A study on the orientation relationship between the scallop-type Cu_6Sn_5 grains and (011) Cu substrate using electron backscattered diffraction

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(Received 4 August 2009; accepted 28 October 2009; published online 4 December 2009)

The wetting reaction between molten Sn and (011) Cu single crystal was investigated. Based on the electron backscattered diffraction technique, the preferential orientation relationships between the scallop-type Cu_6Sn_5 grains and (011) Cu single crystals were detected. The strong texture of Cu_6Sn_5 grains was formed on the normal direction although the Sn/(011) Cu couple was aged at 170 °C for 40 days. This indicates that the Cu_6Sn_5 grains do not desultorily form on the (011) Cu substrate for these scallop-type Cu_6Sn_5 grains. © *2009 American Institute of Physics*. [doi:10.1063/1.3266144]

I. INTRODUCTION

Solder joints are ubiquitous: it has been commonly utilized to join copper wires in electronics packaging field.[1,2] The essential process in solder joining is that the molten solders would react with solid substrates (such as Ag, Cu, Ni) to form several intermetallic compound (IMC) layers (a strong metallic bonding) at the solder/substrate interfaces.[1–4] In this case, a great deal of documents is always concerned with the interfacial reactions between the solder and the substrate.[1–5] But the Cu–Sn system is one of the most essential reactions among these interfacial reactions. The previous studies have reported that the typical scallop-type Cu_6Sn_5 grains would form on the poly-Cu for the Cu–Sn system at the initial state, and then the Cu_3Sn layer would form at the Cu_6Sn_5/Cu interface after the subsequent annealing at the temperatures above 70 °C.[1]

Recently, some new findings indicate that the Cu_6Sn_5 grains with strong texture and regular morphology would form on the (001) and (111) Cu single crystal substrates.[6–8] The regular prism-type Cu_6Sn_5 grains formed on (001) and (111) Cu single crystals are elongated either along two perpendicular directions or along three preferential directions having an angle of 60° between each other. In addition, they also found that there is a preferred orientation relationship between Ag_3Sn and Ag single crystal in reaction between molten Sn and Ag.[9] The morphologies, orientation relationships, and evolution of Cu_6Sn_5 grains formed on the (001) and (111) Cu single crystals have been carefully investigated in the previous researches.[6–8] These results confirmed such an orientation relationship, i.e., $[\bar{2}01]_{Cu_6Sn_5} \| [\bar{1}10]_{(001)Cu}$. Obviously, on the (011) Cu single crystal, there are two perpendicular directions along $[\bar{1}10]_{(001)Cu}$ and $[110]_{(001)Cu}$, while there are three directions with an angle of 60° between each other along $[1\bar{2}1]_{(111)Cu}$, $[\bar{2}11]_{(111)Cu}$, and $[11\bar{2}]_{(111)Cu}$ on (111) Cu. This is why there are two kinds of regular prism-type Cu_6Sn_5 grains formed on (001) and (111) Cu single crystals.[6–8] However, it should be pointed out that $[\bar{1}10]_{(001)Cu}$ is consistent with $[\bar{1}10]_{(110)Cu}$, as a result, the formed Cu_6Sn_5 grains on the (011) Cu single crystal substrate were found to be still scallop-type rather than regular morphology.[8] This gives rise to an interesting question: whether there is still any special orientation relationship or not when the scallop-type Cu_6Sn_5 grains form on the (011) Cu single crystal substrate. In this study, the pure Sn/(011) Cu single crystal couple was employed to further decipher the question above with the help of electron backscattered diffraction (EBSD) technique.

II. EXPERIMENT

In this study, Sn foil was employed as a solder. (011) and (001) Cu single crystal thin plates with a dimension of $10 \times 10 \times 3$ mm^3 were used as substrates. These Cu single crystal samples were ground with 800#, 1000#, 2000# SiC paper and then carefully polished with the 2.5, 1.5, and 0.5 μm polishing pastes. Wetting samples (Sn/Cu) and sandwich samples (Cu/Sn/Cu) were prepared at 260 °C, and were then cooled in air to room temperature. The joint samples were deeply etched with the 5%HCl+3%HNO_3 +CH_3OH (vt%) etchant solution to remove the excess Sn phase so that the reactive phases can be well exposed, but sandwich samples were spark-cut to form some thin plates with a dimension of $10 \times 10 \times 0.6$ mm^3. These thin sandwiches were ground with 800#, 1000#, 2000# SiC papers and then carefully polished with the 2.5 and 1.0 μm polishing pastes. Finally, they were prepared to the samples for EBSD mapping. The morphology of the IMCs was observed by the LEO Supra 35 field emission scanning electron microscope (SEM). Orientation maps were then collected on the selected area using a SEM equipped with a fully automatic EBSD analysis system (Oxford Instruments-HKL Channel). During the EBSD acquisition, a step size of 0.6 μm was chosen.

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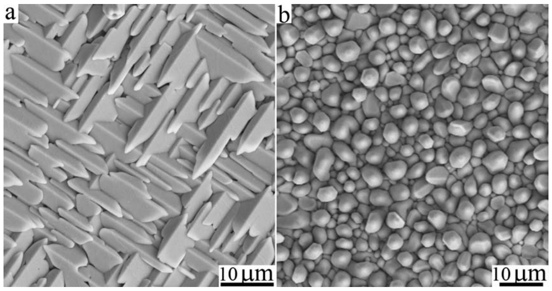

FIG. 1. Typical morphologies of Cu_6Sn_5 grains formed on (a) (001) Cu, (b) (011) Cu single crystals at 260 °C.

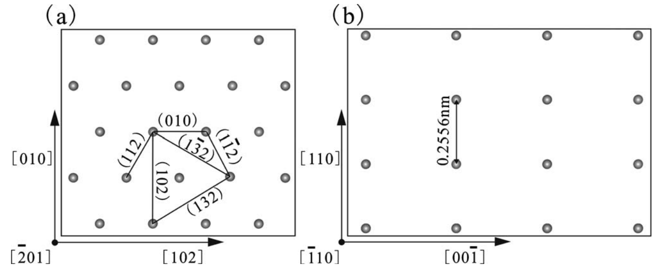

FIG. 3. (a) Structure of Cu_6Sn_5 cell projected from $[\bar{2}01]$ direction; (b) structure of Cu cell projected from $[\bar{1}10]$ direction.

III. RESULT AND DISCUSSION

Figure 1 shows the top-view SEM images of Cu_6Sn_5 grains formed on (001) and (011) Cu single crystals after reaction with Sn at 260 °C, respectively. It is obviously found that the Cu_6Sn_5 grains display regular prism-type along two perpendicular directions, and distribute homogenously on the whole (001) Cu surface,[7,8] as displayed in Fig. 1(a). However, the Cu_6Sn_5 grains display typical scallop-type and homogenously distribute on the whole (011) Cu surface, as displayed in Fig. 1(b), which is similar to the previous observations on polycrystalline Cu substrates.[6–10] Previous results have confirmed that there is a preferential orientation relationship between the elongated Cu_6Sn_5 grains and (001), (111) Cu single crystals,[8] but it seems that there should be no preferential orientation relationship between the Cu_6Sn_5 grains and (011) Cu single crystal because the Cu_6Sn_5 grains also display scallop-type. However, the special morphology is not the unique reason to determine the orientation relationship between the Cu_6Sn_5 grains and Cu single crystal. There may still be some orientation relationships between the scallop-type Cu_6Sn_5 grains and the (011) Cu single crystal because of the special atom array on (011) plane. EBSD and transmission electron microscopy (TEM) are good methods to establish the orientation relationships between IMC grains and the Cu single crystals.[6,8,11] But TEM only concentrates on examination of two grains, while EBSD is able to focus on a large area, including many grains.

Figure 2(a) shows the phase maps using different colors besides the Sn/(011) Cu interface. In Fig. 2(a), the red, green, and gray regions represent Cu, Cu_6Sn_5, and Sn phases, respectively. Obviously, a lot of Cu_6Sn_5 grains form at the Sn/(011) Cu interface except for two Cu_6Sn_5 grains in Sn phase, as displayed by the green region in Fig. 2(a). Through careful observations, the two Cu_6Sn_5 grains were confirmed to form at the Sn grains boundaries, as indicated by the white pane in Fig. 2(a), which is similar to the previous observations.[12] The orientation maps are shown in Fig. 2(b). For the Sn phase, there are only two colors to describe the orientation of Sn, indicating that there are only two kinds of orientations for pure Sn in the selected area. While it can be found that the Cu_6Sn_5 grains mainly have three orientations at the Sn/(011) Cu interface, as displayed by the red, white, and black arrows in Fig. 2(b). It is indicated that there should be some preferential orientation relationship between the scallop-type Cu_6Sn_5 grains and (011) Cu single crystal.

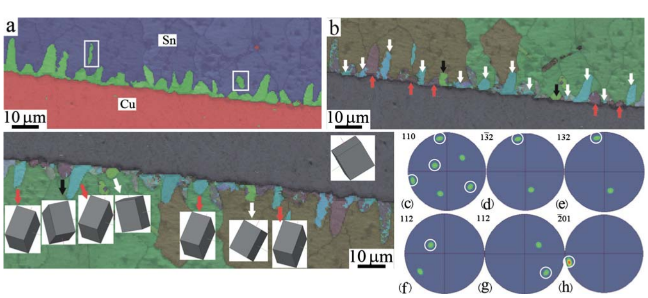

FIG. 2. (Color online) EBSD maps for the Sn/(011) Cu couple: (a) phase map, (b) orientation map; the pole figures (c) Cu single crystal, [(d)–(h)] Cu_6Sn_5 cell.

To further investigate the orientation relationship between the scallop-type Cu_6Sn_5 grains and (011) Cu single crystals, the orientation and pole figures of Cu_6Sn_5 grains and Cu substrate should be obtained. Figures 2(c)–2(h) shows the Cu_6Sn_5 unit cell and the Cu unit cell indicating the grain orientation by EBSD analysis. Three kinds of Cu_6Sn_5 unit cells were detected, as demonstrated by the red, black, and white arrows in Fig. 2. In this case, it can be concluded that there are also some orientation relationships between the (011) Cu substrate and the Cu_6Sn_5 grains, as illustrated in Figs. 2(c)–2(h). Figure 2(c) presents the pole figures of (011) Cu, Figs. 2(d)–2(h) show the pole figures of Cu_6Sn_5 unit cell. According to these pole figures, four kinds of orientation relationships between the Cu_6Sn_5 grains and (011) Cu single crystal can be identified as below

$$\{110\}_{Cu} \parallel (132)_{Cu_6Sn_5}, \quad \{110\}_{Cu} \parallel (1\bar{3}2)_{Cu_6Sn_5},$$

$$\{110\}_{Cu} \parallel (112)_{Cu_6Sn_5}, \quad \{110\}_{Cu} \parallel (\bar{2}01)_{Cu_6Sn_5}.$$

It is indicated that the regular atom array of (011) Cu plays an important role in these orientation relationships between the Cu and the Cu_6Sn_5 grains. Figure 3(a) shows the arrays of Cu atoms in Cu_6Sn_5 along $[\bar{2}01]$ direction. Figure 3(b) presents the arrays of Cu atoms in Cu single crystal along $[\bar{1}10]$ direction. It is known that the plane space of Cu_6Sn_5 lattice is 0.25478 nm along $[\bar{2}01]$ direction based on the η'-Cu_6Sn_5 phase with a monoclinic structure (C_2/c $a=1.1022$ nm, $b=0.7282$ nm, $c=0.9827$ nm, $\beta=98.84°$).[13] The Cu atom space is 0.25560 nm along [110] direction on (011) plane of Cu with face-centered cubic structure (Fm3m, $a=0.25560$ nm), as illustrated in Fig. 3(b). Therefore, based on the difference in the atom spaces above, the misfit (α) of Cu atoms between $[\bar{2}01]$ direction of Cu_6Sn_5 and [110] directions of Cu can be calculated as

$$\alpha = (0.255\,60 - 0.254\,78)/0.254\,78 = 0.32\%. \qquad (1)$$

This indicates that there is the extremely low misfit of Cu atoms between Cu and Cu_6Sn_5 (only 0.32%). It is well known that the interfacial energy will reduce by decreasing the misfit between the IMC and the substrate.[7] If there is a low misfit direction on the (011) Cu substrate, Cu_6Sn_5 would directly nucleate on the low misfit directions and plane after the liquid-state reaction in order to minimize the interfacial energy, leading to the formation of the strong texture in Cu_6Sn_5 grains. For the requirement of minimizing the interfacial energy, the $[\bar{2}01]$ direction of Cu_6Sn_5 would be preferentially formed on the (011) Cu single crystal. According to the crystallographic relations illustrated in Fig. 3(a), the Cu atoms plane in Cu_6Sn_5 along $[\bar{2}01]$ direction would contain six involving planes, i.e., (132), $(1\bar{3}2)$, (112), (010), $(1\bar{1}2)$, (102), respectively. Therefore, the six possible orientation relationships between the Cu_6Sn_5 grains and (011) Cu should be obtained as below

$$\{110\}_{Cu} \parallel (132)_{Cu_6Sn_5} \quad \text{and} \quad [110]_{Cu} \parallel [\bar{2}01],$$

$$\{110\}_{Cu} \parallel (1\bar{3}2)_{Cu_6Sn_5} \quad \text{and} \quad [110]_{Cu} \parallel [\bar{2}01],$$

$$\{110\}_{Cu} \parallel (112)_{Cu_6Sn_5} \quad \text{and} \quad [110]_{Cu} \parallel [\bar{2}01],$$

$$\{110\}_{Cu} \parallel (010)_{Cu_6Sn_5} \quad \text{and} \quad [110]_{Cu} \parallel [\bar{2}01],$$

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

$$\{110\}_{Cu} \parallel (102)_{Cu_6Sn_5} \quad \text{and} \quad [110]_{Cu} \parallel [\bar{2}01].$$

Obviously, based on Fig. 3, the following relationship was not obtained:

$$\{110\}_{Cu} \parallel (\bar{2}01)_{Cu_6Sn_5}.$$

However, it has indeed been gotten in our experimental results. Why? It should be explained based on the crystal structure. As we know, for Cu, {110} planes contain six planes, i.e., (110), (101), (011), $(\bar{1}10)$, $(\bar{1}01)$, $(0\bar{1}1)$. Through careful calculation, the dihedral angles between each two planes have three possible values: 60°, 90°, and 120°, respectively. Based on Fig. 3(a), it is obviously found that the dihedral angle between $(\bar{2}01)$ and (132) planes is 90°. Therefore, when the (132) plane of Cu_6Sn_5 is parallel to one of the {110} planes of Cu, $(\bar{2}01)$ plane of Cu_6Sn_5 may be parallel to one of the {110} planes of Cu. This is why we can get the orientation relationship of $\{110\}_{Cu} \parallel (\bar{2}01)_{Cu_6Sn_5}$ through the pole figures, as displayed in Fig. 2.

In order to further investigate the texture evolution of Cu_6Sn_5 grains during the solid aging procedure, a Sn/(011) Cu couple was aged at 170 °C, and was then etched. At last, the orientation data of each Cu_6Sn_5 grain was collected by EBSD. Figure 4 is the inverse pole figure (IPF) of scallop-type Cu_6Sn_5 on (011) Cu aged at 170 °C for forty days. Notice that the IPF contains about 1000 grains, which makes the texture analysis reliable. Obviously, the Cu_3Sn layer that consumed some Cu_6Sn_5 would form at the Cu_6Sn_5/(011)Cu interface after the aging procedure, but the formation of Cu_3Sn layer did not affect the texture of Cu_6Sn_5. As shown in Fig. 4, the Cu_6Sn_5 grains still show a relatively strong texture in the normal direction (ND) IPF, indicating that the Cu_6Sn_5 grains do not desultorily form on the (011) Cu substrate even if the Sn/(011) Cu couple was aged at 170 °C for 40 days. Also, the rolling direction and transverse direction IPFs show certain weak texture compared with the ND direction.

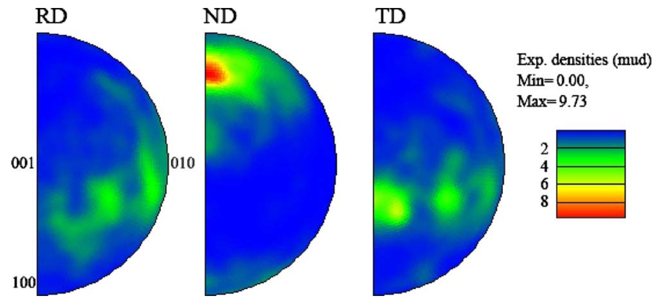

FIG. 4. (Color online) IPF of the Cu_6Sn_5 grains.

In summary, the morphology of the Cu_6Sn_5 grains was typically scallop-type when Sn was reacted with a (011) Cu single crystal. In terms of the EBSD method, it is confirmed that there are still some preferential orientations with low index between Cu_6Sn_5 grains and (011) Cu single crystal. The Cu_6Sn_5 grains still exhibit rather strong texture for the Sn/(011) Cu couple aged at 170 °C for forty days, indicating that the Cu_6Sn_5 grains also tend to grow with special crystallographic relationship because of the preferential nucleation in the initial state.

ACKNOWLEDGMENTS

The authors would like to thank W. Gao, H. H. Su, and J. O. Suh for sample preparation, SEM observations, crystallographic analysis, and stimulating discussion. This work was financially supported by the National Basic Research Program of China under Grant Nos. 2004CB619306 and 2010CB631006, and the National Outstanding Young Scientist Foundation under Grant No. 50625103.

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