Preferential growth and orientation relationship of Ag_3Sn grains formed between molten Sn and (001) Ag single crystal

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The current study shows that there is a preferred orientation relationship between Ag_3Sn and Ag in reaction between molten Sn and Ag. Due to the preferred orientation relationship, the morphology of Ag_3Sn grains formed on (001) Ag single crystal is different from those formed on (011), (358) single crystal Ag, and polycrystalline Ag Facet scallop-type Ag_3Sn grains formed irregularly on (011), (358) single crystal Ag, and polycrystalline Ag; whereas the regular Ag_3Sn grains with parallel edges grew on (001) Ag single crystal, and they were elongated along two perpendicular directions. The orientation relationship between Ag_3Sn grains and (001) Ag single crystal was determined using electron backscattered diffraction. The preferential growth of regular Ag_3Sn grains with parallel edges formed on (001) Ag single crystal can be attributed to their minimum misfit.

I. INTRODUCTION

Sn-Pb solders would be replaced by the lead-free solders in electronic packaging field because of the toxic nature of Pb.[1,2] At present, Sn-Ag, Sn-Cu, Sn-Zn, and Sn-Bi alloys are the most promising lead-solders, which are potential candidates of lead-free solders in electronic packaging field in the future.[2] These soldering joints provide the electrical connection and the mechanical bonding. But intermetallic compounds (IMCs) always form at the interface between the solders and substrates during the reflow procedure.[2–5] Therefore, the solders as well as the morphologies of the formed IMCs should play important roles in the electrical connection and the mechanical properties. However, nearly all of the investigations only focus on the morphology of IMCs formed on polycrystalline substrates, mainly on Cu substrate so far.[6]

More recently, new findings show that the Cu_6Sn_5 grains with strong texture and special morphology formed on the (001) and (111) Cu single-crystal substrates.[7–9] The morphologies, orientation relationships, and evolution of Cu_6Sn_5 grains formed between molten Sn and Cu single crystals have been carefully investigated in these research studies.[7–9] It is indicated that the nucleation, growth, and ripening of Cu_6Sn_5 grains on Cu single crystal are different from those on polycrystalline Cu. However, in electronic packaging field, in addition to the Cu and Ni substrates, Ag is also a good substrate due to its good wettability, antioxidation, and electronic and thermal conductivity.[10–13] This process raises an interesting question: whether the special morphology and the preferential orientation of Ag_3Sn IMC can appear on Ag single-crystal substrate with low index. In this article, to avoid the effect of other elements, the pure Sn/(001) Ag single-crystal couple was used as an example to decipher the question above.

II. EXPERIMENTAL PROCEDURE

In this study, Ag single crystal was used as a substrate and Sn foil was used as a solder. First, Ag single crystal with dimensions of $150 \times 20 \times 10\ mm^3$ was grown by the Bridgman method in a horizontal furnace.[14] The orientation of the Ag single-crystal plate was determined by the electron backscattered diffraction (EBSD) method. Next, some pieces of Ag thin plates with dimensions of $10 \times 10 \times 1\ mm^3$ were spark-cut from the grown Ag single-crystal plate, ensuring that the wetting surfaces are parallel to (001), (011), and (358) planes. Polycrystalline Ag thin plate was also used as substrate for a comparison test. All of the Ag plates were ground successively with 800, 1000, 2000 grade SiC paper and then carefully polished with 2.5- and 1.0-μm polishing pastes. Wetting samples were prepared by reacting Sn foil (~70-μm thick) with these Ag thin plates at 260 °C for different periods. After that, all of the 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 morphology of the Ag_3Sn grains could be fully exposed. LEO super35 scanning electron microscope (SEM; Carl Zeiss, Oberkochen, Germany) was used to detect the morphology and orientation of the Ag_3Sn grains formed on (001) Ag single crystal with the help of EBSD.

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III. RESULTS AND DISCUSSION

Figure 1(a) is a top-view SEM image of Ag_3Sn grains formed on polycrystalline Ag. The morphology of Ag_3Sn grains is irregular faceted scallops. Cu_6Sn_5 faceted scallops have also been detected at the interface of Cu/Sn-Pb.[15] Figure 1(b) shows the SEM image of Ag_3Sn grains on the (001) Ag single crystal reflowed at 260 °C for 30 s. There are many regular Ag_3Sn grains with parallel edges, which are significantly different from the morphology of Ag_3Sn grains formed on polycrystalline Ag. The elongations of Ag_3Sn grains go along two perpendicular directions, which are similar to the Cu_6Sn_5 grains formed on (001) Cu single crystal.[7,9] The morphology of Ag_3Sn grains with parallel edges can still be detected when the reflow time increases to 60 s, as shown in Fig. 1(c). Compared with the samples aged for 30 s, these Ag_3Sn grains are more compact when the couple was reflowed for 60 s. Figures 1(d) and 1(e) show the morphology of Ag_3Sn grains formed on (011) and (358) Ag single crystal reflowed at 260 °C, respectively. These Ag_3Sn grains are irregular faceted prisms, which are different from those on (001) Ag single crystal.

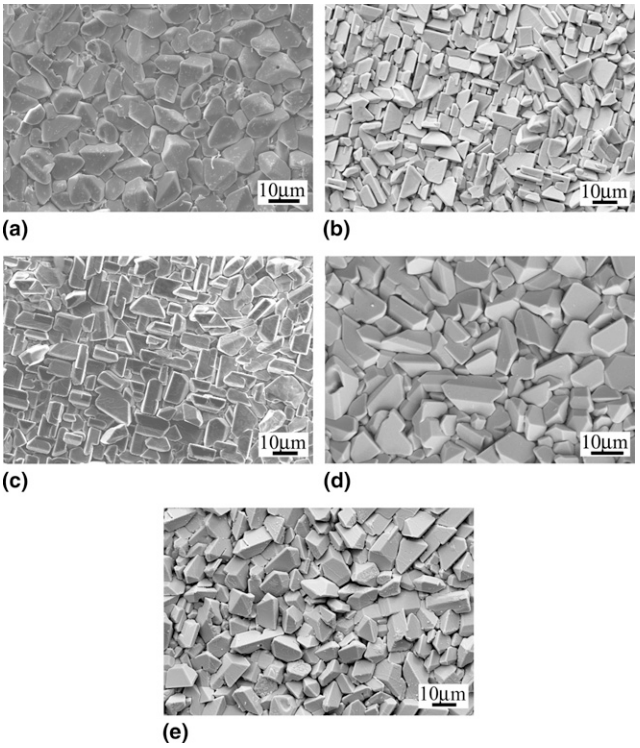

FIG. 1. SEM images of Ag_3Sn grains formed on (a) polycrystalline Ag; (b, c) (001) Ag single crystal reflowed at 260 °C for 30 and 60 s, respectively; (d) (011) Ag single crystal reflowed at 260 °C for 30 s; (e) (358) Ag single crystal reflowed at 260 °C for 30 s.

In addition, on the (001) Ag single crystal, these Ag_3Sn grains with parallel straight edges also display a preferential orientation relationship with Ag single-crystal substrate as the Cu_6Sn_5 grains formed on (001) and (111) Cu single crystals.[7–9] Once the orientation of these Ag_3Sn grains with parallel edges was determined, the orientation relationship between (001) Ag single crystal and Ag_3Sn grains can be established. Although EBSD mapping is always used to determine the orientations of crystals, it is hard to perform on an as-etched rough surface. However, the Kikuchi bands of the local Ag_3Sn grain can be obtained one by one by EBSD because their surfaces are smooth enough for EBSD mapping. Fairhurst et al.[16] have reported that the crystal structure of Ag_3Sn was orthorhombic (*Pmmn*, a = 5.9689, b = 4.78024, c = 5.18439Å). Based on the structure and Kikuchi bands of Ag_3Sn, the orientation relationship between Ag single crystal and Ag_3Sn grains can be established.

Figure 2(a) gives the Kikuchi bands of (001) Ag single crystal. The Kikuchi bands of the Ag_3Sn grains with

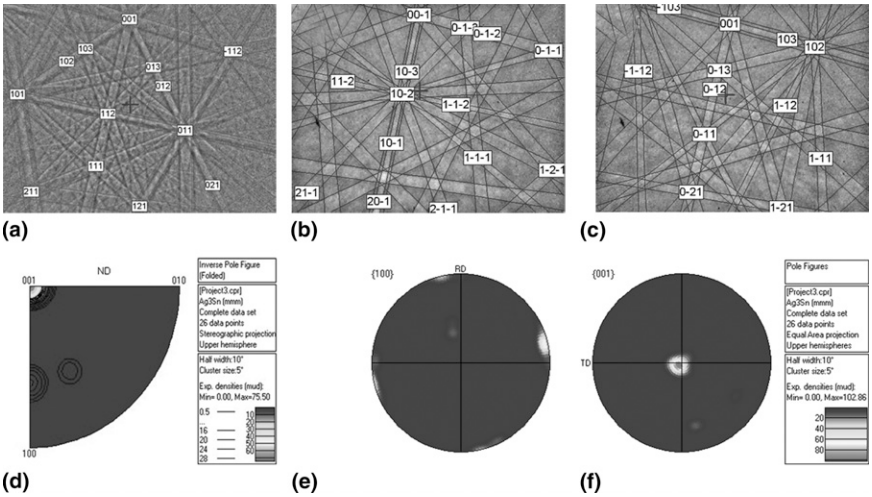

FIG. 2. (a) Kikuchi bands of (001) Ag single-crystal substrate; (b, c) Kikuchi bands of Ag_3Sn grains along two perpendicular directions on (001) Ag single crystal; (d)–(f) normal direction inverse pole figure, {100} pole figure, and {001} pole figure for 26 indexed grains, respectively.

two perpendicular elongation directions are shown in Figs. 2(b) and 2(c). Further analysis indicates that the crystallographic planes of the Ag_3Sn grains elongated along two perpendicular directions are all the (001). To confirm the orientation of Ag_3Sn grain, many Ag_3Sn grains with parallel edges were detected and their orientation distribution is shown in Fig. 2(d). Figures 2(e) and 2(f) show the {100} pole figure and {001} pole figure for one Ag_3Sn grain. These pole figures indicate that the Ag_3Sn grains have strong (001) texture on (001) Ag single crystal. For the Ag_3Sn grains formed on (011) and (358) Ag single crystal, they also show prism morphology with regular facets, but their distribution seems to be at random. As a result, their orientation relationship was not investigated.

As mentioned above, the Ag_3Sn grains not only display special morphology, but also form a strong texture feature on (001) Ag single-crystal substrate. However, such special morphology and the texture of Ag_3Sn grains were not observed on polycrystalline Ag substrates. It is assumed that the interfacial energy must play a crucial role in the nucleation and growth of the Ag_3Sn grains.[7,9] To minimize the interfacial energy between Ag and Ag_3Sn during the reflow procedure, the Ag_3Sn grains would elongate along the lowest misfit directions. Compared with polycrystalline Ag surface, there exists a low misfit direction on the (001) Ag single-crystal surface. Figure 3(a) shows the lattice structure of Ag single crystal along [001] direction. The Ag atom space is 0.2889 nm along [110] or $[\bar{1}10]$ direction. Figure 3(b) shows the lattice structure of Ag_3Sn grain along [100] direction. According to the structure and the lattice constant of Ag_3Sn,[16] the distance of two adjacent Ag atoms was calculated as 0.2984 nm along [100] direction. Then, the misfit of Ag atoms (α_{Ag}) between the [100] direction of Ag_3Sn grain and the [110] or $[\bar{1}10]$ direction of Ag single crystal was calculated as follows:

$$\alpha_{Ag} = (0.2984 - 0.2889)/0.2984 = 3.18\% \quad . \qquad (1)$$

It is obvious that the misfit of Ag atoms at the interface between Ag and Ag_3Sn is rather low. Compared with other orientation directions of Ag single crystal, the Ag_3Sn grains would preferentially nucleate along the [110] or $[\bar{1}10]$ direction of Ag single crystal to decrease the interfacial energy. In addition, the [110] direction is perpendicular to the $[\bar{1}10]$ direction in Ag single crystal. This result is why the Ag_3Sn grains formed on (001) Ag single crystals were elongated along two perpendicular directions, as illustrated in Fig. 1. According to the analysis above, the orientation relationships between Ag and Ag_3Sn are suggested to be as follows:

$$[100]_{Ag3Sn}||[\bar{1}10]_{(001)Ag}, [100]_{Ag3Sn}||[110]_{(001)Ag}, \quad (001)_{Ag3Sn}||(001)_{Ag} \quad .$$

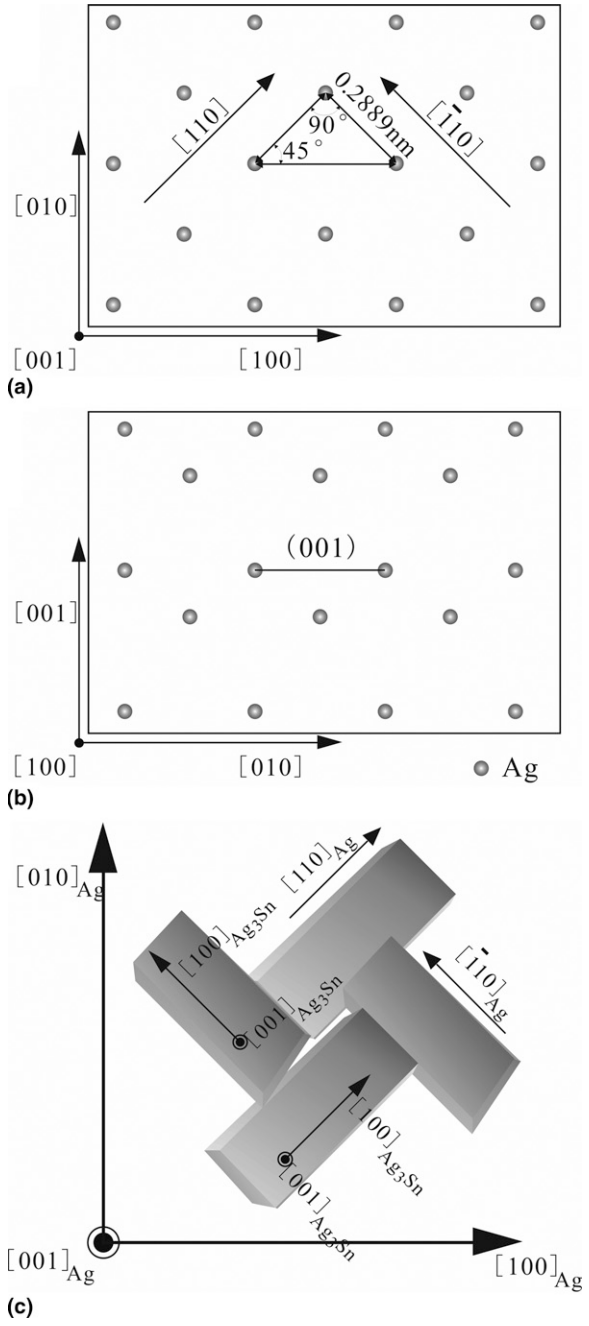

FIG. 3. (a) Illustration of atom array of Ag single crystal along [001] direction; (b) illustration of atom array of Ag_3Sn grain along [100] direction; (c) schematic diagram of morphology and orientations of Ag_3Sn grains formed on (001) Ag single crystal.

To further confirm the orientation relationship between Ag_3Sn grains and (001) Ag single crystal, the cross-section of their interfaces was cut by focus ion beam (FIB) technique, as displayed in Fig. 4. Through analyzing the 3-D model given by the EBSD software, the following can be obtained: $[100]_{Ag3Sn}||[\bar{1}10]_{(001)Ag}$, which is consistent with the orientation relationships

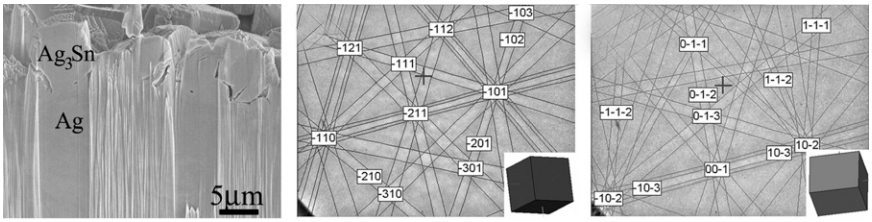

FIG. 4. (a) Cross-section of interface cut by FIB; (b, c) Kikuchi bands and 3-D models of the marked Ag and Ag_3Sn grains, respectively.

described above. This process indicates that on (001) and (111) Cu as well as on (001) Ag, the formed IMCs often display special morphology and orientation relationship with the single-crystal substrates.

IV. CONCLUSION

The morphology and orientation relationship of Ag_3Sn formed on (001), (011), (358) Ag single crystal, and polycrystalline Ag are different. On the (001) Ag single crystal, the regular Ag_3Sn grains with parallel edges go along two perpendicular directions, whereas the facet scallop-type Ag_3Sn grains formed on (011), (358) Ag single crystal and polycrystalline Ag. In addition, it was determined that there is a special orientation relationship between Ag_3Sn grains and (001) Ag single crystal using EBSD and FIB techniques. Combined with the morphologies, orientation relationships, and evolution of Cu_6Sn_5 grains formed on the Cu single-crystal substrates with different orientations,[7,9] the IMC prefers to grow along the [110] and $[\bar{1}10]$ low misfit directions on the special single-crystal substrate and then forms an IMC layer with strong texture, which might affect the interfacial mechanical properties of the solder joints. However, a special texture is not likely for IMC formed on (011), (358) Ag single crystal.

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