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Preferred orientation relationship between Cu_6Sn_5 scallop-type grains and Cu substrate in reactions between molten Sn-based solders and Cu

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A strong crystallographic orientation relationship between the Cu_6Sn_5 scallop-type grains and their Cu substrate has been found by synchrotron micro-x-ray diffraction study. Even though the crystal structures of Cu_6Sn_5 monoclinic and Cu face-centered-cubic are very different, angular distributions of crystallographic directions between Cu_6Sn_5 and Cu revealed a strong orientation relationship. Both SnPb solder and pure Sn showed the same result, indicating that this is general behavior between Sn-based solders and Cu. The strong orientation relation suggests that Cu_6Sn_5 forms prior to Cu_3Sn in the wetting reactions. A total of six different orientation relationships were found. In all the cases, the $\bar{0}1$ direction of Cu_6Sn_5 preferred to be parallel to the 110 direction of Cu with a misfit of 0.24%. Due to pseudohexagonal structure of the Cu_6Sn_5 , the six relationships can be categorized into two groups. From the orientation distribution, one group was found to be less rigid than the other group.

I. INTRODUCTION

Solder joint is ubiquitous; it is used in plumbing and in circuit interconnection in electronic devices. Metallic bonding in solder joints is achieved by the formation of Cu-Sn intermetallic compound IMC of Cu_6Sn_5 and Cu_3Sn at the solder/Cu interface. Because of the wide application of solder, especially the Pb-free solders to consumer electronic products, the study of the wetting reaction of molten solder on Cu has attracted renewed interests lately. Morphology of IMC formation affects the reaction kinetics. It is known that Cu_6Sn_5 has unique scallop-type morphology and Cu_3Sn has a layer-type morphology. The latter forms between the former and the copper substrate. Morphology of the Cu_6Sn_5 depends greatly on composition of solder.¹ Figures 1 a and 1 b show top-view scanning electron microscopy SEM images of Cu_6Sn_5 scallops formed by reaction between molten eutectic SnPb solder and Cu and between molten pure Sn and Cu, respectively. These images were obtained by polishing and etching away the unreacted solder above the IMC. In Fig. 1 a, the shape of the scallops is close to hemisphere. However, in Fig. 1 b, the scallops have faceted morphology.

Assuming a rounded hemispherical surface morphology, the growth of scallop-type Cu_6Sn_5 has been analyzed by a mechanism of nonconservative ripening under constant surface area, while the total volume increases with time.² However, the interface between the scallops and Cu has been investigated, except that it was assumed that the interfacial diffusion of Cu is fast and the diffusion is not a rate limiting step. In spite of the very large body of literature published on the subject of solder/Cu reaction,³⁻¹² the structural information of the interface and the crystallographic orientation re-

lationship between the IMC and Cu is still missing. It is the purpose of this study to determine the orientation relationship and the statistical distribution experimentally.

As shown in Figs. 1 a and 1 b, the surface of the scallop is not flat. Therefore electron backscattered diffraction EBSD, which requires a flat and polished surface, cannot be used to obtain the map of scallop orientation. In addition, EBSD is unable to probe the buried phases, such as the Cu substrate beneath the scallops. On the other hand, the orientation relationship between a particular scallop and its Cu substrate can be determined by cross-sectional transmission electron microscopy TEM, yet a statistical distribution is difficult to obtain. In the present study, we used the synchrotron radiation technique of scanning white beam micro-x-ray diffraction, to map the grain orientation of several thousand scallops with high spatial and angular resolution. Due to the deeper penetration of x rays, information on both the IMC scallops and the buried Cu substrate can be obtained simultaneously. The crystallographic orientation relationship of a very large number of scallops and the substrate can be obtained for statistical studies.

II. EXPERIMENT

A. Sample preparation

Solders with two different compositions were used in current study. Solder with a 55Sn45Pb composition was reacted with Cu to investigate reaction between SnPb solder and Cu. The 55Sn45Pb composition was selected in order to ensure round morphology of Cu_6Sn_5 scallops.¹ To investigate reactions between Pb-free solders and Cu, pure Sn was used to represent various Pb-free solders. This is because compositions of most of Pb-free solders are nearly pure Sn. The 55Sn45Pb solder was prepared by mixing pure Sn 99.999% and Pb 99.998% in a clean quartz ampoule under vacuum,

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(a)

(b)

FIG. 1. Top-view SEM image of Cu_6Sn_5 grains, a formed by the reaction between eutectic SnPb solder and Cu and b formed by pure Sn and Cu. a and b have different morphology.

melting at 1150°C for 1 h, and quenching into ice water. To obtain a quenching rate high enough to produce homogenous alloys, only a small amount of alloy 3 g was made each time. The solders were cut into small pieces 0.5 ± 0.1 mg and melted in mildly activated flux 197 RMA to form a spherical bead.

Copper foil 99.999% was cut into 1 cm 1 cm square pieces, with 1 mm thickness. The Cu pieces were cleaned ultrasonically with acetone and $20\% \text{HNO}_3 + 80\% \text{H}_2\text{O}$ for 30 s to remove organic contaminants on the surface. The acetone cleaning was followed by rinsing with methanol and de-ionized DI water and drying with nitrogen gas. The cleaned Cu foils were annealed at 800°C in clean quartz ampoule under vacuum for 40 days to give a grain size of millimeters. The annealed Cu foils were mechanically polished down through colloidal silica to reduce surface roughness. The polished Cu foils went through additional annealing at 800°C in clean quartz ampoule under vacuum for 48 h to reduce polishing damage. This is because the polishing damage, unremoved, would introduce distortion of Laue spots. After the final annealing, the Cu foils were etched with $5\% \text{HNO}_3 + 95\% \text{H}_2\text{O}$ for 15 s to remove native oxide, and rinsed with DI water followed by drying with nitrogen gas. Then Cu pieces were quickly immersed into hot 197 RMA flux. The flux was used to improve wettability of solder. The

prepared solder bead was dropped onto the Cu foil. The solder bead melted and wetted the surface of the Cu foil by forming a cap. The interfacial Cu_6Sn_5 scallop formation between the molten solder cap and the Cu foil was controlled by varying the reaction time. The 55Sn45Pb solder was reacted with the copper foil at 200°C from 30 s to 8 min. The pure Sn was reacted with Cu at 250°C for 4 min. The reacted sample was quenched down to room temperature in acetone. To expose Cu_6Sn_5 scallops as shown in Figs. 1 a and 1 b, the unreacted solder covering the scallops was removed by mechanical polishing, followed by selective chemical etching. The selective etching was performed by using one part nitric acid, one part acetic acid, and four parts glycerol at 80°C .¹³ While the grain sizes of Cu in the Cu foils were in the millimeter range, the size of each scallop is about 1 – 2 μm , therefore the grain size of Cu_6Sn_5 is much smaller than the grain size of the Cu. Each scallop is a single crystal of Cu_6Sn_5 . The purpose of annealing the Cu is to obtain a very large grain size, then the Laue spots from the Cu will be much stronger than those from the Cu_6Sn_5 , so they can be decoupled in the Laue pattern. Furthermore, we can study the formation of a cluster or colony of scallops on each Cu grain.

B. Sample characterization

The micro-x-ray diffraction experiments were conducted on beamline 7.3.3 at the Advanced Light Source in Lawrence Berkeley National Laboratory.¹⁴ The sample was scanned under a micron size x-ray beam and at each step of scan a white beam Laue diffraction pattern was collected by using a MAR133 x-ray charge coupled device detector. The micro-x-ray beam can penetrate through the Cu_6Sn_5 to reach the Cu, hence, each Laue pattern is a composite of diffraction spots of Cu_6Sn_5 and Cu. The strongest Laue spots came from the Cu, because of the larger grain size and therefore the probing volume of Cu is larger in comparison to that of the Cu_6Sn_5 scallops. The Cu reflections were indexed first to yield Cu grain orientation and then removed from the list of reflections for the subsequent analysis of the Cu_6Sn_5 reflections.

In the early stage of wetting reaction, diffraction peaks from Cu_3Sn were not detected because either the Cu_3Sn did not exist or its grain size and thickness were too small to be visible above the background level. Since the three phases have different structures and symmetries, there is no ambiguity in indexing their Laue spots.

III. RESULTS

The Cu_6Sn_5 undergoes order-disorder type phase transformation near 186°C . The β -phase Cu_6Sn_5 is stable at high temperature and the α -phase is stable at low temperature. Since samples were quenched to room temperature, most of Cu_6Sn_5 scallops maintained the β -phase structure. This was confirmed by trying to analyze the Laue patterns assuming β -phase structure. Most Laue spots could not be indexed when we assumed α -phase structure.

The crystal structure of β - Cu_6Sn_5 has been thought to be hexagonal,¹⁵ but a recent study using electron diffraction

showed that it is actually monoclinic $P2/c$, $a = 9.84$, $b = 7.27$, $c = 9.84$ Å, $\beta = 62.5^\circ$.¹⁶ From the Laue patterns, three-dimensional computer models of crystal structures were simulated to determine the orientation relationships between the Cu and the monocline Cu_6Sn_5 . After constructing models from various data points, six types of orientation relationship between the two phases were found:

$(010)_{\text{Cu}_6\text{Sn}_5} \parallel (001)_{\text{Cu}}$ and $[-110]_{\text{Cu}_6\text{Sn}_5} \parallel [110]_{\text{Cu}}$	1
$(343)_{\text{Cu}_6\text{Sn}_5} \parallel (001)_{\text{Cu}}$ and $[-101]_{\text{Cu}_6\text{Sn}_5} \parallel [110]_{\text{Cu}}$	2
$(\bar{3}4\bar{3})_{\text{Cu}_6\text{Sn}_5} \parallel (001)_{\text{Cu}}$ and $[-101]_{\text{Cu}_6\text{Sn}_5} \parallel [110]_{\text{Cu}}$	3
$(101)_{\text{Cu}_6\text{Sn}_5} \parallel (001)_{\text{Cu}}$ and $[-101]_{\text{Cu}_6\text{Sn}_5} \parallel [110]_{\text{Cu}}$	4
$(141)_{\text{Cu}_6\text{Sn}_5} \parallel (001)_{\text{Cu}}$ and $[-101]_{\text{Cu}_6\text{Sn}_5} \parallel [110]_{\text{Cu}}$	5
$(\bar{1}4\bar{1})_{\text{Cu}_6\text{Sn}_5} \parallel (001)_{\text{Cu}}$ and $[-101]_{\text{Cu}_6\text{Sn}_5} \parallel [110]_{\text{Cu}}$	6

In all the cases, the $\bar{1}01$ direction of Cu_6Sn_5 is aligned parallel to the 110 direction of Cu. Figure 2 a is a map representing the angle between the $\bar{1}01$ direction of Cu_6Sn_5 and the 110 direction of Cu, after 8 min of wetting reaction. The scanned area was $120 \text{ m} \times 120 \text{ m}$, with a step size of 2 m. Most of the spots have the angle close to 0° . Figure 2 b is a histogram of orientation distribution corresponding to Fig. 2 a. The angle is close to zero for the vast majority of data points, indicating a very strong correlation between Cu_6Sn_5 and Cu. Among the data, 17.8% of data points had angle less than 1° and 62.9% had angle less than 5° .

The orientation relationship in Eqs. 1 - 6 can be classified into two groups. This is due to the strong pseudo-hexagonal symmetry around the Cu atoms in Cu_6Sn_5 . Figure 3 a shows the structure of Cu_6Sn_5 projected along the $\bar{1}01$ direction. Copper atoms in the Cu_6Sn_5 are represented by circles. In Fig. 3 b, the crystal planes for the six relationships are labeled with respect to the Cu atom pseudo-hexagon. Relationships involving planes 010, 343, and $\bar{4}3$ belong to the first group "group 1". Relationships with planes 101, 141, and $\bar{1}41$ belong to the second group "group 2". Figure 2 c is the histogram of angle between 001 plane of Cu and group 1 planes of Cu_6Sn_5 after 8 min of reflow. Two peaks are clearly visible. The first peak close to 0° is from the angle between the planes of group 1 and 001 of the Cu substrate. The second peak is from the angle between group 2 planes and 001 of the Cu substrate. The peak from group 2 is much broader than the peak from group 1. The result is similar for all the tested samples indicating that group 2 is a less rigid type of orientation relationship than group 1.

Figure 4 a is a histogram of the angle between the $\bar{1}01$ direction of Cu_6Sn_5 and the 110 direction of Cu, after the pure Sn reacted with an annealed Cu for 4 min at 250°C . The peak is a little broader and the noise level is higher than

FIG. 2. Map and histograms of a sample with 8 min of reflow, indicating a strong orientation relationship between Cu_6Sn_5 and Cu. a Map representing angle between the $\bar{1}01$ direction of Cu_6Sn_5 and the 110 direction of Cu. b Histogram of orientation distribution corresponding to Fig. 2 a. Value is close to zero for the majority of data points. c Histogram of the angle between the 001 plane of Cu and the group 1 planes of Cu_6Sn_5 . The first peak close is from the angle between the planes of group 1 and 001 of Cu. The second peak is from the angle between group 2 and 001 of Cu.

the histogram in the Fig. 2 b. Among the data, 12.8% of data points had values smaller than 1° and 49.8% were smaller than 5° . However, the Cu_6Sn_5 still has a strong dependence on Cu. This suggests that scallops in Pb-free solder reaction should also have the same orientation relationship. Since the Cu_6Sn_5 scallops on pure Sn have faceted morphologies, this result also indicates that the orientation relationship is not affected by the morphology of scallops. Figure 4 b is the histogram of the angle between the 001 plane of the substrate Cu and the group 1 planes of Cu_6Sn_5 . Group 2 is dominant.

Figures 5 a and 5 b are maps of the angle between the 101 direction of Cu_6Sn_5 formed on a large single grain of Cu and the laboratory z axis after 4 and 8 min time of reaction. White spots are data points where the Laue patterns were not clear enough to be indexed due to sample damage. The number of scallops scanned was around 1200 in both

FIG. 3. a Structure of Cu_6Sn_5 projected from the 101 direction. Copper atoms are represented with circles. Cu atoms have strong pseudo hexagonal symmetry. b Crystal planes of the six relationships are labeled with respect to the hexagon composed of copper atoms. They can be categorized into two groups.

FIG. 4. Histograms of the orientation relationship between Cu_6Sn_5 and Cu. Pure Sn was reacted with Cu at 250°C for 4 min. a Histogram of the angle between the 110 direction of Cu and the 101 direction of Cu_6Sn_5 . b Histogram of the angle between angle between the 001 plane of Cu and the group 1 planes of Cu_6Sn_5 . Orientation of Cu_6Sn_5 still strongly depends on the orientation of Cu and the group 2 relationship is dominant.

FIG. 5. a and b are maps of the angle between the 101 direction of Cu_6Sn_5 formed on a large single grain of Cu and the laboratory z axis after 4 and 8 min reflow, respectively, indicating scallops with similar orientation tend to form clusters.

cases. The average diameter of scallops is $1-2\text{ }\mu\text{m}$. But spots with various colors in the orientation maps look much larger than the actual size of the scallops. This indicates that scallops with similar orientation tend to form clusters or colonies. The mechanism of the cluster formation is not understood yet. This can be due to a strong interaction between neighboring scallops during the ripening. However, the difference between clusters was investigated by inspecting computer three-dimensional models. We found that scallops form clusters in three different ways: 1 In some clusters, the $101_{\text{Cu}_6\text{Sn}_5} // 110_{\text{Cu}}$ relationship is not strictly obeyed; 2 the $\bar{1}01$ direction of the Cu_6Sn_5 is parallel to different 110 directions in Cu from cluster to cluster; and 3 some clusters belongs to group 1 while other clusters follow relationship group 2.

IV. DISCUSSION

The reason why the $\bar{1}01$ direction of Cu_6Sn_5 is always parallel to the 110 of Cu is because a small misfit between the two crystal structures can be achieved in such way. Along the $\bar{1}01$ direction of monoclinic Cu_6Sn_5 , Cu atoms are located at intervals of $2.5573\text{ }\text{\AA}$. Since the lattice constant of face-centered-cubic Cu is $a = 3.6078\text{ }\text{\AA}$, the distance between the two atoms along the 001 plane diagonal of the Cu lattice is

FIG. 6. Histograms of the angle between the 110 direction of Cu and the 101 of Cu_6Sn_5 , after a 30 s, b 1, c 4, and d 8 min of reflow, showing influence of the reflow time on the relationship between crystal directions. The Cu_6Sn_5 scallops gradually gain texture as reflow time increases, but the texture starts to decrease with further increase of the reflow time.

$$\frac{\bar{a}_{\text{Cu}}}{\bar{a}_{\text{Cu}_6\text{Sn}_5}} = \frac{3.6078}{2.5511} = 1.414$$

Thus the misfit between Cu and Cu_6Sn_5 is

$$f = \frac{2.5511 - 2.5573}{2.5511} = 0.00244 = 0.24\%.$$

The existence of a strong orientation relationship between the Cu_6Sn_5 and the Cu suggests that at the nucleation stage the Cu_6Sn_5 forms prior to the Cu_3Sn . The lattice structure of Cu_3Sn is orthorhombic with the Cu_3Ti type¹⁷ and Cu_3Sn does not have any low index plane or direction having a small misfit with either Cu or Cu_6Sn_5 . If Cu_3Sn were

FIG. 7. Histograms of the angle between the 001 plane of Cu and the group 1 planes of Cu_6Sn_5 , after a 30 s, b 1, c 4, and d 8 min of reflow, showing influence of the reflow time on the relationship between crystal planes.

formed before Cu_6Sn_5 , the latter would not possibly have developed an orientation relationship with Cu. However, a cross-sectional TEM study will be required for a critical investigation.

Influence of the reflow or reaction time on the orientation relationship is shown in Fig. 6, where histograms of the angle between the 110 direction of Cu and the $\bar{0}1$ direction of Cu_6Sn_5 are given. If the orientation of Cu_6Sn_5 depends strongly on Cu, the majority of the data will have a value close to 0° . At 30 s, which was the earliest reaction time of our measurement, the distribution shown in Fig. 6 a is quite random. The distribution at 1 min Fig. 6 b shows a stronger correlation between the Cu_6Sn_5 scallops and the Cu grain. The histogram is bimodal. At this moment, the origin of the bimodal distribution is not understood. The correlation becomes very strong at 4 min Fig. 6 c, but weakens at 8 min Fig. 6 d. This change in distribution can be explained from the nucleation and growth of Cu_6Sn_5 and Cu_3Sn . The Cu_6Sn_5 scallops should nucleate first with a certain degree of randomness, resulting in a distribution such as that in Fig. 6 a. During the growth and ripening of Cu_6Sn_5 scallops, scallops not following the orientation relationship will be consumed first to reduce their higher interfacial energy with Cu. Hence, the fraction of scallops with a good orientation relationship will continue to increase. This explains why the distribution gradually becomes more concentrated toward 0° , as shown in Figs. 6 a-6 c. After a certain amount of time, the orientation relationship between Cu_6Sn_5 and Cu will be affected by the nucleation and growth of Cu_3Sn between them. Formation of the Cu_3Sn is by a solid state reaction between Cu_6Sn_5 and Cu.¹⁸ Growth of the Cu_3Sn may not be uniform and Cu_3Sn nucleate and grow nonuniformly, grain by grain. After a long reflow time, some of the Cu_3Sn grains will become thick and incoherent to both Cu_6Sn_5 and Cu. The presence of incoherent grains of Cu_3Sn may tilt the Cu_6Sn_5 scallops in order to release the misfit strain energy. The Cu_6Sn_5 scallops can be tilted easily. It is because they are surrounded by liquid solder, which does not provide any physical restriction.

Influence of reflow time on the angle between the crystal planes is shown in Figs. 7 a-7 d. Figures 7 a-7 d are histograms of the angle between the group 1 planes of Cu_6Sn_5 and the 001 plane of Cu, with 30 s, 1, 4, and 8 min of reflow time. As mentioned earlier, while the peaks from group 1 are sharp, the peaks from group 2 are rather broad. This means that the group 2 relationship is less rigid and can better accommodate the lattice mismatch. As shown in Fig. 7 a, initially the distribution is random due to the random nucleation of Cu_6Sn_5 scallops. At 1 min, the group 2 relationship starts to become dominant. But at 4 min, group 1 is dominant. At 8 min, group 1 is still dominant, but the peak from group 2 has increased. In short, group 2 is dominant in the early stage up to 1 min, but group 1 is dominant over group 2 in the later stage, indicating that group 1 is thermodynamically more stable than group 2. However, as the reflow time further increases, the population of group 2 will start to increase. In the nucleation stage, the less rigid group 2 should be preferred, so that Cu_6Sn_5 scallops can accommodate the initial randomness. But since group 1 is more stable

FIG. 8. Pure Sn was reacted with Cu at 250°C for 2 min. a Histogram of the angle between the 001 plane of Cu and the group 1 planes of Cu_6Sn_5 . b Map of the angle between the 100 direction of Cu and the in-plane x axis. There are three grains. c Map of the angle between the group 1 planes of Cu_6Sn_5 and the 001 plane of Cu. There is no obvious influence from the orientation of Cu.

than group 2, group 1 becomes dominant at 4 min. However, as the reflow time increases further up to 8 min, the Cu_3Sn between Cu_6Sn_5 and Cu starts to become thicker. To accommodate the lattice mismatch from the formation of Cu_3Sn , group 2 starts to appear again.

For the case of the reaction between pure Sn and Cu, group 2 becomes dominant earlier than the case of 55Sn45Pb and Cu. Figure 8 a is a histogram of the angle between the group 1 Cu_6Sn_5 planes and the 001 Cu plane, after pure Sn reacted with Cu for 2 min. Group 2 is already dominant. This is because Cu_3Sn has grown faster due to a higher reaction temperature in the pure Sn case. Both Figs. 4 a and 6 c are histograms of the angle between the $\bar{0}1$ direction of Cu_6Sn_5 and the 110 direction of Cu after 4 min reflow. The solder used in Fig. 4 a is pure Sn and in Fig. 6 c is 55Sn45Pb. The histogram in Fig. 4 a has a broader peak and a higher noise level compared to the one in Fig. 6 c, indicating that scallops are more randomly oriented due to faster growth of the Cu_3Sn . Influence of the Cu substrate orientation was also examined as a candidate to determine which

one of the two groups will be dominant. Figure 8 b is the map of the angle between the 100 direction of Cu and the in-plane x axis laboratory x axis. Figure 8 c is the map of the angle between the 100 plane of Cu and the group 1 planes of Cu_6Sn_5 . The white spots are data points where the Laue patterns were not clear enough to be indexed due to sample damage. There are three Cu grains in the scanned area. If the orientation of Cu has an effect on cluster formation, whether group 1 or group 2 will be dominant can be determined, because there should be some correlation between Figs. 8 c and 8 d. However, there is no clear correlation observed. Other samples with multiple copper grains were also examined, but there was no obvious influence from the orientation of the Cu grains.

V. SUMMARY

A strong crystallographic orientation relationship between the Cu_6Sn_5 scallops and the Cu substrate in the wetting reaction between molten Sn-based solders and Cu has been determined. Six types of the orientation relationship between Cu_6Sn_5 and Cu were found. In all of them, the $\bar{0}1$ direction of Cu_6Sn_5 is always parallel to the 110 direction of Cu with a misfit of 0.24%. The six orientation relationships can be classified into two groups because of the strong pseudohexagonal symmetry of Cu atoms in Cu_6Sn_5 . The distribution of the angles between the crystallographic planes of Cu and Cu_6Sn_5 showed that one group has a less rigid orientation relationship than the other group. The strong crystallographic orientation relation suggests that Cu_6Sn_5 forms prior to Cu_3Sn . We have also found that in the early stage of

reaction, the orientation distribution of Cu_6Sn_5 scallops is rather random. The Cu_6Sn_5 scallops gradually gain texture as reflow time increases, but the texture starts to decrease with further increase of the reflow time because of the growth of Cu_3Sn between the Cu_6Sn_5 and the Cu.

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