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Cu$_6$Sn$_5$ crystal growth mechanisms during solidification of electronic interconnections

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ABSTRACT

The growth mechanisms of primary Cu$_6$Sn$_5$ are studied in Sn-Cu alloys and solder joints by combining EBSD, FIB-tomography and synchrotron radiography. With increasing cooling rate and Cu content, Cu$_6$Sn$_5$ crystals developed from faceted hexagonal rods to grooved rods, in-plane branched faceted crystals and, finally, to nonfaceted dendrites. This range of growth morphologies has been rationalised into a kinetic microstructure map. Cu$_6$Sn$_5$ hexagonal rods grew along [0001] bounded by $\{10\bar{1}0\}$ facets and Cu$_6$Sn$_5$ dendrites branched along <405> in the $\{10\bar{1}0\}$ planes. The faceted to nonfaceted transition indicates a kinetic interface roughening transition and a gradual change in mechanism from lateral growth governed by anisotropic attachment kinetics to continuous growth governed by diffusion and curvature. Finally, it is shown that the full range of Cu$_6$Sn$_5$ morphologies that grew for different composition and cooling rate combinations in bulk alloys can be engineered to grow in solder joints made with a single composition (Sn-0.7 wt%Cu/Cu) by altering the peak temperature and the cooling rate.

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1. Introduction

With the miniaturization of Pb-free solder joints, intermetallics occupy an increasing proportion of the solder joint volume and impact more significantly on the reliability of electronics [1]. In some cases, fully intermetallic interconnections are favoured and can be made by micro-bumps or transient liquid phase soldering [2–5]. Cu$_6$Sn$_5$ is of particular interest because it is commonly found as primary crystals in the bulk solder and as the interfacial reaction layer in joints between Cu substrates and most Sn-rich solders. Thus, there has been increasing interest in methods to control the size and morphology of primary Cu$_6$Sn$_5$ [6–9].

Primary Cu$_6$Sn$_5$ has been reported to grow with various morphologies such as needles [10–12], hollow rods [11,13], X-shapes [9,14,15], Y-shapes [8,9], H- and M-shapes [16,17] and as dendrites [6,18]. Since many of these studies have been based on arbitrary 2D cross sections, it is not clear how many of these morphologies are separate growth forms in 3D. The growth direction of the rod-like Cu$_6$Sn$_5$ is reported to be [0001] and the growth facets are usually

$\{1\bar{1}00\}$-type Cu$_6$Sn$_5$ planes [15,16,19,20]. The crystallographic directions and facets of the other growth forms are not known. Although markedly different primary Cu$_6$Sn$_5$ morphologies have been observed [8–11,13–17], there has been little work on the transitions between these growth forms nor on the mechanisms responsible for the range of Cu$_6$Sn$_5$ morphologies.

In this work, we grow primary Cu$_6$Sn$_5$ with a wide range of morphologies by altering the Cu content and cooling rate during equiaxed solidification. We characterise the 3D morphology, the crystallographic growth directions and facets, and study the growth mechanisms for each morphology. The results are then rationalised into a kinetic microstructure map including a faceted to nonfaceted growth transition. Finally, we explore how this understanding can be applied to control the primary Cu$_6$Sn$_5$ morphology in Sn-0.7Cu/Cu joints (all compositions are given in wt% unless otherwise stated).

2. Experimental methods

Alloys containing 0-4.2Cu were prepared by mixing 99.9%Sn with a Sn-10Cu master alloy in a graphite crucible, melting in a resistance furnace and holding at 450 °C for 1 h. The melt was then

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drawn into borosilicate glass tubes of inner diameter 4 mm with vacuum. 500 ± 0.5 mg samples were made by cutting the resulting rods and $\varnothing500$ μm solder BGA balls and joints were made following procedures detailed in Ref. [15].

The Sn-xCu alloys were solidified at controlled cooling rates in the range 0.03—100 K/s using the following procedures. 500 ± 0.5 mg samples were first placed in two quartz tubes held vertically at the same level in a forced air convection oven in order to ensure similar thermal profiles. Both samples were melted and held at 450 °C before a BN-coated 0.5 mm K-type thermocouple was inserted into one of the samples. After 30 min holding at 450 °C, the samples were cooled by opening the door to different positions generating different reproducible cooling rates. Faster cooling rates were achieved by submerging the bottom of the quartz tubes in media with higher thermal conductivity, i.e. sand or water. Cooling rates were measured from the cooling curves recorded by the immersed thermocouple and microstructure analysis was performed on the samples without a thermocouple.

For real-time observation by synchrotron radiography at the BL20XU beamline of the SPring-8 synchrotron, Sn-1.1Cu, Sn-4.2Cu and Sn-10Cu alloys were rolled to ~50 μm thickness. Samples were fixed between two SiO$_2$ sheets and a ~50 μm thick polytetra-fluoroethylene (PTFE) sheet was used as a spacer. The experimental set-up was similar to previous research [7,10,21—23] and a 21 keV beam was used. The transmission imaging field of view was 877 μm × 658 μm (1920 × 1440 pixels) with a resolution of 0.457 μm per pixel. The exposure time was 150 ms per frame and the frames were recorded at 6.67 frames per second.

To study primary Cu$_6$Sn$_5$ in Sn-0.7Cu/Cu solder joints, samples were held at different peak temperatures ranging from 240 °C to 390 °C for 5 min before being cooled at one of two cooling rates. A cooling rate at ~30 K/s was applied by removing a joint from the oven and placing rapidly under an extraction fan. The cooling rate was measured by a thermocouple attached to the Cu substrate near the joint. Cooling at 0.67 K/s was performed in a DSC by heating at 0.33 K/s up to the same peak temperatures, holding for 5 min and cooling at 0.67 K/s.

Samples were mounted in Struers VersoCit acrylic cold mounting resin and prepared following standard metallographic procedures. A Zeiss Auriga field emission gun scanning electron microscope (FEG-SEM) was used to investigate the cross sections and a Bruker e-Flash electron backscatter diffraction (EBSD) detector and Bruker ESPRIT 2.1 software were used to measure the crystal orientations. For the investigation of the three-dimensional morphology and growth directions of Cu$_6$Sn$_5$, some samples were etched in a solution of 5% NaOH and 3.5% orthonitrophenol in distilled H$_2$O at 60 °C for approximately 15 min to selectively dissolve the matrix βSn. Single crystal intermetallics were then placed on a stub and studied by analytical SEM. For 3-dimensional (3D) characterisation of Cu$_6$Sn$_5$ dendrites, ~30 × 30 × 50 μm volumes were serially-sliced using a dual column focused ion beam/ SEM microscope (FIB-SEM, FEI Helios NanoLab 600). The slice step was 100 nm and the milling current was 2.8 nA. Raw images were segmented using Image J and Matlab, and 3D reconstruction was performed in Avizo 9.

3. Results and discussion

3.1. Solidification microstructure map for primary Cu$_6$Sn$_5$

Fig. 1 shows the range of primary Cu$_6$Sn$_5$ growth morphologies that developed in samples with Cu contents in the range 0.7—4.2Cu solidified at cooling rates in the range 0.03—100 K/s. The top row shows the typical appearance of these morphologies in 2D sections. The bottom row shows the equivalent 3D morphologies after

selective dissolution of the βSn matrix. These morphologies can be classified into three major categories, (i) faceted hexagonal rods (e.g. Fig. 1A), (ii) grooved and/or branched faceted crystals (e.g. Fig. 1B and C), and (iii) dendrites (e.g. Fig. 1D and E).

Fig. 2A is a solidification microstructure map, summarising the cooling rate and composition combinations where the different primary Cu$_6$Sn$_5$ morphologies were observed. It can be seen that faceted growth (e.g. Fig. 1A—C) occurs at fairly slow cooling rates <~3.7 K/s, whereas dendritic growth (e.g. Fig. 1D—E) occurs for Cu contents >2.3 wt% and cooling rates ≥~3.7 K/s. This map shows that there is a transition from hexagonal rods to grooved and branched faceted crystals as the Cu content increases from 0.7Cu to 4.2Cu at low cooling rate, and that there is a faceted (blue symbols) to dendritic (red symbols) growth transition with increasing cooling rate in Sn-2.3Cu and Sn-4.2Cu. The growth mechanisms for each morphology and the transitions between them are discussed in sections 3.2—3.4.

Fig. 2A also shows the composition and cooling rate combinations that produced no primary Cu$_6$Sn$_5$ (i.e. microstructures that were either fully-eutectic or βSn dendrites plus eutectic). Note in Fig. 2A that, at low cooling rate, some primary Cu$_6$Sn$_5$ formed in hypoeutectic compositions (e.g. Sn-0.7Cu at 0.03 K/s) and, at high cooling rate, primary Cu$_6$Sn$_5$ did not form in some hypereutectic compositions (e.g. Sn-1.1Cu at >28 K/s). The boundary between microstructures without primary Cu$_6$Sn$_5$ and those containing primary Cu$_6$Sn$_5$ can be understood and calculated from cooling curve measurements and a simple competitive solidification model, as shown next.

Fig. 2B is a typical cooling curve and its derivative for a Sn-4.2Cu sample. The release of latent heat as Cu$_6$Sn$_5$ nucleates and grows is clearly detected in the green derivative curve in Fig. 2B, and the onset of Cu$_6$Sn$_5$ latent heat release, T_{onset}^{Cu6Sn5} was found from the departure of the derivative curve from the baseline. Here the measured temperature at which latent heat release was first detected is a combination of the nucleation undercooling and growth undercooling for primary Cu$_6$Sn$_5$. The onset of Cu$_6$Sn$_5$ latent heat release, T_{onset}^{Cu6Sn5} is plotted against cooling rate in Fig. 2D. It can be seen that T_{onset}^{Cu6Sn5} decreases strongly with increasing cooling rate. T_{onset}^{Cu6Sn5} was converted to an undercooling using $\Delta T_{onset}^{Cu6Sn5} = T_{Liq}^{Cu6Sn5} - T_{onset}^{Cu6Sn5}$ and an empirical exponential fit was found as shown on Fig. 2D.

The nucleation of βSn and subsequent recalescence is also clearly detected in Fig. 2B and the nucleation undercooling for βSn, $\Delta T_n^{\beta Sn}$, was defined as the βSn-Cu$_6$Sn$_5$ eutectic temperature (226.9 °C) minus the nucleation temperature prior to recalescence. $\Delta T_n^{\beta Sn}$ was found to be relatively high and near-constant at 19—25 K for all compositions and cooling rates studied [24]; any influence of cooling rate on this undercooling was masked by the scatter in the data.

To calculate the boundary between microstructures without primary Cu$_6$Sn$_5$ and those containing primary Cu$_6$Sn$_5$, the following competitive solidification condition was applied: primary Cu$_6$Sn$_5$ forms if it can nucleate and grow before βSn nucleates. This is equivalent to: Cu$_6$Sn$_5$ forms if the primary Cu$_6$Sn$_5$ onset temperature is higher than the βSn nucleation temperature, i.e. if T_{onset}^{Cu6Sn5} in Eq. (1) is larger than $T_n^{\beta Sn}$ in Eq. (2).

$$T_{onset}^{Cu6Sn5} = T_{Liq}^{Cu6Sn5} - \Delta T_{onset}^{Cu6Sn5} \qquad (1)$$

$$T_n^{\beta Sn} = T_E - \Delta T_n^{\beta Sn} \qquad (2)$$

Where the Cu$_6$Sn$_5$ liquidus temperature, T_{Liq}^{Cu6Sn5}, was expressed as a function of bulk composition, C$_0$, using a polynomial fit to the Sn-Cu phase diagram in Fig. 2C based on ThermoCalc database TCSLD3.0 [25], $T_E = 226.9$ °C is the βSn-Cu$_6$Sn$_5$ eutectic temperature and