In Situ Heating Transmission Electron Microscopy Observation of Nanoeutectic Lamellar Structure in Sn–Ag–Cu Alloy on Au Under-Bump Metallization

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Abstract: We investigated the microstructural evolution of Sn96.4Ag2.8Cu0.8 solder through in situ heating transmission electron microscopy observations. As-soldered bump consisted of seven layers, containing the nanoeutectic lamella structure of AuSn and Au5Sn phases, and the polygonal grains of AuSn2 and AuSn4, on Au-plated Cu bond pads. Here, we found that there are two nanoeutectic lamellar layers with lamella spacing of 40 and 250 nm. By in situ heating above 140 °C, the nanoeutectic lamella of AuSn and Au5Sn was decomposed with structural degradation by sphering and coarsening processes of the lamellar interface. At the third layer neighboring to the lamella layer, on the other hand, Au5Sn particles with a zig-zag shape in AuSn matrix became spherical and were finally dissipated in order to minimize the interface energy between two phases. In the other layers except both lamella layers, polycrystal grains of AuSn2 and AuSn4 grew by normal grain growth during in situ heating. The high interface energy of nanoeutectic lamella and polygonal nanograins, which are formed by rapid solidification, acted as a principal driving force on the microstructural change during the in situ heating.

Key words: in situ heating, Sn–Ag–Cu solder, UBM, microstructure, TEM, STEM

INTRODUCTION

Eutectic and near-eutectic solders containing Sn and Pb had been frequently used in the past, because of their low cost, low melting point, and superior mechanical properties (Kim & Tu, 1996; Tu & Zeng, 2001). However, since the use of all hazardous substances in electronic devices was prohibited by Restriction of Certain Hazardous Substances Directive announced in 2006, lead-free Sn-based solder alloys have been commonly developed in packaging materials of electronic devices (Abtew & Selvaduray, 2000; Kim et al., 2003; Ho et al., 2007; Tang et al., 2008; Chinnam et al., 2011).

Under-bump metallization (UBM) soldering technique is recently applied to the integrated circuits of next-generation semiconductors. In our previous study, the Sn–Ag–Cu UBM solder exhibits the microstructural complexity owing to the rapid quenching rate resulting from small feature size under few tens of micrometers, including various crystal phases, nanoeutectic dendrite structure, and those complex multilayers (Bali et al., 2008). Therefore, it is a critical issue to investigate thermal degradation behaviors of the UBM solder, which can crucially affect the mechanical failure and electrical properties at high temperature (Amagai et al., 2002; Kang et al., 2002; Deng et al., 2005; Keller et al., 2011). However, research results on the mechanisms of microstructural change and phase transition induced by thermal aging of solder have not been reported so far, because it is practically very hard to fabricate a transmission electron microscopy (TEM) sample of the micro-sized UBM bump by conventional TEM sampling methods. In this study, we investigated thermally activated kinetic behavior at the interface between the Sn–Ag–Cu solder and Au plate in the UBM solder through in situ heating observations of a TEM sample prepared by focused ion beam (FIB) milling technique.

MATERIALS AND METHODS

Lead-free Sn96.4Ag2.8Cu0.8 solder was melted at ~270 °C using a diode laser beam with the wavelength of 1,084 nm. The molten solder was then impinged onto the Au (~2-μm-thick)-plated Cu bond pads under N2 atmosphere at room temperature. The solidification time was ~20 ms, thus resulting in a rapid quenching rate of the order of 105 K/s. A TEM sample was fabricated by FIB ion milling, and then was mounted on a TEM heating holder (Gatan 625) for the
in situ heating TEM and scanning TEM (STEM) observations up to 180°C. The phase and composition in each layer of the UBM solder was determined by convergent beam electron diffraction characterizations and energy-dispersive spectroscopy measurements in TEM nanoprobe mode, respectively.

**Results and Discussion**

Figure 1 shows a scanning electron microscopy (SEM) image of a packaged UBM solder (Fig. 1a), and the cross-sectional SEM (Fig. 1b) and TEM (Fig. 1c) images observed after FIB ion milling. The Figures 1b and 1c have one-to-one correspondence in the microstructure. In the UBM solder solidified at 220°C, which is a solidus temperature of the UBM solder, various eutectic phases, which can be observed in binary Au–Sn alloy, were formed along the rapid heat flux. As shown in Figures 1b and 1c, the solder is distinguished by seven layers (A–G), which was thermodynamically interpreted in our previous work (Bali et al., 2008). The six layers (A–F) can be observed in Figure 1c, but Layer G was unfortunately milled away during TEM sampling by FIB. Through our previous result (Bali et al., 2008) and more detailed TEM observations in this study, we can precisely identify the crystallographic information of each layer. Layers A and B consist of fine and coarse lamellar structures, respectively, with the eutectic phases of Au₅Sn and AuSn. Although Layer C has the same eutectic phases of Au₅Sn and AuSn as Layers A and B, it has a normal casting structure rather than a lamellar structure. In the Layers D and E, polycrystals and equiaxed grains are developed at each layer with different phases of orthorhombic AuSn₂ and AuSn₄. The AuSn₄ phase in Layer E shows a different growth behavior in Layer F, where the AuSn₄ phase protrudes into Sn matrix in Layer G. In the final Layer G, the AuSn₄ grains are isolated in Sn matrix. The characteristics of microstructural change and phase transition observed during in situ heating of as-soldering were summarized in Table 1, including in situ TEM results at 140 and 180°C. Unlike the SEM image (Fig. 1b), the Layer A of Figures 1c, 2, and 3 consists of an interesting nanoeutectic structure.

Figure 2 shows the overall microstructure change of UBM solder during the in situ heating of an FIB-milled TEM sample, which is the first report on thermal behavior of UBM solder with elevated temperature. Up to in situ heating of 120°C, all layers of the UBM solder (Fig. 2a) are

**Table 1.** The Characteristics of Phase Transition and Microstructural Change of Layers A–G Revealed through In Situ Heating Transmission Electron Microscopy (TEM) Observations of the Under-Bump Metallization (UBM) Solder in Figure 1c.

<table>
<thead>
<tr>
<th>Layer</th>
<th>100°C</th>
<th>140°C</th>
<th>180°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Nanosize eutectic dendrite of Au₅Sn and AuSn</td>
<td>Dissociation of lamellar wall for reducing interface energy</td>
<td>Dissociation of nanosize lamellar wall</td>
</tr>
<tr>
<td>B</td>
<td>Normal eutectic dendrite of Au₅Sn and AuSn</td>
<td>Dissolution of Au₅Sn nanoparticles in AuSn</td>
<td>Complete dissolution of Au₅Sn nanoparticles in AuSn</td>
</tr>
<tr>
<td>C</td>
<td>AuSn including isolated Au₅Sn with zig-zag shape</td>
<td>Growth of isolated Au₅Sn by Oswald ripening</td>
<td>AuSn₂ polycrystalline growth into AuSn single crystal</td>
</tr>
<tr>
<td>D</td>
<td>Equiaxed AuSn₂</td>
<td></td>
<td>Elongated AuSn₂</td>
</tr>
<tr>
<td>E</td>
<td>Equiaxed AuSn₄</td>
<td></td>
<td>Equiaxed AuSn₄</td>
</tr>
<tr>
<td>F</td>
<td>Coarse dendritic structure with ~1-μm-thick dendrites of AuSn₄ growing into Sn matrix</td>
<td></td>
<td>Growth of AuSn₄ grain</td>
</tr>
<tr>
<td>G</td>
<td>Isolated AuSn₄ in Sn matrix</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. a: A scanning electron microscopy (SEM) image of a packaged under-bump metallization solder, (b) a cross-sectional SEM image, and (c) a transmission electron microscopy image observed after focused ion beam ion milling, which is corresponding to (b) in position and magnification.

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Figure 2. Microstructural change of under-bump metallization solder acquired during in situ heating at (a) 100°C, (b) 140°C, and (c) 180°C.

Figure 3. Transmission electron microscopy images of Layers A–C observed at higher magnification during in situ heating at (a) 100°C, (b) 140°C, and (c) 180°C.
scarcely changed from as-solder. A notable small change begins at the nanoeutectic structure of Layer A at 140°C (Fig. 2b), but unfortunately it is not observed in the Figure 2b owing to a low magnification (see Fig. 3b for more detail). On the other hand, microstructural change of other layers is negligible. At 180°C, as shown in Figure 2c, all layers show remarkable change. The nanolamellar structure is collapsed and the interfaces between Layers B, C, and D migrate. The detailed observations on the phase and microstructural evolution of each layer during in situ heating will be explained in Figures 3 and 4 through TEM and STEM observation.

Figure 3 shows Layers A–C observed at higher TEM magnification during in situ heating. Layers A, B, and C consist of two binary phases of AuSn and Au5Sn with different structure, showing a gray contrast for AuSn and a dark contrast for Au5Sn. At 100°C (Fig. 3a), Layers A and B consist of a nanoeutectic lamellar structure of AuSn and Au5Sn, but Layer A has extremely small interlamellar spacing of 40 nm, compared with thick interlamellar spacing of 250 nm for Layer B. In Layer B, interestingly, the AuSn columnar contains Au5Sn nanoparticles distributed like small dark spots, which may be formed from an Au-rich area trapped locally in AuSn owing to rapid quenching. Layer C shows a eutectic structure having Au5Sn islands of zig-zag shape in the AuSn phase. The unique eutectic structure emerges when the contents of Au in AuSn during solidification are low, so that lamellar structure cannot be formed and thereby Au5Sn nanoparticles should be precipitated. The zig-zag shape indicates that crystallographically specific orientation relationship exists between matrix AuSn and precipitated Au5Sn (Bali et al., 2008). At 140°C, the nanoeutectic lamellar structure of the Layer A begins to collapse as shown in a rectangle of Fig. 3b. Even though the lamellar structure of Layer B seems to be more stable than that of Layer A at the same temperature, Au5Sn nanoparticles in lamellar AuSn phase disappear by dissociation of Au5Sn and diffusion of the dissociated Au atoms into lamellar walls. On the other hand, Au5Sn nanoparticles in Layer C lose the zig-zag shape by the decomposition and diffusion mechanism same as Au5Sn in AuSn of Layer B (indicated by the circle in Fig. 3b). The dissipation mechanism of Au5Sn in Layers B and C is very similar to Oswald ripening phenomena.

At 180°C, the lamellar structure of the Layer A is changed to round shape, of which grains consist of two phases of Au5Sn and AuSn. Interestingly, it seems to harmonize with Layer B by expanding interlamellar spacing. Layer B shows the lamellar structure with a very clear contrast owing to the complete dissipation of Au5Sn islands in AuSn. A principal driving force leading to the microstructural change of Layers A–C with increasing temperature was due
to the high interface energy between Au5Sn and AuSn. Therefore, the nanoeutectic lamellar structure might be decomposed at the lowest temperature, because many interfaces formed at the nanoeutectic lamellar structure provide microstructure instability of UBM solder.

Figure 4 shows the magnified TEM images of Layers E and F in Fig. 2, which is rotated by about 90°. Up to an in situ heating temperature of 140°C, Layers D–F maintained the initial structure without the microstructural change that occurred in Layers A–C. At 180°C, equiaxed AuSn4 grains in Layer E slightly grew by normal grain growth mechanism, whereas the elongated AuSn4 grains in Sn in Layer F changed to equiaxed shape without phase change, as shown by arrows in Figures 4c and 4d, showing a high-angle annular dark-field image of Figure 4c. Here, the equiaxed single phases of AuSn2 and AuSn4 in Layers D and E are more stable than the two phases of Layer F, including the elongated AuSn4 grains in Sn matrix. Unfortunately, in situ heating TEM experiments above 180°C were not performed in this study, because the TEM sample fabricated by FIB was bent at high temperature. In this work, the structural stability of each layer depended on the interface area between grain boundaries or phase boundaries.

**Conclusion**

We investigated the phase transition and thermal stability of Sn96.4Ag2.8Cu0.8 solder manufactured by laser process through in situ heating. The microstructure change of UBM solder up to 120°C was scarcely changed. As-soldered bump consisted of seven layers on an Au-plated Cu bond pad, sequentially containing the nanoeutectic lamella structure of AuSn and Au5Sn phases, the equiaxed grains of AuSn2 and AuSn4, and the elongated AuSn4 grains in Sn matrix. Above an in situ heating temperature of 140°C, the lamellar structure of Layer A with the highest interface energy was first decomposed, and had thick lamellar spacing. The AuSn nanoparticles and zig-zag-shaped AuSn islands in AuSn at Layers B and C were thermally decomposed and disappeared by the complete diffusion of the excess Au toward interfaces. At 180°C, the equiaxed AuSn2 and AuSn4 grains in Layers D and E showed normal grain growth behavior, whereas the elongated AuSn4 grains in Sn matrix in Layer F gradually changed to equiaxed shape. In this way, the specific UBM solder manufactured by rapid quenching process showed the various thermal behaviors by thermal activation process to minimize the interface energy at each layer during in situ heating.

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