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Dramatic morphological change of scallop-type Cu_6Sn_5 formed on (001) single crystal copper in reaction between molten SnPb solder and Cu

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Wetting reaction between molten Sn-based solders and Cu produces scallop-type Cu_6Sn_5. In the present wetting study, a (001) single crystal Cu is used as substrate and a dramatic change in the morphology of Cu_6Sn_5 is observed: instead of scallop type, the authors observed a rooftop-type Cu_6Sn_5 grains, elongated along two preferred orientation directions. This was confirmed by electron beam backscattered diffraction and white beam synchrotron x-ray microdiffraction. The results indicate that the nucleation, growth, and ripening behavior of Cu_6Sn_5 on single crystal substrate can be quite different from the conventional case of wetting on randomly oriented polycrystalline Cu substrates. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2761840]

Because of the wide application of solder, especially Pb-free, in consumer electronic products, the study of the wetting reaction of molten solder on Cu has attracted considerable interests.[1–9] Metallic bonding in solder joints is achieved through the formation of Cu–Sn intermetallic compounds of Cu_6Sn_5 and Cu_3Sn at the Cu/solder interface. The Cu_6Sn_5 has a unique scallop-type morphology, and the Cu_3Sn has a layer-type morphology. The latter forms between the former and the copper substrate. Figure 1 is a top-view scanning electron microscopy (SEM) image of Cu_6Sn_5 scallops on a polycrystalline Cu substrate after the remaining solder was etched away. The scallops appear rounded and there are deep channels between them.[10] The crystal structure of the low temperature phase η-Cu_6Sn_5 is monoclinic.[11] Our recent study using white beam synchrotron micro-x-ray diffraction showed that the formation of Cu_6Sn_5 on Cu has a set of preferred orientation relationships.[12] There are six types of preferred orientation relationships between the two phases, and in all cases the $[\bar{1}01]$ direction of Cu_6Sn_5 is parallel to the $[110]$ direction of Cu. The six orientation relationships are as follows:

$$(010)_{Cu_6Sn_5} \parallel (001)_{Cu} \text{ and } [\bar{1}01]_{Cu_6Sn_5} \parallel [110]_{Cu}, \quad (1)$$

$$(343)_{Cu_6Sn_5} \parallel (001)_{Cu} \text{ and } [\bar{1}01]_{Cu_6Sn_5} \parallel [110]_{Cu}, \quad (2)$$

$$(\bar{3}4\bar{3})_{Cu_6Sn_5} \parallel (001)_{Cu} \text{ and } [\bar{1}01]_{Cu_6Sn_5} \parallel [110]_{Cu}, \quad (3)$$

$$(101)_{Cu_6Sn_5} \parallel (001)_{Cu} \text{ and } [\bar{1}01]_{Cu_6Sn_5} \parallel [110]_{Cu}, \quad (4)$$

$$(141)_{Cu_6Sn_5} \parallel (001)_{Cu} \text{ and } [\bar{1}01]_{Cu_6Sn_5} \parallel [110]_{Cu}, \quad (5)$$

$$(\bar{1}4\bar{1})_{Cu_6Sn_5} \parallel (001)_{Cu} \text{ and } [\bar{1}01]_{Cu_6Sn_5} \parallel [110]_{Cu}. \quad (6)$$

This is because a low misfit of 0.24% between the Cu atoms can be achieved along the $[\bar{1}01]_{Cu_6Sn_5}$ direction and the $[110]_{Cu}$ direction. The above relationships can be classified into two groups based on the strong pseudohexagonal symmetry around Cu atom in Cu_6Sn_5 when projected along the $[\bar{1}01]$ direction (Fig. 2). Crystal planes in Eqs. (1)–(3) correspond to edges of the Cu hexagon (group 1) and Eqs. (4)–(6) correspond to diagonals of the Cu hexagon (group 2).

Since the low misfit directions between Cu_6Sn_5 and Cu lie on the (001) plane of Cu, it is of interest to investigate the behavior of Cu_6Sn_5 formed on (001) single crystal Cu. Single crystal Cu substrates were purchased from Goodfellow and they have a diameter of 1 cm and a thickness of 0.25 cm. The surface was carefully polished, cleaned, and etched before being immersed in flux. Wetting samples were prepared by reacting small beads (~0.5 mg) of 55Sn45Pb (in wt %) solder with the (001) single crystal copper in flux at 200 °C with different reaction times ranging from 30 s to

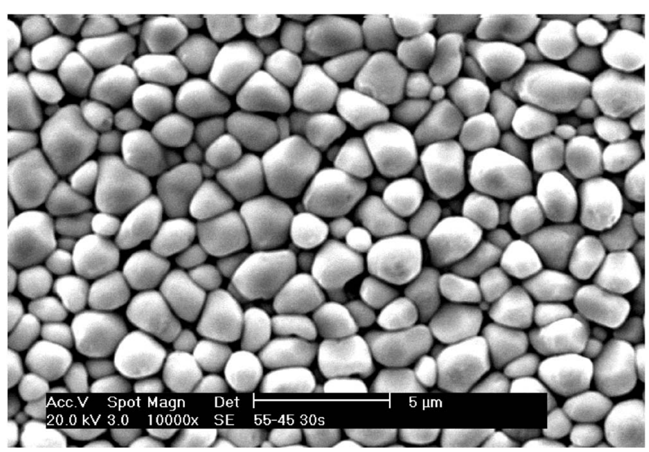

FIG. 1. Top-view scanning electron microscopy (SEM) image of Cu_6Sn_5 scallop-type grains on a Cu.

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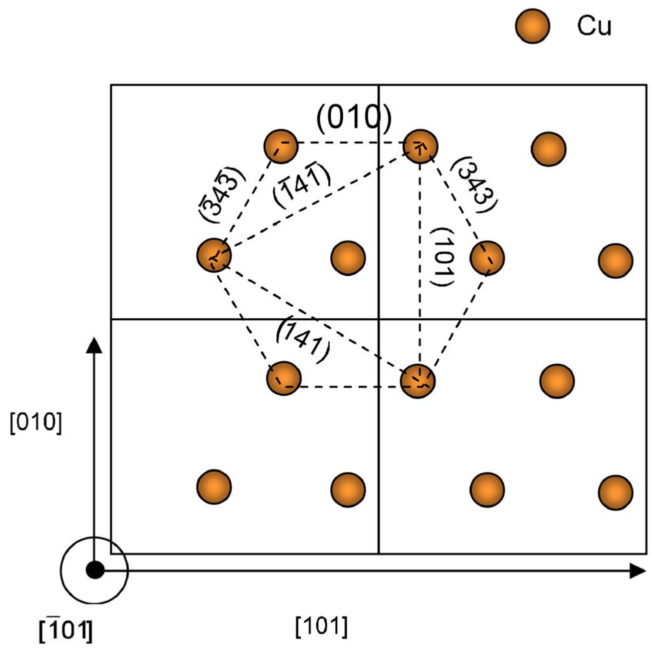

FIG. 2. (Color online) Structure of Cu_6Sn_5 projected from the $[\bar{1}01]$ direction.

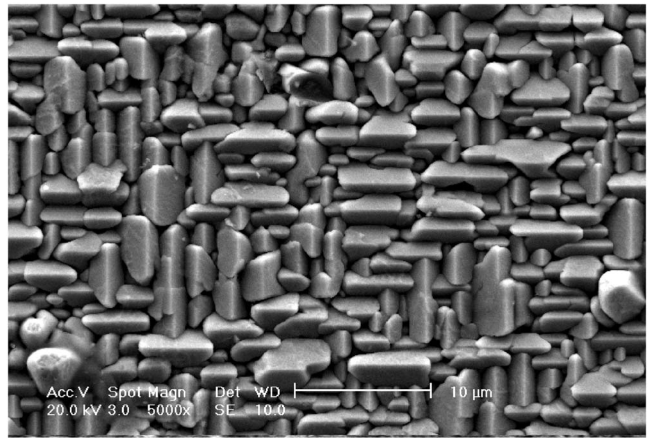

FIG. 3. Morphology of rooftop-type Cu_6Sn_5 formed on (001) Cu.

4 min. The molten solder forms a cap on the Cu upon wetting. After a given time of reaction, samples were quenched to room temperature by dipping them into acetone. After solidification, the unreacted solder was removed by mechanical polishing, followed by selective chemical etching in order to expose the interfacial Cu_6Sn_5 scallops.

Figure 3 shows the morphology of Cu_6Sn_5 formed on (001) Cu substrate. Elongated and rooftop-type Cu_6Sn_5 grains were distributed on the entire surface. The elongations go along two perpendicular directions. We hypothesized that Cu_6Sn_5 should elongate along the low misfit direction in order to minimize interfacial energy with Cu. Electron beam backscattered diffraction (EBSD) analysis was performed to verify the elongation direction. Because of the high roughness of the sample (see Fig. 3), performing EBSD mapping is an issue. However, since each grain is a single crystal, a single Kikuchi pattern coming from a selected spot of an elongated grain is enough to determine its orientation. Kikuchi patterns were obtained separately from the (001) single crystal Cu substrate and Cu_6Sn_5 grains, and we found that Cu_6Sn_5 grains are elongated along two different ⟨110⟩ directions. Figure 4(a) is a Kikuchi pattern from the Cu substrate. Figures 4(b) and 4(c) are the respective Kikuchi patterns of an elongated grain and of another grain elongated perpendicularly to the first one. The analysis indicated that the (001) plane of Cu is perpendicular to the surface normal, and that the ⟨110⟩ directions are nearly parallel (within 4°) to the laboratory x and y axes. The Kikuchi pattern shown in Fig. 4(b) indicated that the $[\bar{1}01]$ direction of Cu_6Sn_5 is parallel to the [110] direction of Cu. One of the "group 2" planes was parallel to the (001) plane of Cu. For the Kikuchi pattern in Fig. 4(c) the $[\bar{1}01]$ direction of Cu_6Sn_5 was perpendicular to the $[\bar{1}01]$ direction of the other Cu_6Sn_5 and was parallel to the $[\bar{1}10]$ direction of Cu. Again, one of the group 2 planes was parallel to the (001) plane of Cu. In summary, from EBSD, it was confirmed that Cu_6Sn_5 grains were elongated along their $[\bar{1}01]$ direction, parallel to the ⟨110⟩ directions of the single crystal Cu.

To obtain statistical data of the orientation distribution, synchrotron white beam micro-x-ray diffraction was performed. The micro-x-ray diffraction experiments were conducted on beamline 7.3.3 at the Advanced Light Source in Lawrence Berkeley National Laboratory.[13] The sample with 4 min reaction time was scanned under a micron size x-ray beam. At each step of scan, a Laue pattern was collected using an x-ray charge coupled device detector. The micro-x-ray beam can penetrate through the Cu_6Sn_5 and reach the Cu. Therefore, each Laue pattern is a composite of diffraction spots from Cu_6Sn_5 and Cu. The strongest Laue spots came from the Cu due to its larger grain size and thus contribution to the signal. 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.

Figure 5(a) is a histogram of the angles between the [001] direction of Cu and the $[\bar{1}01]$ direction of Cu_6Sn_5, after the 4 min reaction at 200 °C. An area of 25×30 μm^2 was scanned with a step size of 0.5 μm in both x and y directions. There is a strong peak at 90°, indicating that the $[\bar{1}01]$ directions of most of the Cu_6Sn_5 scallops are lying on the (001) plane of Cu. Figure 5(b) is a histogram of the angles between the [010] direction of Cu and the $[\bar{1}01]$ direction of Cu_6Sn_5. There are two peaks: one peak is at 45° and the other is at 135°. It indicates that the $[\bar{1}01]$ directions of most of the Cu_6Sn_5 grains are parallel to the [110] or $[\bar{1}10]$ direc-

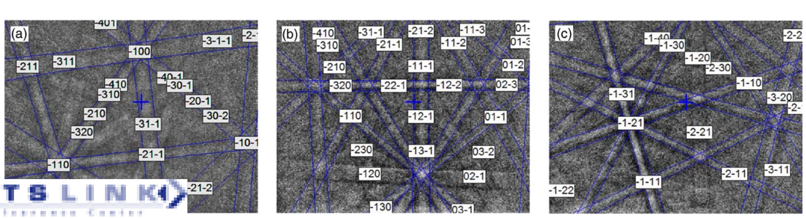

FIG. 4. (Color online) Kikuchi patterns from the EBSD analysis. (a) Kikuchi pattern from the Cu substrate. (b) and (c) are Kikuchi patterns of a Cu_6Sn_5 grain and another grain perpendicular to the first scallop, respectively.

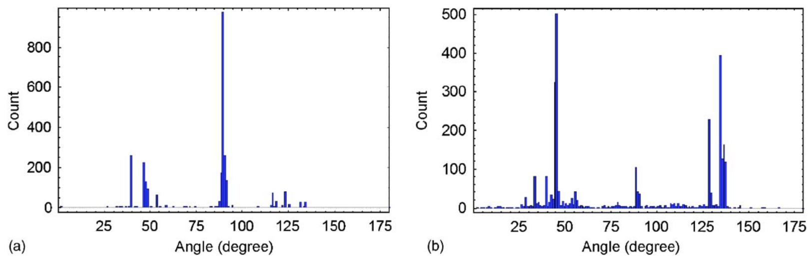

FIG. 5. (Color online) (a) Histogram of angle between the [001] direction of Cu and the [$\bar{1}$01] direction of Cu_6Sn_5, after 4 min reflow at 200 °C. (b) Histogram of angle between the [010] direction of Cu and the [$\bar{1}$01] direction of Cu_6Sn_5.

tion of Cu. The above results confirm the existence of a strong preferred orientation relationship between Cu_6Sn_5 and (001) Cu on the bases of EBSD and synchrotron micro-x-ray diffraction.

The dramatic change in morphology of Cu_6Sn_5 suggests that nucleation, growth, and ripening mechanisms of the elongated Cu_6Sn_5 can be different from the rounded scallop-type Cu_6Sn_5. Figure 6 is a SEM image of Cu_6Sn_5 scallops on (001) Cu after 30 s reflow. Clearly Cu_6Sn_5 already has very strong texture. The strong texture of Cu_6Sn_5 indicates that nucleation of the Cu_6Sn_5 is not random but rather oriented when (001) Cu is used as a substrate. Soldering is a reactive wetting. When molten solder spreads on copper, dissolution of copper substrate takes place at the interface.[14] If the orientation of substrate copper is a high-index (*hkl*) plane, more copper will be required to be dissolved away in order to expose the low misfit ⟨110⟩ crystal directions and {001} planes of Cu. Therefore, the nucleation of Cu_6Sn_5 will not have enough time to nucleate with the preferred orientation if the Cu substrate is a high-index plane, and random nucleation will become dominant. However, if the substrate is a (001) single crystal Cu, Cu_6Sn_5 can directly nucleate on the low misfit direction and plane. As a result, Cu_6Sn_5 grains will have an oriented nucleation and textured growth.

FIG. 6. (Color online) SEM image of Cu_6Sn_5 grains on (001) Cu, after 30 s reflow.

Due to the strong orientation relationship between the elongated Cu_6Sn_5 and (001) Cu, as shown in Fig. 3, we expect a lower interfacial energy between them than that between the round scallop-type Cu_6Sn_5 and polycrystalline Cu, as shown in Fig. 1. Indeed when we etched the Cu_6Sn_5, we found that the elongated Cu_6Sn_5 on (001) has lasted much longer in the etchant. The lower interfacial energy will improve the impact fracture toughness of the interface.

In summary, a dramatic change in morphology of Cu_6Sn_5 was found when Sn-based solder was reacted with a (001) single crystal Cu. Grains of Cu_6Sn_5 become elongated along the two low misfit directions between Cu_6Sn_5 and Cu. The relationship between the morphology and the crystallographic orientation was verified by EBSD study. Statistical distribution data obtained by white beam synchrotron micro-x-ray diffraction agreed with the EBSD study. The Cu_6Sn_5 already showed strong texture at 30 s of wetting reaction, indicating that the grains tend to nucleate with texture.

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[1]H. K. Kim, K. N. Tu, and P. A. Totta, Appl. Phys. Lett. **68**, 2204 (1996).
[2]K. N. Tu and K. Zeng, Mater. Sci. Eng., R. **34**, 1 (2001).
[3]S. K. Kang and S. Purushothaman, J. Electron. Mater. **27**, 1199 (1998).
[4]K. H. Prakash and T. Sritharan, Acta Mater. **49**, 2481 (2001).
[5]Y. G. Lee and J. G. Duh, J. Mater. Sci. **10**, 33 (1999).
[6]G. Ghosh, J. Mater. Res. **19**, 1439 (2004).
[7]D. R. Frear, J. W. Jang, J. K. Lin, and C. Zhang, JOM **53**, 28 (2001).
[8]J. Y. Tsai, Y. C. Hu, C. M. Tsai, and C. R. Kao, J. Electron. Mater. **32**, 1203 (2003).
[9]K. S. Kim, S. H. Huh, and K. Suganuma, J. Alloys Compd. **352**, 226 (2003).
[10]K. N. Tu and K. Zeng, Mater. Sci. Eng., R. **34**, 1 (2001).
[11]A. K. Larsson, L. Stenberg, and S. Lidin, Z. Kristallogr. **210**, 832 (1995).
[12]J. O. Suh, Ph.D. thesis, UCLA, 2006.
[13]N. Tamura, R. S. Celestre, A. A. MacDowell, H. A. Padmore, R. Spolenak, B. C. Valek, N. M. Chang, A. Manceau, and J. R. Patel, Rev. Sci. Instrum. **73**, 1369 (2002).
[14]W. J. Boettinger, C. A. Handwerker, and U. R. Kattner, in *The Mechanics of Solder Alloy Wetting and Spreading*, edited by F. G. Yost, F. M. Hosking, and D. R. Frear (Van Nostrand Reinhold, New York, 1993), pp. 130–140.