Directional growth of Cu$_3$Sn at the reactive interface between eutectic SnBi solder and (100) single crystal Cu

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The growth mechanisms of Cu$_3$Sn at the interface between eutectic SnBi solder and Cu were investigated by transmission electron microscopy. On (100) Cu the interfacial reaction during reflow resulted in a columnar growth of Cu$_3$Sn along Cu [100] with a special crystallographic relationship of $\langle 210 \rangle_{\text{Cu3Sn}} || \langle 402 \rangle_{\text{Cu}}$ and $\langle 122 \rangle_{\text{Cu3Sn}} || \langle 010 \rangle_{\text{Cu}}$. In the subsequent solid-state aging new triangular Cu$_3$Sn grains nucleated and grew at the triple junction sites of the interface between Cu and two adjacent Cu$_3$Sn grains.

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Intermetallic compounds (IMCs) are essential elements of solder interconnections in modern electronic devices. The compounds are typically formed by the chemical reaction between the active species in a solder alloy, most often Sn, and the device metallization, such as Cu, during reflow soldering or solid-state aging. Much interest has arisen from the realization that IMCs are not only necessary for the development of a solder bond but also play a critical role in determining the reliability of solder interconnections. Since the 1970s, an extensive amount of research, both experimental and theoretical, has focused on the thermodynamics, kinetics, structural and other properties of IMCs in wetting and solid-state reactions [1–10]. The reaction products between Cu and Sn have received the most attention, because Cu is a common metallization and is highly solderable.

The reaction of Sn and Cu often results in two IMCs, Cu$_6$Sn$_5$ and Cu$_3$Sn. For an Sn–Cu reaction couple after short reflow (a few seconds), Cu$_3$Sn is either absent or too thin to be resolved by scanning electron microscopy [11]. For most solder joints on Cu, Cu$_6$Sn$_5$ forms first between Sn and Cu, grows quickly and is often much thicker than the Cu$_3$Sn layer in wetting and solid-state reactions. Therefore, most studies on Sn–Cu reactions have focused Cu$_6$Sn$_5$ by either examining it solely or mixing it together with Cu$_3$Sn. These studies have shown that Cu$_6$Sn$_5$ follows a scallop-type growth mechanism in wetting reactions but undergoes a transition to layer-type growth in the subsequent solid-state reactions [7,11–13]. On the other hand, despite its slower development, the Cu$_3$Sn layer plays a critical role in determining the reliability of a solder/Cu interface as the Cu$_3$Sn or its interface with Cu is prone to voiding either by the Kirkendall effect or by solute segregation [8,14]. Since voids are formed as the Cu$_3$Sn phase grows, understanding the growth mechanism of the Cu$_3$Sn phase is necessary to addressing reliability concerns on interfacial voiding. Although some studies have analyzed the thermodynamics and kinetics of Cu$_3$Sn growth [15,16], the growth mechanism of the Cu$_3$Sn phase remains unclear.

This study aimed to elucidate the growth mechanisms of Cu$_3$Sn using transmission electron microscopy (TEM), which not only can distinguish phases as small as several nanometers, but can also resolve structural relationship between the parent and product phases. To simplify the crystallographic analysis, (100) single crystal Cu was chosen as the substrate. In the early stage, growth of Cu$_3$Sn phase was found to follow a columnar growth mechanism in which the Cu$_3$Sn product phase bears well-defined crystallographic orientations to the Cu crystal. In the subsequent aging, fast feeding of the reactive species along the column
boundary prompted nucleation of Cu₃Sn at the triple junction sites where the column boundary intersected with Cu crystal. Further growth of the Cu₃Sn into equiaxed grains at the triple junctions terminated the directional growth for Cu₃Sn.

The single crystal Cu (100) sheets (10 mm × 2.5 mm × 2 mm) were first surface polished and rinsed in acetone and distilled water. Pairs of the copper sheets were then covered with a commercial eutectic SnBi solder paste, aligned, clamped and heated to the reflow temperature to form a solder joint before the specimens were air-cooled to room temperature. The reflowing process was held at 443 K for about 3–5 s. Solid-state aging was performed in silicone oil at 393 K for up to 168 h.

To prepare TEM foils, 300 μm thick slices were cut from the solder joint by a low-speed saw. The slice was mechanically grounded to a final thickness of 40 μm and ion-milled (Gatan model 691 PIPS) at 5.0 keV and 5 μA with a low milling angle (less than 6°). Both a JEM-2010 and an FEI Tecnai F30 electron microscope were used to carry out TEM observations at an accelerating voltage of 200 and 300 kV, respectively.

The crystal structure of Cu₃Sn has been studied widely since 1927 [21,22]. Its basic unit is orthorhombic, which may be disordered or ordered, or have a long-period superlattice [23]. A basic orthorhombic lattice with dimensions of \( a = 0.5514 \) nm, \( b = 0.4765 \) nm and \( c = 0.4329 \) nm [24] was adopted in this study, which was verified by our electron diffraction works.

The interfacial microstructure of the as-reflowed sample is presented in Figure 1a, where two IMC layers – Cu₆Sn₅ and Cu₃Sn – were present. As a reaction product of Cu and Cu₆Sn₅, the Cu₃Sn layer stayed in-between Cu and Cu₆Sn₅. For clarity, the Cu/Cu₆Sn₅ and Cu₃Sn/Cu₆Sn₅ interfaces are indicated by black and white arrows, respectively. Next to the (100) single crystal Cu, the Cu₃Sn layer was relatively uniform, with a thickness of about 150 nm. The layer was made up of columnar grains whose grain boundaries were generally perpendicular to the substrate surface. After 24 h of aging at 393 K, Cu₃Sn grains grew and the layer thickness increased to about 300 nm (Fig. 1b). Although the interfaces of Cu/Cu₃Sn and Cu₃Sn/Cu₆Sn₅ (indicated by black and white arrows, respectively) became slightly rough, Cu₃Sn grains still maintained a columnar morphology and the column boundaries were perpendicular to (100) Cu surface. Therefore, the growth direction of the columnar Cu₃Sn grain was parallel to [100]ₐₖ.

The growth direction was verified by selected-area electron diffraction (SAED) and high-resolution electron microscopy (HREM) observations. Figure 2a shows the SAED patterns from Cu₃Sn/Cu interface, including both \([122]₁ₐₖ₁₃₈\) and \([010]₁ₐₖ\) patterns. The diffraction spots from Cu substrate were marked and indexed in white, while those from Cu₃Sn were in black. The spots of \((210)ₐₖ₃₈\) and \((402)ₐₖ\) coincide, indicating an orientation relationship of

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(210)ₐₖ₃₈ || (402)ₐₖ || [122]₁ₐₖ₁₃₈ || [010]₁ₖ
\]

The corresponding HREM image of the interface is shown in Figure 2b, in which the lattice image of Cu₃Sn can be taken as constructed with \((011)\) and \((210)\) planes with spacings of 0.320 and 0.239 nm, respectively. On the Cu side, individual \((200)\) planes are clearly observed while \((002)\) planes are not. These \((002)\) planes have a planar spacing of 0.18 nm, which is close to the TEM resolution of 0.17 nm used in this study. The lattice image also indicates that the Cu₃Sn/Cu interface is essentially parallel to the \((200)\)ₐₖ plane, or the growth direction of Cu₃Sn is along \([100]ₐₖ\).

As is well known, in the wetting reaction liquid Sn reacts with Cu to first form Cu₆Sn₅. The initial formation of Cu₆Sn₅ comes from the solid-state reaction between Cu₆Sn₅ and Cu in the reflowing process. In Sn/Cu or Sn-rich alloy/Cu couples, such as SnAgCu/Cu, SnAg/Cu and SnCu/Cu, only a Cu₆Sn₅ layer is clearly visible; the Cu₃Sn layer is either absent or too thin to be detected for a short reflow time [4]. In this regard, the eutectic SnBi/Cu system is different. As shown in Figure 1a, a uniform layer of Cu₃Sn was already formed after reflow as Sn diffusion toward Cu is limited by non-reacting Bi. During wetting reaction, a substantial amount of Bi was left behind at the Cu₆Sn₅/solder interface due to the consumption of Sn from SnBi solder to form...
Cu₆Sn₅. This Bi-rich layer together with the newly formed Cu₆Sn₅ layer can act as a barrier layer for Sn diffusion to Cu substrate [17]. As Sn flux is reduced, a rich supply of Cu atoms at the Cu/Cu₆Sn₅ interface should create a favourable condition for the formation of Cu₆Sn₅, especially since there is a large driving force to form Cu₆Sn between Cu and Cu₆Sn₅ [1]. In the previous study of polycrystalline Cu and eutectic SnBi, a Cu₆Sn₅ layer was also observed after reflowing [18]. Compared to the case of the polycrystalline Cu substrate, the Cu₆Sn₅ layer on the single crystal Cu in this work was more uniform, bound by two smooth interfaces.

The columnar growth and the crystallographical relationship observed in this study have not been reported before for Cu₆Sn, even though a couple of recent studies have uncovered the orientational relationships for Cu₆Sn [19,20]. The columnar growth has resulted from the following favourable growth conditions. First is the fast directional feed of reacting species normal to Cu₆Sn/Cu interface in the early stage of the reaction, because the diffusion distance is shortest in this direction. Second is the presence of multiple nucleation sites at the Cu₆Sn/Cu interface and the lack of other heterogeneous nucleation sites in the early part of the growth process. Moreover, there is a large driving force for Cu₆Sn phase to nucleate according to the Sn–Cu binary phase diagram. Once nucleated, Cu₆Sn crystals can grow rapidly without nucleation of new grains. The third is the need for Cu₆Sn crystals to maintain a special orientational relationship of Eq. (1) with Cu. So far, the relationship in Eq. (1) is the only one found and its uniqueness still remains a question. However, the preference of the [1 2 2]Cu₆Sn||[0 1 0]Cu significantly reduces the nucleation and growth of Cu₆Sn crystals along other orientations.

In the subsequent solid-state aging process, the columnar Cu₆Sn₅ layer formed in the reflowing process continued to grow. In addition, new Cu₆Sn grains were found at the Cu/Cu₆Sn interface after the sample was aged for 48 h at 393 K. It was observed that these new grains, which have triangular morphology, as marked by white dots in Figure 3, nucleated at the triple junction sites between Cu and two columnar Cu₆Sn grains. With prolongation of the solid-state aging, more and more Cu₆Sn grains nucleated, grew and aggregated to form a second Cu₆Sn layer, which was made up of equiaxial grains developed from triangular grains. Figure 4 shows the interfacial microstructure of the solder joint aged for 168 h. On the Cu substrate there were two distinct Cu₆Sn layers: an initial columnar layer (layer 1) and a newly formed equiaxed layer (layer 2), whose interface is marked with white dots. The appearance of the equiaxed Cu₆Sn grains marked the end of the directional growth process for Cu₆Sn.

The triple junction nucleation and the formation of new equiaxed layer of Cu₆Sn are closely related to the diffusion of Sn during solid-state aging. In the early stage of the growth process, Cu₆Sn layer is very thin so that the diffusion distances for reacting species are very short. However, as the Cu₆Sn layer becomes thicker, Sn diffusion through the long column becomes increasingly more difficult, especially in comparison with the diffusion along the column boundaries, which should still be very fast. Therefore, the grain boundaries in the columnar Cu₆Sn layer, which are perpendicular to the Cu₆Sn/Cu interface, can act as fast channels for supplying reacting species. Consequently, the intersection of the columnar boundary and the Cu₆Sn/Cu interface become enriched in the reacting species, prompting formations of new Cu₆Sn at these triple junction sites as triangular grains (see Fig. 3). Once a triangular grain is precipitated, the original columnar grain boundary is split into two grain boundaries between triangular/ columnar Cu₆Sn grains. This enables new nucleation on these new triple junction sites at the triangular/ columnar grain boundaries, whose number is multiplied due to the splitting. Finally, newly formed triangular grains grow into equiaxial grains and aggregate to form an equiaxed layer. The protrusion of equiaxial Cu₆Sn grains (in layer 2) into the columnar Cu₆Sn layer (layer 1) at the grain boundaries, indicated by arrows in Figure 4, provides direct evidence to support the above explanation.

In summary, TEM investigations were carried out to study the growth mechanism of Cu₆Sn in the reactions between eutectic SnBi solder and (100) single crystal

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**Figure 3.** TEM images of the sample aged for 48 h showing (a) nucleation and (b) growth of triangular Cu₆Sn grains at the triple junction sites of the Cu/Cu₆Sn interface and columnar Cu₆Sn grain boundaries.

**Figure 4.** TEM image of the sample aged for 168 h showing the formation of equiaxed Cu₆Sn layer (layer 2) between the columnar Cu₆Sn layer (layer 1) and the Cu substrate. The grain boundaries between the columnar Cu₆Sn grains are indicated by arrows.
Cu. During reflow, the reactions between solid-state Cu$_6$Sn$_5$ and Cu resulted in columnar growth of Cu$_3$Sn grains along Cu [100] with a preferred orientation relationship of \( (210)_{\text{Cu}_6\text{Sn}_5} || (402)_{\text{Cu}_3\text{Sn}} || [122]_{\text{Cu}_6\text{Sn}_5} || [010]_{\text{Cu}} \). In the subsequent solid-state aging, the directional growth of Cu$_3$Sn continued in the columnar mode until the columnar layer grew to a thickness at which supply of the reacting species became so limited that the columnar growth was replaced by preferential nucleation and growth of new Cu$_3$Sn grains at the triple junction sites of the Cu/Cu$_6$Sn interface and Cu$_3$Sn grain boundaries. Upon further growth, the equiaxed grains formed a second layer of Cu$_3$Sn between the Cu and the columnar Cu$_3$Sn, creating a double-layered Cu$_3$Sn structure.

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