Growth mechanism of duplex structural Cu$_2$(In,Sn) compound on single crystalline Cu substrate

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ABSTRACT

The growth mechanism of duplex structural Cu$_2$(In,Sn) compound formed between eutectic SnIn solder and single crystalline Cu during reflowing and solid-state aging was systematically investigated using a top-view technique. The fine-grain Cu$_2$(In,Sn) had a granular morphology and distributed homogeneously without any growth orientation, while textured coarse-grain Cu$_2$(In,Sn) displayed preferential growth on different Cu surface planes. It was observed that on (100) or (111) single crystalline Cu substrates, the coarse-grain Cu$_2$(In,Sn) compound had regular and elongated shuttle-type morphology along two perpendicular (90°) or three intersecting (120°) Cu directions, respectively. But on (102) Cu surface the grains grew like elongated stripes along only one (010)Cu direction. Electron beam backscattered diffraction (EBSD) revealed the growth orientation relationships between them, which are $(0001)_{	ext{Cu}_2(	ext{In,Sn})}/(011)_	ext{Cu}$, on (100)Cu and (111)Cu, and [1 0 1]$_{(010)_{	ext{Cu}}}$ on (102)Cu surface. These orientation relationships enable the minimum misfit (2.3–2.9%) of the array of Cu atoms between coarse-grain Cu$_2$(In,Sn) compound and single crystalline Cu substrate.

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1. Introduction

The morphologies of intermetallic compounds (IMCs) formed between different kinds of Sn-based solders and polycrystalline Cu had been studied by many researchers [1–7], and the morphology evolution of IMC has great effect on the reliability of the solder joint, especially for those grown on single crystalline substrates. For example, Suh et al. [8,9] studied the liquid-state wetting reaction between SnPb solder and (001) Cu, and observed a rooftop-type Cu$_6$Sn$_5$ grains elongated along two preferred orientation directions comparing with the normal scallop-type Cu$_6$Sn$_5$ grown on single crystalline Cu substrate. Zou et al. [10] investigated the morphologies and orientation relationships of Cu$_6$Sn$_5$ grains formed between liquid-state Sn and (001), (011), (111) and (123) Cu systematically. According to their study, the regular prism-type Cu$_6$Sn$_5$ grains formed on (001) and (111) Cu single crystals, but on (011) and (123) substrates the Cu$_6$Sn$_5$ grains were mainly scallop-type with only a few regular prism-type grains. Shang et al. [11,12] conducted a comprehensive TEM study on the growth mechanism of Cu$_6$Sn$_5$ on polycrystalline and single crystalline Cu substrates, and found that the columnar Cu$_6$Sn$_5$ grains grew on single crystalline (100) Cu with preferred orientation relationship. Recently, Chen et al. [13] utilized EBSD and HRTEM to reveal the preferred orientation relationship between (Cu,Ni)$_5$Sn$_3$ and Ni substrates, and find that the interface between Cu$_6$Sn$_5$ and Ni is coherent.

Besides the above-mentioned Sn-based lead-free solders, the binary eutectic SnIn solder has the advantages of lower melting temperature, better wettability, better ductile properties [14,15] and longer fatigue life [16]. Owing to the participation of In element in the interfacial reactions between solder and substrates, SnIn solder joint exhibits particular and different characters such as the morphologies and phase species of IMC, which will influence the mechanical property and service reliability of the interconnects in application. However, fewer researchers have paid attention to the morphology characterization and growth orientation of In-containing IMC. According to our knowledge, the evolution of duplex structural Cu$_2$(In,Sn) compound on single crystalline Cu substrates has never been reported before.

In this study, the growth mechanism of duplex structural Cu$_2$(In,Sn) IMC was investigated by scanning electron microscope (SEM) with a top-view etching techniques. Preferential growth of coarse-grain Cu$_2$(In,Sn) was observed on (100), (111) and (102) single crystalline Cu substrates, whose crystallographic orientation relationship was revealed by electron beam backscattered diffraction (EBSD).
2. Experimental procedures

2.1. Sample preparation

The solder used in this study was eutectic 48Sn52In alloy, and the substrate was single crystalline Cu. The (100) and (111) Cu plates (40 × 4 × 2 mm$^2$) were commercially purchased with polished and clean surfaces (the roughness is below 0.5 nm). The single crystalline Cu (102) plates (40 × 4 × 2 mm$^2$) were cut from a bulk Cu single crystal by electro-discharge machine, whose crystallographic orientation was determined by EBSD. These single crystalline (102) Cu surfaces were first ground successively with SiC papers and carefully polished with 1 and 0.5 μm diamond paste, and then rinsed in acetone, distilled water and dried in turn. Wetting SEM samples were prepared by putting eutectic SnIn thin foil on the polished Cu sheets, and then heated to the reflow temperature (160°C) for 5 s to form a solder joint. Solid-state aging was carried out at 60°C in an electric furnace for different days.

2.2. Morphology observation

In order to clearly reveal the morphologies of the IMC formed between eutectic SnIn solder and Cu from the top, the unreacted solder should be removed completely. The surface excess solder was mechanically polished first, and then was carefully etched with the 20% H$_2$O$_2$ + 80% CH$_3$COOH (vol:3) etchant solution which has the advantage of low etching rate and less effect on the Cu substrate. The etched samples were rinsed with distilled water in an ultrasonic bath for 10 min to clear away the residual etchant solution and then dried. All the clean samples were observed with a LEO super35 scanning electron microscope with an energy dispersive spectrum (EDS) system to characterize the morphologies of the IMC and to perform compositional analyses.

2.3. Orientation relationship determination

As the preferential growth of coarse-grain Cu$_2$(In,Sn) IMC was observed on single crystalline Cu substrate, EBSD was performed to study the orientation relationships between them using LEO super35 SEM. Since each elongated IMC grain is a single crystal, the Kikuchi patterns coming from selected spots of elongated grains are feasible to determine the crystallographic orientation. Because the EBSD method is very sensitive to the roughness degree of the sample surface, thus after SEM observations the samples were properly ion-milled again by LEICA EM RES101 to get a smooth surface for EBSD experiments.

3. Results and discussion

3.1. Morphology evolution of fine-grain Cu$_2$(In,Sn) on single crystalline Cu substrate

The duplex structural Cu$_2$(In,Sn) compound, which is made up of a fine-grain and a coarse-grain sublayers with the same hexagonal crystal structure, has been identified on polycrystalline Cu substrate in our previous works [17,18]. According to our recent study on the interfacial reaction between eutectic SnIn solder and single crystalline Cu substrate, cross-sectional characterization revealed that this duplex structural Cu$_2$(In,Sn) was also formed between Cu(In,Sn)$_2$ layer (tetragonal crystal structure) and Cu substrate. To clarify their morphology more precisely in a wide visual field, top-view observations were carried out by etching off the top residual SnIn solder, the Cu(In,Sn)$_2$ compound layer, the coarse-grain Cu$_2$(In,Sn) sublayer, and fine-grain Cu$_2$(In,Sn) sublayer in turn. Fig. 1a shows the image of duplex structural Cu$_2$(In,Sn) compound formed on (111)Cu after reflowing at 160°C for 5 s. Coarse-grain Cu$_2$(In,Sn) sublayer is on the top of fine-grain Cu$_2$(In,Sn) sublayer with elongated morphology showing preferential growth, which will be described and discussed in the following sections. The fine Cu$_2$(In,Sn) grains have granule-type morphology with smaller grain size, and distributes homogeneously on the entire (111)Cu substrates. Fig. 1b and c reveal the morphology evolution of fine-grain Cu$_2$(In,Sn) during solid-state aging at 60°C for 1 and 5 days, respectively. It can be seen that fine-grain Cu$_2$(In,Sn) grains increased slightly with the same granular morphology. Further increase of aging time up to 30 days results in bigger grain size of the fine Cu$_2$(In,Sn) compound as shown in Fig. 1d. The fine-grain Cu$_2$(In,Sn) formed on (100)Cu and (102)Cu surfaces was also investigated, and the same granular morphology as that in Fig. 1 was observed without any preferential growth on different Cu surface planes.

Although fine-grain Cu$_2$(In,Sn) compound was formed on Cu substrate directly, interestingly it is the coarse-grain Cu$_2$(In,Sn) but not fine-grain Cu$_2$(In,Sn) that show certain regularity and preferential growth on single crystalline Cu substrate, which has never been reported before. It is known that the occurrence and sequence of IMC formation are determined by the highest driving force and the minimum Gibbs energy naturally. Lee et al. [19] successfully predicted the first formation of IMC at the interfaces between Cu substrate and Sn–Pb, Sn–Bi and Sn–Zn binary eutectic solders. However, due to the lack of related thermodynamic data of the Cu$_2$(In,Sn) and Cu(In,Sn)$_2$, it was difficult to prove the formation sequence of IMC in eutectic SnIn/Cu system, especially Cu(In,Sn)$_2$ has coarse- and fine-grain duplex structural sublayers. Their studies only concluded that Cu$_6$(SnIn) IMC could not form first at eutectic Sn–In/Cu interface. However, the texture structure of coarse-grain Cu(In,Sn)$_2$ in Fig. 1 could be explained by the same growth phenomenon of Cu$_6$(SnIn) in other system. According to the study of Wang and Chen [20] on the interfacial reactions between Sn–0.7Cu wt.% and Ni, it is reported that the coarse-grain Cu$_6$(SnIn) grains display near hexagonal prism-shape and form first, while the fine-grain Cu$_6$(SnIn) grains nucleate later on the larger grains. Therefore, it could be deduced that the coarse-grain Cu$_2$(In,Sn) compound nucleated first with regular elongated morphologies during wetting reaction between 48Sn52In solder and single crystalline Cu substrate, while granule fine-grain Cu$_2$(In,Sn) formed later in the following solid reaction between coarse-grain Cu$_2$(In,Sn) and Cu. Since the coarse-grain Cu$_2$(In,Sn) compound formed first on single crystalline Cu substrate, preferential growth and orientation relationship were kept.

3.2. Preferential growth of coarse-grain Cu$_2$(In,Sn) on single crystalline Cu substrates

3.2.1. Growth morphology of coarse-grain Cu$_2$(In,Sn) on (100) Cu

Fig. 2 shows top-view SEM images of coarse-grain Cu$_2$(In,Sn) grains on (100) single crystalline Cu substrates after reflowing at 160°C for 5 s and aging at 60°C for different time. It can be obviously seen that the coarse-grain Cu$_2$(In,Sn) grains show a regular shuttle-type morphology and distribute homogeneously on the entire (100) Cu surfaces after reflowing in Fig. 2a. The most interesting thing is that the shuttle-type coarse-grain Cu$_2$(In,Sn) prefer only two elongated directions which are perpendicular to each other with an intersecting angle of 90°, which is consistent with the strong textured Cu$_6$(SnIn) or (Cu$_2$Ni)$_3$(SnIn)$_5$ grains on (001) Cu studied by Suh et al. [8,9], Zou et al. [10] and Chen et al. [13]. However, the coarse-grain Cu$_2$(In,Sn) grains show shuttle-type morphology in this study, which is different from the rooftop-type or the prism-type of Cu$_6$(SnIn) grains on single crystalline (100) Cu [8–10,13]. Comparing coarse-grain Cu$_2$(In,Sn) grains formed after reflowing with those further aged at 60°C until 15 days, it was found that the size and morphology of coarse-grain Cu$_2$(In,Sn) changed slightly at this initial stage as shown in Fig. 2a–c. However, the regularity of coarse-grain Cu$_2$(In,Sn) grains becomes weaker, which should be affected by the growth of fine-grain Cu$_2$(In,Sn) adjacent to Cu substrates. As shown in Fig. 1, fine-grain Cu$_2$(In,Sn) grew continuously on single crystalline Cu with increased aging time. These fine Cu$_2$(In,Sn) grains could protrude into the coarse-grain Cu$_2$(In,Sn) sublayer and locate between two adjacent coarse Cu$_2$(In,Sn) grains to weaken the growth regularity of coarse-grain Cu$_2$(In,Sn) grains. Further increasing the aging time up to 30 days resulted in a dramatic change in size and morphology of the coarse-grain Cu$_2$(In,Sn) grains in Fig. 2d. Except for a much bigger grain size, the grain morphology changed from one dimension elongation into poly-facet shape, although parts of
them still align along two perpendicular directions. This should be due to the change of surface energy of coarse Cu$_2$(In,Sn) grains from higher surface energy with elongated morphology to lower surface energy with poly-facet shape.

3.2.2. Growth morphology of coarse-grain Cu$_2$(In,Sn) on (111) Cu

The morphologies of coarse-grain Cu$_2$(In,Sn) grains formed on (111) single crystalline Cu substrates after reflowing at 160°C for 5 s and aged at 60°C for different time were shown in Fig. 3. It is obvious that the same shuttle-type coarse-grain Cu$_2$(In,Sn) compound formed on the whole (111) single crystalline Cu surfaces. The most typical phenomenon is that the elongated shuttle-type coarse-grain Cu$_2$(In,Sn) grains align along three directions with intersection angles of 60° or 120°, which is different from those observed on (100) single crystalline Cu surfaces in Fig. 2. This morphology was kept to the aging time of 15 days with a slight increase of grain size as displayed in Fig. 3a–c. The dramatic change in morphology and size of coarse-grain Cu$_2$(In,Sn) grains appears in the aging process up to 30 days as indicated in Fig. 3d, where the elongated shuttle-type grains grow into poly-facet grains also, which shows the same phenomena as that on (100)Cu.

3.2.3. Growth morphology of coarse-grain Cu$_2$(In,Sn) on (102) Cu

In order to study the evolution of coarse-grain Cu$_2$(In,Sn) formed on other single crystalline Cu surfaces, (102) surface was selected as the substrate and the results were shown in Fig. 4. Fig. 4a–d shows top-view SEM images of the evolution of coarse-grain Cu$_2$(In,Sn) compound during aging for up to 30 days. It could be seen that the morphology of coarse-grain Cu$_2$(In,Sn) grains on (102) Cu is elongated stripe-type, which differs from the shuttle-type one formed on (100) and (111) Cu surfaces. These elongated stripe-type Cu$_2$(In,Sn) grains align along only one direction of (102) Cu surface. The grain size of coarse Cu$_2$(In,Sn) grains increases slightly during aging, and the regularity of preferred orientation directions was also affected by the growth of fine-grain Cu$_2$(In,Sn) grains for long time solid-state aging.
It is concluded that after reflowing at 160 °C for 5 s, coarse-grain Cu$_2$(In,Sn) grains formed on (100), (111) and (102) single crystal-Cu substrates have elongated shuttle or strip-like morphology with certain regularity and preferred growth directions. During solid-state aging at 60 °C, these coarse-grain Cu$_2$(In,Sn) grains have a trend of grain size coarsening, regularity weakening, and morphological changing from elongated to poly-facet shape.

3.3. Orientation relationships between coarse-grain Cu$_2$(In,Sn) and single crystalline Cu substrates

3.3.1. Growth orientation of coarse-grain Cu$_2$(In,Sn) on (100) and (111) Cu

The preferential growth of coarse-grain Cu$_2$(In,Sn) grains on (100) and (111) Cu single crystals with elongated morphology, implies that there exist orientation relationships during the nucleation and growth of coarse-grain Cu$_2$(In,Sn) on these substrates. To verify this, EBSD experiments were performed on both Cu substrate and coarse-grain Cu$_2$(In,Sn) grains. Since each elongated coarse-grain Cu$_2$(In,Sn) grain is a single crystal, Kikuchi patterns from selected spots of coarse-grain Cu$_2$(In,Sn) compound are enough to determine orientations. Fig. 5a and d are Kikuchi bands from (100) and (111) Cu surfaces after etching off IMC layers formed on them, while Fig. 5b and e show Kikuchi patterns from elongated coarse-grain Cu$_2$(In,Sn) on (100) and (111) Cu respectively. A live description of 3D crystal orientations of perpendicularly arrayed coarse Cu$_2$(In,Sn) on (100) Cu was shown in Fig. 5c, and that of equilaterally arrayed coarse Cu$_2$(In,Sn) on (111) Cu was presented in Fig. 5f. It was found that the coarse-grain Cu$_2$(In,Sn) compound elongated along [0001]$_{Cu_2(In,Sn)}$ direction on (100) and (111) Cu surfaces. Basing on the careful analyses of Kikuchi patterns, the orientation relationships between coarse-grain Cu$_2$(In,Sn) and Cu are determined as follows:
In grains were only observed on (001) and (111) Cu axes are parallel and parallel-to-each other at an angle. Fig. 7c shows Kikuchi bands of (100) single crystalline Cu surface (a) and the formed coarse-grain Cu$_2$(In,Sn) (b) together with the illustration of two perpendicular coarse-grain Cu$_2$(In,Sn) on (100) Cu surface (c), and those of (111) Cu (d) and coarse-grain Cu$_2$(In,Sn) (e) which distributed in three directions on (111) single crystalline Cu surface (f).

The atomic model of these orientation relationships between Cu$_2$(In,Sn) and Cu is shown in Fig. 6. To keep this growth orientation, a low or minimum misfit of Cu atomic arrays between coarse-grain Cu$_2$(In,Sn) and Cu should exist from the viewpoint of lower nucleation energy. Fig. 6a shows one third of the whole Cu$_2$In cell due to the equivalence property of primitive hexagonal structure of Cu$_2$In, in which the intersecting axis between (11−20) (the black lines) and (12−30) (the blue lines) crystal planes is exactly [0001]$_{Cu_2In}$ direction, and the spacing between two Cu atoms along [0001]$_{Cu_2In}$ is 0.5232 nm. Fig. 6b and c show the arrays of Cu atoms on (100) and (111) crystal planes of Cu unit cell, in which the nearest atomic spacing between two Cu atoms is 0.2556 nm along [011]$_{Cu}$ direction. However, the spacing between the first and third Cu atoms is doubled as 0.5112 nm. Therefore, when coarse-grain Cu$_2$(In,Sn) grows along [0001]$_{Cu_2In}$ and parallels to [011]$_{Cu}$ on single crystalline Cu substrate, the atomic misfit between them can be calculated as \( \Delta = 2(0.5232 − 0.5112)/(0.5232 + 0.5112) = 2.3\% \). As part of In atoms were substituted with Sn and the radius of Sn is less than that of In, the actual misfit between Cu$_2$(In,Sn) and Cu substrate should be less than 2.3\%. Viewed on (100) Cu surfaces the [011]$_{Cu}$ and [01−1]$_{Cu}$ axes are perpendicular to each other as shown in Fig. 6b, while [1−10]$_{Cu}$, [0−11]$_{Cu}$ and [−101]$_{Cu}$ axes intersect with each other at an angle of 60° or 120° on (111) Cu substrate (see Fig. 6c). When coarse-grain Cu$_2$(In,Sn) grow along these directions with the orientation relationships described in formulas (1) and (2), morphological regularity will be presented as shown in Figs. 2 and 3.

3.3.2. Growth orientation of coarse-grain Cu$_2$(In,Sn) on (102) Cu

Fig. 7a shows Kikuchi bands of coarse-grain Cu$_2$(In,Sn) grains on (102) Cu substrates as well as 3D crystal orientations of coarse-grain Cu$_2$(In,Sn) at the upper-right corner and that of Cu at the lower-right corner. EBSD results revealed that the (11−2−3) crystal plane of coarse-grain Cu$_2$(In,Sn) grains are parallel to (102) plane of Cu. Fig. 7b is the SEM image of coarse-grain Cu$_2$(In,Sn) grains showing that these grains indeed elongate along only one direction, which was determined as [1−100]$_{Cu_2In}$ direction. Fig. 7c shows partial structure of Cu$_2$In cell and the structure of Cu cell. According to this atomic model, the spacing between two Cu atoms along [1−100]$_{Cu_2In}$ direction is 0.7437 nm, while that between the first and third Cu atoms along [010]$_{Cu}$ direction on (102) surface is 0.7228 nm. Hence the atomic misfit between them is calculated as 2.9\%, which is small and can minimize the nucleation energy during growth. The orientation relationship between coarse-grain Cu$_2$(In,Sn) and (102) Cu is identified as:

\[
Cu(102) : \{11 − 2 − 3\}_{Cu_2In}/\{110\}_{Cu}, \quad \text{and} \quad [1 − 100]_{Cu_2In}/\{010\}_{Cu}
\]

It was reported that preferential growth of regular prism-type Cu$_3$Sn$_5$ grains were only observed on (001) and (111) Cu substrates, while on (011), (123) and other single crystalline Cu...
surfaces the formed Cu$_3$Sn grains had irregular scallop-type morphology without growth orientation relationship. In this study, coarse-grain Cu$_2$(In,Sn) grains formed on (102) Cu surfaces also displayed regular stripe-type morphology, and kept a growth orientation relationship with (102) Cu as shown in formula (3). The actual atomic misfit between them will be less than 2.9% due to the substitution of In atoms by some Sn atoms.

It is necessary to point out that besides the growth morphology and orientation relationship, the growth kinetics of Cu$_2$(In,Sn) IMCs could also be affected by the different single crystalline Cu substrates. However, since coarse- and fine-grain Cu$_2$(In,Sn) compounds have the same crystal structure with similar phase contrast in the cross-sectional SEM images, it is difficult to distinguish the interface between them to carry out a precise study on their growth kinetics at different Cu surface planes. According to our previous study on the growth kinetics of Cu$_3$Sn on (100)Cu and (111)Cu, first principle calculations revealed that (111)Cu plane has a lower surface energy of about 0.45 eV than that of (100)Cu plane (about 0.57 eV) [12]. It means the release of Cu atoms for IMC growth will be more difficult on (111)Cu (more stable with lower energy). Hence the growth of Cu$_2$(In,Sn) IMCs on (100)Cu should be faster than that on (111)Cu, which need to be clarified with a comprehensive study basing on well-designed experiments and precise analyses.

4. Conclusions

The growth mechanism of duplex structural coarse- and fine-grain Cu$_2$(In,Sn) IMC between eutectic SnIn solder and single crystalline Cu substrate were systematically investigated using SEM and EBSD. It was concluded that during wetting reaction between 48Sn52In solder and single crystalline Cu substrate at 160 °C, granule fine-grain Cu$_2$(In,Sn) distributed homogeneously on Cu surface without orientation relationship between them, while coarse-grain Cu$_2$(In,Sn) compound had elongated morphology and showed preferential growth on different single crystalline Cu substrates. During solid-state aging at 60 °C for up to 30 days, the grain size of both coarse- and fine-grain Cu$_2$(In,Sn) increased. However, the growth regularity of coarse-grain Cu$_3$Sn was weakened, and its morphology changed from elongated one into poly-facet shape due to the growth of fine-grain Cu$_2$(In,Sn) underneath.

There are orientation relationships during the nucleation and growth of coarse-grain Cu$_2$(In,Sn) compound on single crystalline Cu, whose atomic misfits are less than 2.3–2.9% between their crystallographic structures. On (100) single crystalline Cu substrates, shuttle-type coarse-grain Cu$_3$Sn nucleated and grew along two perpendicular (011)$_{Cu}$ directions with orientation relationship of $\{11-20\}_{Cu}^{2}$(In,Sn)//$\{100\}_{Cu}$, $\{12-30\}_{Cu}^{2}$(In,Sn)//$\{101\}_{Cu}$, and $\{0001\}_{Cu}^{2}$(In,Sn)//$\{011\}_{Cu}$. In the case of (111) Cu surfaces, coarse-grain Cu$_3$Sn also had a shuttle-type morphology, and formed along three (011)$_{Cu}$ directions (in intersecting angles of 60° or 120°) with orientation relationship of $\{11-20\}_{Cu}^{2}$(In,Sn)//$\{111\}_{Cu}$, $\{12-30\}_{Cu}^{2}$(In,Sn)//$\{111\}_{Cu}$, and $\{0001\}_{Cu}^{2}$(In,Sn)//$\{011\}_{Cu}$. However, reflowed coarse-grain Cu$_2$(In,Sn) aligned along only one (010)$_{Cu}$ direction with a stripe-type morphology on (102) single crystalline Cu surfaces, whose orientation relation was determined as $\{11-2-3\}_{Cu}^{2}$(In,Sn)//$\{102\}_{Cu}$ and $\{1-100\}_{Cu}^{2}$(In,Sn)//$\{010\}_{Cu}$.

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