverse pole figure maps (IPF-Z) of 12 Cu/Sn-3Ag-0.5Cu/Cu joints that were cooled from ~240 °C in either a DSC at 0.33 K s\(^{-1}\) or an industrial reflow oven at 1–5 K s\(^{-1}\). Wireframe unit cells are superimposed on each main orientation using the mean Euler angles of that grain. All joints with multiple grains are solidification twins with a common \(<100>\) axis and common (100) plane indicated by cross-hatching on the unit cells.  
**b** Cyclic twinning in one joint shown by translating the unit cells into the \(101\) and \(301\) cyclic twin configurations\(^35\) with the parallel \(100\) planes and \(101\) and \(301\) twinning planes shaded.  
**c** \(<100>\) and \(<001>\) pole figures showing the highly variable \(\beta\)Sn grain orientations in 33 joints.  
**d** The distribution of angles between [001]Sn and the plane of the Cu substrate.
Fig. 2 Lattice match between $\beta$Sn and a family of transition metal stannides. a Each crystal structure is shown in an equivalent orientation as a stacking of distorted-square antiprisms. A single distorted antiprism with Sn atoms on the vertices and a T atom at the center is shown underneath FeSn$_2$. Red planes represent the similar net of Sn atoms in each structure. The black square on each net of Sn atoms indicates the projection of the corresponding unit cell, and its position is determined by the origin for the crystallographic settings in Table 1. b $\beta$Sn unit cell and (100) plane. c Planar lattice match between the (100) of $\beta$Sn and the red planes containing Sn nets in the IMCs, showing the atomic mismatch of 24 atoms surrounding the origin labeled ‘O’ (unrelaxed structures). Here $\alpha$CoSn$_3$ is used as the example.

Electron flow direction or temperature gradient suffer the most severe electromigration$^{18-25}$ or thermomigration damage$^{26}$. Thermomechanical fatigue is influenced by $\beta$Sn grain orientations$^{27}$ by inducing stresses between adjacent grains of different orientations$^{27-31}$, and by inducing stresses between the substrate and solder, which are highest when the $\beta$Sn c-axis is nearly parallel with the substrate plane as this induces the maximum CTE mismatch$^{13, 17, 32, 33}$. In shear fatigue, joints with the $\beta$Sn c-axis nearly parallel with the substrate plane and at ~20°–60° with the shear direction are more resistant than other $\beta$Sn orientations$^{34}$. From this, it can be seen that the optimum $\beta$Sn orientation is different for different failure modes.

While research continues on the optimum $\beta$Sn orientations for overall solder joint reliability, it would be beneficial if a method could be developed to reliably control $\beta$Sn orientations in ball grid array (BGA) and flip chip joints. The challenge is overviewed in Fig. 1, which shows the $\beta$Sn microstructures and orientations in typical Cu/Sn-3Ag-0.5Cu/Cu BGA joints, which are similar to those widely reported in the literature$^{13, 18, 35-37, 31, 32}$. Figure 1a are electron backscatter diffraction (EBSD) inverse pole figure maps of $\beta$Sn with respect to the direction of current flow (Z). Unit cell orientations are plotted on each grain using the Euler angles of the mean orientation of the grain. It can be seen that some of the joints contain a single $\beta$Sn grain and some contain two or three $\beta$Sn grains. The orientations of $\beta$Sn grains in 33 such joints are plotted relative to the direction of current flow in Fig. 1c. The $c$-axes, i.e., the <001>, are oriented differently in every joint and are at a wide range of angles from the plane of the substrate (Fig. 1d). Thus, each joint will be unique in its response to electromigration, mechanical loading, and thermal cycling, and it is likely that an array of joints interconnecting a component will contain at least one joint which is poorly oriented and will act as a weak link.

The joints in Fig. 1 are all single-grain or cyclic-twinned $\beta$Sn grains, similar to refs$^{13, 18, 35-37}$. The cyclic twinning can be seen from the superimposed unit cells on the two/three grain joints in Fig. 1a that always share a common (100)$^{35}$ as indicated by the cross-hatched planes on the unit cells, and from Fig. 1b, which focuses on the cyclic twins in the bottom-right joint from Fig. 1a. Note that the three unit cells have been translated into the (101) cyclic twin and the (301) cyclic twin configurations, which are both consistent with ~60° rotations about a common <100>$^{35}$. Since the joints are all either single grain or twinned, it can be inferred that $\beta$Sn solidified from a single nucleation event. The location of this nucleation event is one of the Cu$_6$Sn$_5$ intermetallic compound (IMC) layers near where the solder ball meets the Cu pad as discussed in ref. 38. The orientation(s) of $\beta$Sn in Sn-Ag-Cu solder joints are determined by a stochastic nucleation event and the key to controlling the $\beta$Sn orientation(s) is to identify methods to tightly control this nucleation event.

Here we develop a novel method to study heterogeneous nucleation mechanisms, where droplets of Sn are solidified on the facets of IMCs and the nucleation undercooling and resulting orientation relationships (ORs) are measured. Combining this method with a lattice matching approach to nucleate design, we identify a family of transition metal stannides that catalyze $\beta$Sn
nucleation and give useful orientation control. We next demonstrate a simple bonding technique to incorporate the nucleant particles into BGA solder joints to give precisely controlled βSn microstructures and grain orientations tailored to best resist a predefine failure mode.

Results

Prediction of nucleant phases. In order to control the orientation of βSn, we seek seed crystals that can be attached to the pads on the printed circuit board (PCB) side or the component side. The requirements of such a heterogeneous nucleant are: it must be the most potent nucleant in contact with the liquid solder, and generate a useful and reproducible OR with βSn; it must be bondable onto the pad or metallization; it should be a solderable prototype of PtSn₄⁴⁶ and similar lattice parameters, and does not exist in equilibrium at βSn nucleation temperatures. Therefore, PtSn₄, αCoSn₃, and βIrSn₄ were explored in this study.

Nucleation mechanisms. As shown in Fig. 3a–c, αCoSn₃, PtSn₄, and βIrSn₄ single crystals all grew with a faceted plate morphology and their largest facets are parallel with the planes of Sn nets in Fig. 2a (i.e., the red planes that are predicted to catalyze βSn nucleation). In Fig. 3a–c, the growth facets and directions have been determined by EBSD as indicated by the unit cells inset in each figure that were plotted from the EBSD-measured Euler angles. To explore βSn nucleation mechanisms on these largest facets of all IMCs, Sn droplets were solidified on each of them, the nucleation undercooling was measured by differential scanning calorimetry (DSC), and the ORs and microstructures were measured by EBSD. Experimental details are as given in the Methods section. Figure 3d shows the typical result of solidifying tin droplets onto the largest IMC facets, using βIrSn₄ as an example. The EBSD IPF-Y map and pole figures show that all five tin droplets are single-grain and that the βSn has one of two reproducible orientations with respect to the orientation of the βIrSn₄, either [001]Sn[100]βIrSn₄ (green droplets) or [001]Sn[010]βIrSn₄ (yellow droplets) as indicated in the orientation map and pole figures. However, these are just two variants of the same OR since βIrSn₄ is tetragonal (i.e., a=b) (Table 1). EBSD maps in all X, Y, and Z directions of these five droplets in Fig. 3d are given in Supplementary Fig. 1. The measured ORs and their frequency of occurrence when tin droplets solidified on the three IMCs are emphasized in the Edge-to-Edge model⁴¹,⁴⁵ and is also the worst matching closely packed direction in the interfacial plane for all nucleants studied here which makes it a useful single value for the goodness of lattice match in this case.

Second, the planar disregistry was calculated as the average angle-corrected disregistry of 24 atoms surrounding an origin atom as shown in Fig. 2c. This is similar to the Bramfitt approach⁴⁰ but involves 25 matching atoms rather than 4 to account for the geometry of this lattice match, and can be calculated as Eq. (1):

\[
\delta_{\text{Planar}} = \frac{\sum_{i=1}^{24} \delta_{\text{disreg}} \times \cos(\theta_i)}{24} \times 100.
\]

Disregistry results are given in Table 1 for eight transition metal stannides from the family in Fig. 2. The IMCs which have disregistries <10% calculated by both methods are highlighted in Table 1. These five highlighted phases are potentially good catalysts for βSn nucleation. Among them, PdSn₄ has the prototype of PtSn₄⁴⁶ and similar lattice parameters, and βCoSn₃ does not exist in equilibrium at βSn nucleation temperatures⁴⁸. Therefore, PtSn₄, αCoSn₃, and βIrSn₄ were explored in this study.

**Table 1 Lattice match between Sn net planes of βSn and selected transition metal stannides**

| Phase | Space group | Pearson's symbol | Lattice parameters (Å) | Ref. | Sn net plane | \( \delta_{100-\text{Sn}} \) (%) | \( \delta_p \) (%) |
|-------|-------------|-----------------|------------------------|------|--------------|-------------------|---------------|
| Sn    | I4/ amd     | tI4             | a: 5.831 b: 5.831 c: 3.182 | 49   | (100)        | <100>Sn           | -             |
| AuSn₄ | Aba2        | o520            | a: 6.512 b: 6.516 c: 11.707 | 50   | (008)        | [100]AuSn₄        | 11.7 9.4 |
| PtSn₄ | Ccca        | o520            | a: 6.418 b: 11.366 c: 6.384 | 51   | (080)        | [001]PtSn₄        | 9.5 8.5 |
| PdSn₄ | Ccca        | o520            | a: 6.442 b: 11.445 c: 6.399 | 46   | (080)        | [001]PdSn₄        | 9.6 8.3 |
| αCoSn₃| Cmca        | o532            | a: 16.864 b: 6.268 c: 6.270 | 52   | (600)        | [010]CoSn₃        | 7.5 6.2 |
| MnSn₄ | I4/mcm      | tI12            | a: 6.644 b: 6.644 c: 5.421 | 53   | (001)        | <100>MnSn₄        | 13.9 11.5 |
| FeSn₂ | I4/mcm      | tI12            | a: 6.545 b: 6.545 c: 5.326 | 54   | (001)        | <100>FeSn₂        | 12.2 10.2 |
| βIrSn₄| I4/acd      | tI40            | a: 6.310 b: 6.310 c: 22.770 | 47   | (0016)       | <100>βIrSn₄       | 8.2 7.2 |
| βCoSn₃| I4/acd      | tI64            | a: 6.275 b: 6.275 c: 33.740 | 52   | (0024)       | <100>βCoSn₃       | 7.6 6.1 |

\( \delta_{100-\text{Sn}} \) is the linear disregistry between <100>Sn and the parallel direction in each stannide).

\( \delta_p \) is the planar disregistry defined in Eq. (1) and Fig. 2c. Phases with disregistries <10% are typeset in bold.

\( \delta_{\text{disreg}} \) is the Bramfitt linear disregistry.
PtSn₄, and droplets solidifying on the facets of single-crystal IMCs. a–c Typical αCoSn₃, PtSn₄, and IrSn₄ single crystals. The growth habit is shown in the inserts using unit cell orientations measured by EBSD. The largest facets are parallel to the Sn net plane in Fig. 2a in each phase. The angular deviation of each pair of near-parallel planes is given as the mean value and standard deviation.

Table 2 Measured ORs between βSn and IMCs

| Droplets | Measured OR                          | Frequency of occurrence | δ₁₀₀<010>Sn (%) | δ₉₀ (%) |
|----------|--------------------------------------|-------------------------|-----------------|--------|
| αCoSn₃/βSn | (100)₃βSn(100)₃CoSn₃<001>₃βSn<010>₃CoSn₃ | 25 out of 41             | 7.49            | 6.16   |
| βIrSn₄/βSn | (100)₂βSn(100)₂IrSn₄<001>₂βSn<010>₂IrSn₄ | 16 out of 41             | 7.53            | 6.18   |
| PtSn₄/βSn  | (100)₂βSn(100)₂PtSn₄<001>₂βSn<010>₂PtSn₄ | 36 out of 36             | 8.1             | 7.2    |
| PtSn₄/βSn  | (100)₂βSn(100)₂PtSn₄<001>₂βSn<010>₂PtSn₄ | 36 out of 36             | 8.1             | 7.2    |

The frequencies of occurrence and disregistry of each OR are also given.

Summarized in Table 2. Noticeably, PtSn₄ and αCoSn₃ each have two reproducible ORs with βSn, but the frequency of occurrence suggests one of these two ORs in each case is more prevalent than the other. This can be understood by noting that PtSn₄ and αCoSn₃ are orthorhombic but they are only slightly distorted from tetragonal (Table 1). Thus, the lattice match is similar in both ORs (see Fig. 2a, b) and, in each case, the more frequently measured OR has a slightly lower (better) disregistry compared with the other OR (Table 2), which indicates the lower disregistry likely results in lower interfacial energy. All measured ORs (Table 2) between each IMC and the βSn are quantified in Fig. 3e as stereographic projections with respect to the largest facet plane of each IMC. The mean angular difference and the standard deviation of these parallel planes are quantified in Fig. 3e, where it can be seen that all pairs of near-parallel planes had mean angular differences of <4°.

The nucleation potencies of these three IMCs were evaluated from DSC of ~20 μm tin droplets solidifying on the IMC facets. Typical DSC curves and the definition of the nucleation undercooling are given in Fig. 4a, b. Figure 4c shows the nucleation undercooling vs. the lattice match expressed as both the planar disregistry and the linear disregistry along <100>Sn (for nucleants with two ORs, the worse δ₁₀₀<010>Sn and δ₉₀ (Table 2) are plotted). The nucleation undercooling is significantly...
suppressed compared with the solidification of ~20 μm droplets on inert oxidized Al substrates (58 ± 15 K). It can also be seen in Fig. 4c that the lower the disregistry, the smaller the nucleation undercooling in both methods of quantifying lattice mismatch, consistent with nucleant potency theories[39–41]. At the same time, in Fig. 4c, note that the nucleation undercoolings of ~20 μm droplets on the IMC facets are not very small compared with potent nucleants in other systems (e.g., Al on Al3Ti[43]). However, importantly, the ORs in Table 2 formed in 182 out of 182 droplets and, irrespective of which OR formed, the [001] of tetragonal βSn was always in the plane of the largest facet of the IMC. Thus, these ORs are not only reproducible but also useful since, by controlling the orientation of the largest facet in a joint, these IMCs have the potential to be used as seed crystals to control the orientation of the [001] of βSn in solder joints.

βSn grain structure and orientation control in solder joints. Since the natural growth shape of primary αCoSn3, PtSn4, and βIrSn4 crystals are thin plates (Fig. 3a–c) whose main facet is the desired nucleation plane, seed crystals were obtained by dissolving the matrix βSn and using the largest natural growth facet as a seed crystal without the need to take slices from a wafer of IMC. To incorporate a PtSn4, αCoSn3, or βIrSn4 seed crystal into BGA solder joints, they were first bonded to Cu pads using a form of transient liquid phase bonding (TLPB), where the IMC seed crystal remained solid during the TLPB. An immersion tin coating was applied to Cu pads and the nucleant IMC was laid flat with the main facet in the plane of the pad as shown in Fig. 5a using αCoSn3 as an example. The αCoSn3 was then TLPB to the pad by a reflow of 5 min at 240 °C, which resulted in the Cu/CoSn3/CoSn3/αCoSn3 layers shown in Fig. 5b. Since PtSn4, αCoSn3, and βIrSn4 are all solderable surfaces using a standard ROL-1 flux, these nucleant-modified pads were then used in the same manner as a Cu-OSP substrate and solder joints were made following the procedure in the Methods section. Figure 5c shows the cross-section of a typical Cu/Sn-3.5Ag + IMC/Cu solder joint after double reflow where the bottom Cu pad contains a TLPB αCoSn3 seed crystal and a 550 μm Sn-3.5Ag ball was used. The microstructure consists of primary Cu6Sn5, βSn dendrites with [110] growth directions indicated by the blue arrows, βSn + Ag5Sn + Cu6Sn5 interendritic eutectic, and a bonded αCoSn3 particle on the bottom substrate. Note that a large αCoSn3 seed crystal has been used in this example to make it feasible to polish to a cross-section containing the seed crystal and measure the OR. The EBSD IPF-Z map of the βSn phase is shown in Fig. 5d, which indicates that the joint contains a single crystal of βSn. Figure 5e is the EBSD IPF-Z map of the αCoSn3 phase. In both maps, the unit cell wireframes of these two phases are superimposed to show the OR, which is also indicated by pole figures in Fig. 5f where near-parallel directions are indicated with circles, squares, and triangles. The OR is consistent with that in Table 2 from droplet studies. Due to the special placement of the αCoSn3 particle, the nucleated single βSn grain is oriented with [100] or [010] across the joint and with [001] parallel with the substrate plane, i.e., the c-axis of βSn is in the substrate plane. Note that, even though primary and interfacial Cu6Sn5 are present prior to βSn nucleation, the nucleation of βSn always occurred on the seed crystal because they (αCoSn3, PtSn4, βIrSn4) are more potent nucleants than Cu6Sn5. Primary Ag5Sn plates were not observed here because the seed crystals require only a relatively small undercooling for βSn nucleation. Further examples of the phases

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**Fig. 4** Nucleation undercooling vs. lattice mismatch. Typical DSC curves and definition of nucleation undercooling in a) a single ~20 μm Sn droplet on the (001) facet of a βIrSn4 single crystal and b) a freestanding single ~20 μm Sn droplet. c) The nucleation undercooling for βSn in ~20 μm Sn droplets on the IMC facets vs. planar disregistry and linear disregistry along <100>Sn. d) The nucleation undercooling of 550 μm Cu/SAC305 + IMC/Cu solder joints vs. planar disregistry and linear disregistry along <100>Sn. Each datapoint and error bar represent the mean nucleation undercooling and standard deviation from at least 25 measurements. All samples were measured on inert oxidized Al substrates.
**Fig. 5** Microstructure at different stages of processing in a Cu/Sn-3.5Ag + nucleant/Cu joint. 

**a** A typical immersion tin-coated Cu substrate with an IMC nucleant bonded on top. 

**b** Cross-section of a typical transient liquid phase bonded (TLPB) αCoSn₃ seed crystal (i.e., a cross-section through **a**). 

**c** Cross-section of a typical Cu/Sn-3.5Ag + αCoSn₃/Cu solder joint after double reflow. Blue arrows show <110> βSn dendrite branching directions. 

**d** EBSD IPF-Z map of the βSn phase. 

**e** EBSD IPF-Z map of the αCoSn₃ seed crystal. The unit cell orientation of each phase is superimposed on each map. 

**f** Pole figures of the βSn and αCoSn₃ phases. The pairs of triangles, circles, and squares indicate the near-parallel planes that are consistent with the OR in Figs. 2c, 3

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**Fig. 6** c-axis orientation control in Cu/Sn-3Ag-0.5Cu or Sn-3.5Ag + nucleant/Cu joints. 

**a-c** Typical EBSD IPF-Z maps and unit cell wireframes. 

**a** αCoSn₃, 

**b** PtSn₄, and 

**c** βIrSn₄. 

**d** Summarized βSn pole figures of 67 solder joints and a histogram of the angles between [001]Sn of these joints and the substrate plane. This range of orientations is optimum for resisting electromigration according to refs18–25
are shown in Supplementary Fig. 2. EBSD maps in all X, Y, and Z directions of the joint in Fig. 5c are given in Supplementary Fig. 3.

Similar results to Fig. 5 were obtained using PtSn3 and βIrSn4 as seed crystals, although a longer time and higher temperature (180 min at 300 °C) were needed to TLPB these IMCs to Cu pads. Figure 6a–c are 30 typical EBSD orientation maps (IPF-Z) of Cu/solder + IMC/Cu joints made with αCoSn3, PtSn3, or βIrSn4 seed crystals and either Sn-3.0Ag-0.5Cu or Sn-3.5Ag solder. The IMC seed crystals have a wide distribution of sizes from ~20–150 μm (length of the longest edge of the plate) and some are TLPB to the seed crystals have a wide distribution of sizes from ~20 μm on the seed crystal giving orientation control. It can also be seen that the nucleation undercooling is smaller for 550μm BGA joints than for ~20 μm that the nucleation undercooling is smaller for 550μm BGA joints than for ~20 μm Cu/SAC305/Cu joint (17 ± 1 K) but nucleation always occurred on the seed crystal giving orientation control. It can also be seen that the nucleation undercooling is smaller for 550μm BGA joints than for ~20 μm droplets when they solidify on the equivalent facet planes but similar orientation control occurred in both.

**Discussion**

The approach in Figs. 5 and 6 gives a c-axis orientation perpendicular to the direction of current flow which has been shown to give optimum resistance to electromigration and thermomigration in solder joints in past work18–25,26. For some applications, alternative orientations may be preferred and the βSn c-axis may need to be tailored to suit the application. For example, it has been shown by Arfaei et al. 34 that shear fatigue performance is best when the βSn c-axis is near-parallel with the substrate plane and at ~20–60° angle with the shear direction. This can be achieved with the current approach since the crystallographic orientation of the IMC plates can be readily determined from the macroscopic shape of the plate, and the IMC plates can be pick-and-placed to have a tightly controlled rotation angle. To demonstrate this, in Fig. 7a, αCoSn3 particles have been bonded along the edge of an array of Cu pads with edges parallel with the X direction (the assumed shear direction). This makes the c/b axis of each αCoSn3 particle at ~45° with the X direction, as shown by the configuration in Fig. 7d. Therefore, after double reflow, the final βSn grain orientations in these joints are controlled to have the c-axis at ~45° with the X direction due to heterogeneous nucleation on the seed crystal. This can be seen in the EBSD IPF-X and IPF-Z maps in Fig. 7c and the summarized IPF-X in Fig. 7e. The red highlighted region in Fig. 7e represents the optimum shear fatigue performance range determined in ref. 34, assuming that X is the shear direction.

For applications where thermomechanical fatigue is the dominant issue, the current technique could be altered to fix the nucleant IMC to have the largest facet perpendicular with the substrate plane and one edge parallel with the substrate plane. By doing this, the final joint would have the βSn c-axis at ~45° with the substrate plane, which would eliminate the worst situation for the thermomechanical fatigue (i.e., c-axis parallel with the substrate13, 17, 32, 33). As the understanding of the role of crystal orientation on solder joint performance improves in the future, the approaches overviewed here open the possibility to tailor the c-axis orientation to best resist the dominant failure mode.

Here, orientation control has been demonstrated for the first-generation Pb-free solders, Sn-3Ag-0.5Cu and Sn-3.5Ag. The latest generation solders under development commonly additionally contain Ni, Bi, In, etc. It is shown in the Supplementary Fig. 7 that similar orientation control can be achieved in solders with these additions. The seed crystals remain effective with these
additions because they do not react with the seed crystals or introduce a more potent nucleation phase. For example, the Ni addition mostly influences the Cu6Sn5 phase, which is a less potent nucleant than the seed crystals, and these Bi and In additions introduce extra (Bi) and (Ag,In) phases that form later during solidification and do not strongly affect the nucleation of βSn. The successful orientation control in these Ni-, Bi-, and In-containing solder alloys indicates that this orientation control method is likely to be applicable to solder compositions developed in the future. Thus, it is suggested that the development of solders for optimum reliability could be tackled with a double approach of alloy design and orientation control.

In summary, seed crystals for solder joints create new design opportunities for electronic components manufacturing, opening the possibility of designing joints to combat different failure mechanisms and increasing the reproducibility of microstructures across solder arrays. The simple bonding step that incorporates the nucleants onto Cu pads is well suited to pick-and-place technology and the seed crystals are expected to be compatible with future improvements in solder alloy design. Most notably, the droplet solidification technique developed here has the potential to accelerate nucleation discovery in other systems by generating statistically significant datasets on nucleation ORs in a relatively short time.

**Methods**

**Synthesis of intermetallic single crystals.** PtSn4, αCoSn5, and βIrSn4 single crystals were grown in Sn-rich liquid by cooling hypereutectic Sn-0.2Pt, Sn-0.1Co, and Sn-1Ir (mass%) alloys at 0.33 K s⁻¹. For reusing in the Tornado LFR400 reflow oven, some joints were refrigerated subsequently in the DSC to measure the nucleation undercooling. Substrates were cut to ~3 × 3 mm² for DSC measurements. N₂ atmosphere was used in all reflowing cases.

**Data availability.** The EBSD and DSC datasets generated during the current study are available in the Zenodo repository (doi: 10.5281/zenodo.884113).

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Z.L.M., S.A.B. and C.M.G. developed the nucleants; Ta,N., Te,N., K.S. and Z.L.M. optimized methods for incorporating nucleant particles into joints; Z.L.M. performed the experiments; Z.L.M. and C.M.G. wrote the paper with inputs from the other authors.

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Competing interests: The authors are co-inventors on a patent entitled "Solder joint and bonding method", Japanese patent number: 2017-133073.

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