MICROSTRUCTURE CONTROL OF UNI-DIRECTIONAL GROWTH OF η-CU_6SN_5 IN MICROBUMPS ON (111) ORIENTED AND NANOTWINNED CU

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ABSTRACT

The growth of η and η'-Cu_6Sn_5 has been proven as a preferential growth behavior on single crystal copper. However, a layer of single crystal copper is not possible to be electroplated. It can not be utilized in the electronic industry. In this paper, we electroplated an array of (111) uni-directional Cu pad followed by electroplating SnAg2.3. After being reflowed at 260°C for 1 minute, the η-Cu_6Sn_5 showed a preferential growth to (0001) plane. As reflow time extended, the preferential growth behavior would change. The intensity of (0001) decreased while that of $(2\bar{1}\bar{1}3)$ increased. It means the preferential growth of η-Cu_6Sn_5 would change during reflow. Eventually, the preferred orientation of η-Cu_6Sn_5 changed to $(2\bar{1}\bar{1}3)$ after 5 minutes of reflowing. It is also found that this preferential growth behavior of Cu_6Sn_5 would be affected by the quality of (111) uni-directional Cu.

Key words: Intermetallic compounds; Soldering; Copper;

INTRODUCTION

The use of conventional Sn-Pb solder alloy in consumer products has been forbidden since 2006 due to RoHS (Restriction of Hazardous Substances Directive). Some new alloy system such as Sn-Ag, Sn-Cu, Sn-Ag-Cu are therefore developed and studied. These alloy systems are all massive tin matrix with minor addition, typically less than 5 wt%, of other metal elements. For this reason, the study of metallurgical reaction and mechanical behavior between tin and copper or nickel substrates are carefully concerned in recent years. Among all the factors, growth of Sn-Cu and Sn-Ni intermetallics draw many attentions since the intermetallic would act not only as a mechanical joint but also a brittle interface at the same time due to its nature.

As the trend goes to minimize the packaging size, the volume fraction of tin in solder joints is decreased. In micro-bumps, the solder height is only 5-20μm. It turns out that the tin might be consumed during reflow process. In that way, the Cu_6Sn_5 would control the properties of solder joints and prevent the early failure caused by Sn orientation.[1] Also, Cu_6Sn_5 can be employed in Li-ion batteries as anode materials due to its favorable properties such as lower cost and storage capacity.[2][3] So, it is beneficial to control the properties of Cu_6Sn_5 by controlling its orientations.

The growth of η and η'-Cu_6Sn_5 has been proven as a preferential reaction with single-crystal Cu substrates. Suh et al. found that the preferential growth behavior between η'-Cu_6Sn_5 and (001) single crystal Cu.[4][5] Zou et al. found the η'-Cu_6Sn_5 a very strong texture on (001), (011), (111) and (123) single crystal Cu substrate.[6][7]. However, for the electroplating technology nowadays, it is unlikely to electroplating single crystal metals on silicon wafers. On poly-crystalline Cu, Kumar et al have reported that the orientations of Cu_6Sn_5 grains formed on were random and had no preferential relationship. [8] So, the preferred orientation behavior can not be used in electronic industries. In this paper, we produce a layer of (111) uni-directional Cu by electroplating. The SnAg 2.3 was used as solder materials. The orientations relationship between uni-directional Cu and Cu_6Sn_5 were examined. Also, the effect of quality of uni-directional Cu on the orientation of Cu_6Sn_5 was discussed.

EXPERIMENTAL PROCEDURE

To examine the relationship between the Cu_6Sn_5 and (111) uni-directional Cu pad, which can be utilized in 3D-IC packaging, Cu pads were electroplated by various current densities of 1 ASD (amps per square decimeter) and 8 ASD. Then, the solder alloy of SnAg2.3 is electroplated.

In the first part, the bump die was reflowed at 260°C for 1 and 5 minutes to grow Cu_6Sn_5. Then, after cooling in the air, the sample was grinded by abrasive papers of #1000, #2000, and #4000 followed by polishing with Al2O3 powder of 1.0μm and 0.3μm. Finally, we use colloidal silicas to remove the surface layer, which might be damaged during the process of polishing. We observe the morphology and the orientation image map from cross section view and top view after grinding and polishing.

In the second part, we jointed two single bumps together to make a complete solder joint and then made them reflowed for several minutes. Samples were grinded by using abrasive papers #400, #1000, #2500 and #4000 after air cooling, and then also polished by Al_2O_3 of 1 and 0.3 μm and colloidal silica. Focus ion beam technique was also adopted in cross-sectional observation. The images of solder joints were taken by JOEL FE-SEM 7001. Orientation maps, inversed pole figures and pole figures were collected by EDAX EBSD system. The XRD and TEM would also adopted to justify the experimental results.

The monoclinic η'-Cu_6Sn_5 has been found by A.K. Larsson et al. [9] in 1994. Ever since that, the crystal structure of Cu_6Sn_5 has become controversial. Larsson has reported the transformation temperature of Cu_6Sn_5 from η' to η is 186 ^oC. However, since the process of making solder joints includes reflow at up to 260 ^oC and cooling down to room temperature. The real stable phase after the joints were made is not sure. Ghosh reported on the η↔η'-Cu_6Sn_5 kinetics and transformation energy.[10] Laurila et al. showed that time for the η to η' transformation was insufficient with typical cooling rates after soldering.[11][12] Therefore, the η-Cu_6Sn_5 would be remained as a metastable phase. Nogita et al. also make a TTT diagram about the phase transformation of Cu_6Sn_5. They conclude that under 70 ^oC, the η-Cu_6Sn_5 in the joint could hardly transform into monoclinic structure.[13] Nogita have also found that the Ni has a effect to stabilize the structure of η-Cu_6Sn_5. [14][15] And Schwingenschlögl has further proven it with first principles calculations.[16] The most common combination used as under bump metallization layer in packaging industry is Cu and Ni. Therefore, after reflowing, the solder must contain some Ni atoms, making the intermetallics $(Cu,Ni)_6Sn_5$, which is more stable as hexagonal crystals. So, the orientation relationships between η-Cu_6Sn_5 and Cu are more important.

EXPERIMENTAL RESULT

1. The (111) Uni-Directional Cu

To make a preferential relationship between intermetallics and copper useful in packaging industry, the copper must be able to be electroplated. In that way, the single crystal copper is so far unpractical to be adopted. The (111) uni-directional Cu with nano-twins were first found by Li et al. and they also did lots of research about the mechanical and electrical properties.[17][18] In our experimental, we made several arrays of Cu pads by electroplating with some particular combinations of Cu seed layer and electroplating setups. With these configurations, we made an array of Cu pads with (111) uni-directional Cu. The diameter and thickness of copper pad are 100 μm and 20 μm respectively.

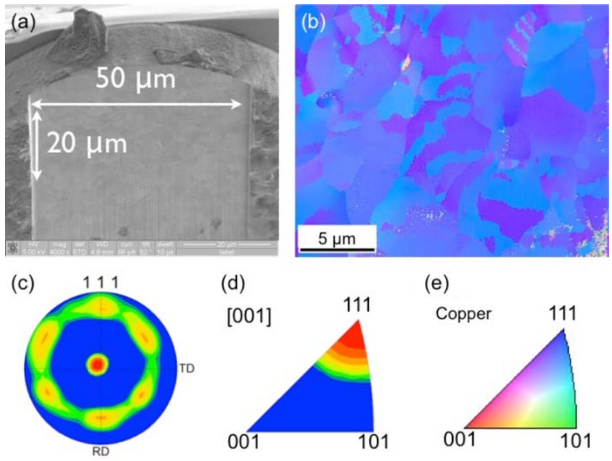

Figure 1. a) The plane-view of (111) uni-directional Cu Pads; **b)** the orientation image map, **c)** the (111) pole figure and **d)** the inversed pole figure of Cu pads; (e) the reference figure.

To examine the consistence of the orientations of copper, we created a flat surface on the copper pads by focused ion beam. The created area with length of 50 μm and width of 20 μm is shown in figure 1(a). By using EBSD, the colors of copper grains were all blue or blue purple in the orientation image map of figure 1(b). With the reference figure 1(e) about the orientation of copper, the orientations of copper on the pads were confirmed to be either (111) or close to (111). It means that the surface of copper is (111). Since the copper has a crystal structure of face-centered cubic, the direction of [111] is therefore normal to the surface. The grain size of electroplated copper is about 2 - 5 μm. The (111) pole figure of figure 1(c) proves that the pole is along the normal direction of surface. And by this figure, it is suggested that the (111) pole of Cu is not exactly normal to the surface. However, the angle difference between (111) pole of Cu and the normal direction of Cu surface is less than 10 degrees. Also by the inversed pole figure, the orientation was confirmed again.

In addition, a TEM sample was prepared by FIB. In figure 2(a), the bright field image was taken and the grain of copper was observed. The diffraction patterns of 3 adjacent grains were taken separately and then superimposed on each other in figure 2(b). It shows that these grains were all with a pole of (111) and only few rotating degrees exist between different grains. Although the Cu is still polycrystalline, the orientation is preferred to (111). And it is possible to electroplate (111) uni-directional Cu.

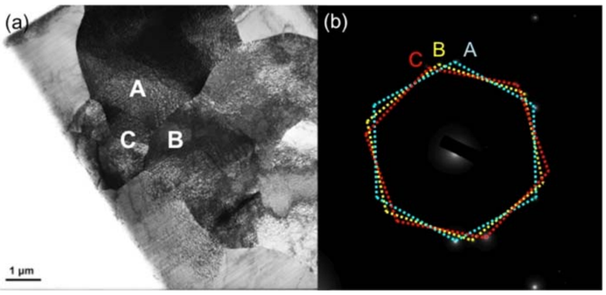

Figure 2. a) The TEM image of Cu pads from top-view; **b)** the diffraction patterns of three adjacent Cu grains.

The Preferential Orientation Relationship In Bump-Die Structure.

The SnAg2.3 was electroplated on (111) uni-directional Cu pad. The reflowing temperature was set to be 260 ^{o}C. After reflowing for 1 minute, the chip was carefully mounted by low-temperature epoxy. To show the cross-sectional area of single side bump, the sample was gridded and polished. The focused ion beam was adopted to perform a final cut. Since there were Cu, Cu_6Sn_5 and Sn coexisting, the advantage of adopting FIB is to make a cut precisely at the desired position and to a definite thickness. Also, by performing the FIB technique, the strain-free surface can be revealed for both 3 phases.

Figure 3(a) shows the cross-section of a bump die after final cut by focus ion beam. The void inside Cu pad was damaged during grinding and those inside Sn was because of the flux. The red rectangle area was carefully observed by EBSD. Figure 3(b), (c), (d) show the orientation image maps of Sn, Cu_6Sn_5 and Cu. The orientation map shows the orientation of these phases in the direction perpendicular to silicon chip. In other words, the orientation relationships along the direction of growth of these phases are shown in figures. And again the color of orientation image maps would represent the orientation of phases.

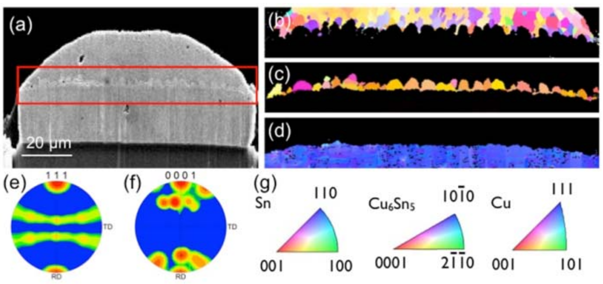

Figure 3. a) The cross-sectional area observed in bump die structure. The orientation image maps of **b)** Sn, **c)** Cu_6Sn_5 and **d)** uni-directional Cu. **e)** the (111) pole figure of Cu. **f)** the (0001) pole figure of η-Cu_6Sn_5; **g)** the reference figure.

As displayed in figure 3(d), the grain of Cu is columnar and the color of Cu is blue with some interlaced bands on it. Corresponding to figure 3(g), the orientations of (111) Cu was assured again. The interlaced bands are confirmed as nano-twins with only 5 - 20 nm of twin spacing. The grain size of intermetallics is about 8-μm widths and 2-μm height. Each scallop has different colors, indicating that each scallop is a single grain of Cu_6Sn_5. These intermetallics are all in the color of red and orange. It suggested that the intermetallic have certain preferred orientation on the (111) Cu pads. By reference of figure 3(g), the orientation of intermetallics is close to (0001). To assure this result, we examine the pole figure of (0001) of intermetallics and that of (111) Cu. In figure 3(e), the (111) pole figure of Cu showed the (111) pole was majorly align with the rolling direction of Cu. Combined with figure 3(f), the (0001) pole figure of Cu_6Sn_5, the (0001) pole were also along the rolling direction. As mentioned in section 3.1, [111] direction of Cu is not exactly normal to the surface, so the pole figure of both Cu and Cu_6Sn_5 showed some leaning behavior. The degree of leaning is few. With these results, the orientation relationship between (111) Cu and η-Cu_6Sn_5 can be clearly justified: $\{111\}_{Cu} \parallel \{0001\}_{Cu6Sn5}$. Since the Cu/Sn couple was reflowed at 260 ^{o}C for only 1 minute, the Cu_3Sn may form little. These orientation relationships are credible because the intermetallics contacted with Cu directly.

Effect of Reflowing Time On The Orientation Relationship

To obtain a general view on the orientation of every intermetallic on one Cu pad, the surface of intermetallic are revealed by grinding and polishing from top surface. Since the intermetallics in section 3.2 were too small and hard to be reached while grinded by human hands, the sample was further reflowed for 4 minutes more to make intermetallics larger.

Figure 4(a) shows the SEM image of Cu pad with Sn and Cu_6Sn_5 on it. The islands on the Cu pad were Cu_6Sn_5 formed during reflow. Between them are the residue tin phase. With the orientation image map of figure 4(b), the colors of intermetallics were red, orange and yellow. It should be noticed that some noisy signals were shown on the figure. These noises at center of the pad are mainly because of the residues left while polishing. And because we revealed the plan-view of intermetallic by grinding from the top of solder ball, the shape of hemisphere makes the peripheral area of pad bumpy. That also makes some noises around the pad.

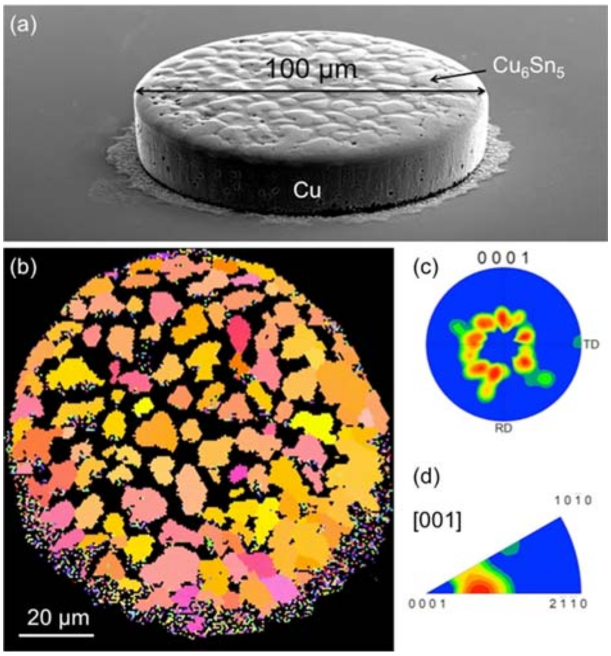

Figure 4. a) The SEM image from plane-view of Cu_6Sn_5; **b)** the orientation image map of Cu_6Sn_5 from top-view; **c)** the (0001) pole figure and **d)** the inversed pole figure of Cu_6Sn_5

There are something different from those reflowed for only 1 minute. First, more Cu_6Sn_5 grains appears in yellow in figure 4(b). It indicates that the orientation of intermetallics had been changed from (0001) toward (20). The (0001) pole was dispersed from the center of normal direction in figure 4(c). It also means that the (0001) plane of η-Cu_6Sn_5 were not parallel to the (111) plane of copper substrate. By the accumulated result of figure 4(d), the inversed pole figure showed that the major orientations of intermetallics have been changed. Many researches have already shown the morphology of Cu_6Sn_5 would change after reflowed at higher temperature or for longer time. The other intermetallics of Cu3Sn start to grow at the interface between copper and Cu_6Sn_5 then. The formation of Cu_3Sn would break the preferential growth relationship because the Cu_6Sn_5 would then grow on Cu_3Sn, rather than Cu.

The Preferential Orientation Relationship in a Solder Joint

The preferential relationship between Cu_6Sn_5 and Cu could be used in real packaging joints. The solder joints were fabricated by joining two bump-dies together. We flipped one chip with uni-directional Cu pads and SnAg2.3 and then stacked it on another one. The joints were then reflowed at 260 ^{o}C for 3 minutes in total to make the joints compact. The sample was then grinded and polished. And the focused ion beam was used to make the final cut.

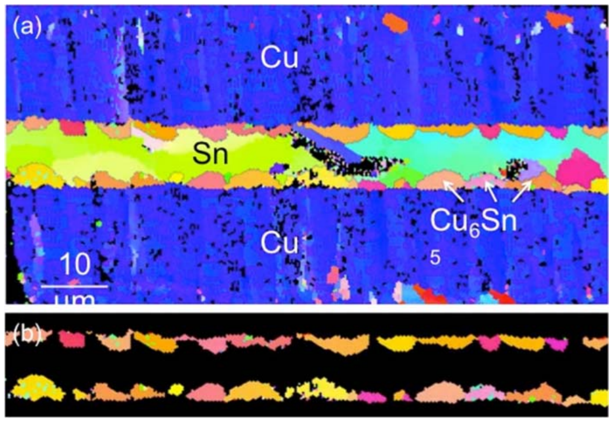

Figure 5. The orientation image maps of **a)**the solder joints reflowed at 260 ^{o}C for 3 minutes; **b)** the Cu_6Sn_5.

Figure 5(a) shows the orientation image maps of the joints. The Cu pad was blue, because it was a uni-directional structure from the bottom to the top. By the reference figure 3(g), it can be sure that the whole column was all (111)-oriented and with nano-twin on each grain. There were some grains showing different colors rather than blue on the bottom side. It might be a transition region from the seed-layer and the uni-directional Cu. The mechanism is not clear yet. The scallop-type Cu_6Sn_5 appeared in the color of red, orange and yellow. Figure 5(b) shows the layer of Cu_6Sn_5 separately. The middle part was remaining SnAg2.3. As noted in previous section, the orientation of Cu along the direction perpendicular to the silicon chip was (111) and that of Cu6Sn5 was close to (0001).

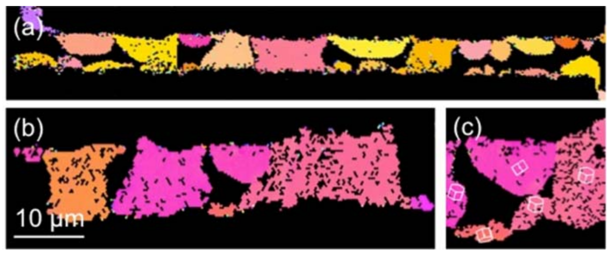

Figure 6. The orientation image maps of η-Cu_6Sn_5 after the solder joints were reflowed at 260 ^{o}C for **a)** 4 minutes and **b)** 5 minutes; **c)** the magnified image for figure 6(b).

As we reflowed the other joint for 4 minute, some of the intermetallics contacted each other and seemed to be merged together in figure 6(a). It should be noted that the unequal growth rate of Cu_6Sn_5 on each side of Cu pad. It is mainly because of the unequal Cu flux during reflowing. This phenomenon has been reported in our previous study [19]. And the orientation map of Cu_6Sn_5 in this figure shows that the two intermetallics became one single grain as soon as they were jointed. It could express some natural properties of Cu_6Sn_5. Although each grain has its own orientation, these grains would merge into one single grain as one reached another. Mind that the intermetallics were small after 3 minutes of reflowing. So they needed to grow first and then they can contact with each other. The reaction must be such fast that it can be finished in less than one minute at 260 ^{o}C.

The reflow time was further increased for 1 more minutes for other joints. The total reflow time was 5 minutes. The results are shown in figure 6(b). Most of the intermetallics were merge together. The orientations of these intermetallics were still close to (0001). By the magnified image of figure 6(c), the white hexagons represent the exact orientations of each -Cu_6Sn_5. As illustrated by this figure, the (0001) planes of hexagons were almost parallel to the Cu pads whether they were at the top or bottom chip. All the c-axis of hexagons lied along the direction perpendicular to the Cu pads. The two grains started to merge together, and their orientations seemed to be similar. However, the mechanism is still under research.

DISCUSSION

Coherence Between η-Cu_6Sn_5 and (111) Uni-Directional Cu

There have been lots of researches about the preferential growth of η'-Cu_6Sn_5 on Cu. The crystal structure of η'-Cu_6Sn_5 is monoclinic ($C\tilde{2}c$, a = 11.022 Å, b = 7.282 Å, c = 9.827 Å, β = 98.84o). However, in the introduction part, we have provided lots of study showing that the η-Cu_6Sn_5 would be mainly presented in solder joints. In in this study, we mainly focused on the preferential growth behavior between η-Cu_6Sn_5 (P63/mmc, a = 4.2032 Å, c = 5.1107 Å) and the (111) uni-directional Cu. The crystal structure of Cu are face-centered Cubic with a = b = c = 3.610 Å.

By our experimental results in section 3.2, the (0001) plane of η-Cu_6Sn_5 was parallel to (111) plane of Cu at the early stage of reflowing. After superimposing the Cu atoms of these two planes, we could barely found any directions that are of lower lattice mismatch through whole plane. So it is difficult to explain this coherent relationship by matching the Cu lattice. Nevertheless, in this study, although the Cu pads were made uni-directional and also the surface of Cu pad was totally (111)-planed, it was still a poly-crystalline structure. Figure 2(b) has already proven that there were rotating behaviors between adjacent copper grains. In this way, it is not a totally ordered arrangement of Cu atoms on the surface. Also, the grain size of Cu_6Sn_5 was larger than that of columnar Cu, indicating that the η-Cu_6Sn_5 must grow on several grain of Cu. So it is not possible to have a whole low lattice mismatch through entire area.

The spontaneous reaction between Cu and Sn makes the formation of Cu_6Sn_5. It is obvious that the total energy between Cu-Sn must be lower than Cu-Cu.[11] We should discuss the coherence between the Sn inside η-Cu_6Sn_5 and Cu. However, it's hard to achieve since Sn atoms are hard to be located in the hexagonal Cu_6Sn_5. Moreover, the tin atoms in the hexagonal Cu_6Sn_5 lie on the plane close $(2\bar{1}\bar{1}3)$. By now, we can only conclude that the (0001) plane of η-Cu_6Sn_5 must be parallel to (111) plane of uni-directional Cu due to its favorable lower energy state.

CONCLUSION

The uni-directional Cu with surface covered by (111) plane can be made by electroplating. The shape of Cu grain was columnar. The diameters of these columnar grains were 2 – 5 µm. After electroplating SnAg2.3 on the Cu pad and then reflowed at 260 oC, the η-Cu_6Sn_5s have shown a preferential growth relationship on the uni-directional Cu. At the early stage of reflowing, the orientations of Cu_6Sn_5 were preferred at (0001). As the time of reflow extended, the orientations of Cu_6Sn_5 would change to be preferred at $(2\bar{1}\bar{1}3)$. Since the uni-directional Cu was still poly-crystal metal, the coherence must be achieved by Cu-Sn bonding at the interface between Cu pads and the intermetallics. Electroplating parameters would affect the quality of uni-directional Cu and therefore affecting the preferential behavior of Cu_6Sn_5. With the technique of electroplating (111) uni-directional Cu, it is possible to control the orientations of intermetallics in the solder joints.

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