Effect of Laser Irradiation on Generation and Growth of Whiskers in Tin-Electroplated Film*

Yutaka Mitooka1, Koji Murakami1, Makoto Hino1, Masao Takamizawa2 and Jun Takada3

1Industrial Technology Research Institute of Okayama Prefectural Government, Okayama 701-1296, Japan
2OM Sango Co. Ltd., Okayama 700-0971, Japan
3Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan

In order to suppress generation and growth of whiskers, the effect of laser irradiation on tin-electroplated film on copper was studied by scanning electron microscopy and X-ray diffraction method. In the case of as-plated film, whiskers were generated on the electroplated tin film of 1 μm thickness within 432 ks. Residual stress of this film and the number of whiskers increased with the amount of copper-tin intermetallic compounds (Cu5Sn5) which developed between the plated film and the copper substrate. On the other hand, in electroplated tin film subjected to diode laser of 300 W for 100 to 1000 ms, no whiskers were formed even after 10 Ms. Residual stress of tin after laser irradiation was tensile at first, then, the stress did not change appreciably after 2.6 Ms. Uniform layer of Cu5Sn5 was formed immediately after laser irradiation, and the morphology showed no meaningful change even after 10 Ms. Whiskers are thought to be suppressed by covering the interface between tin and copper with layer of Cu5Sn5 and by reducing nonuniformity of stress field. [doi:10.2320/matertrans.M2009132]

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1. Introduction

Electroplated films of tin-lead alloy have been widely used as surface treatment for terminals in electronic equipment for its good wettablity with solder. However, lead-free process must be urgently established since the use of lead is strictly banned by RoHS (Restriction of Hazardous Substances) directives. Pure tin is the most preferable1) from the viewpoints of low environmental load, low cost and less consumption of natural resources. In this case, whiskers which easily grow on tin films must be suppressed in order to avoid short circuits and resulting malfunctions.2)

The present authors have conducted a research on the mechanism of whisker growth on tin electroplated films3,4) and on the behavior of lead in tin-lead films.5) According to the previous reports, generation and growth of whiskers are considered to be due to nonuniformity of residual stress caused by copper-tin intermetallic compound (Cu5Sn5) which preferably grows on the grain boundaries of tin. In the case of the tin-lead film on copper substrate and the tin film on nickel substrate, uniform layer of intermetallic compound develop at the interface between the plated film and substrate immediately after deposition. This mode of change in microstructure which reduces nonuniformity in the system is considered to successfully suppress growth of whiskers.

In this research, heat treatment by laser irradiation was conducted to obtain the above uniform microstructure in the system of electroplated film of tin on copper substrate. Development of copper-tin intermetallic compound and changes in residual stress of the tin film after laser irradiation were evaluated, examining the correspondence to the growth of whiskers.

Table 1 Electroplating conditions.

<table>
<thead>
<tr>
<th>Bath</th>
<th>Alkanol sulfonic acid (Ishihara Chemical Co., Ltd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>AS-S15 (133 kg/m3-solution)</td>
</tr>
<tr>
<td>Acid</td>
<td>MS-A (100 kg/m3-solution)</td>
</tr>
<tr>
<td>Additive</td>
<td>HS-5 (30 × 10−3 kg/m2-solution)</td>
</tr>
<tr>
<td>Thickness</td>
<td>1 μm</td>
</tr>
<tr>
<td>Current density</td>
<td>5 × 102 A/m2</td>
</tr>
<tr>
<td>Anode</td>
<td>Rolled Sheet of tin for Hull cell test (Yamamoto-MS Co., Tokyo)</td>
</tr>
<tr>
<td>Temperature</td>
<td>298 K</td>
</tr>
</tbody>
</table>

2. Experimental

Electroplating of tin (1 μm) on rolled sheet of copper (1 300 μm) was conducted under conditions of Table 1. In the following sentences, electroplated film of tin is expressed as ‘plated film’ unless otherwise mentioned. Diode laser irradiation was carried out the electroplated tin film of 1 μm thickness. The specimens were heat-treated by diode laser (Laser Line Co., Ltd. LDF600-1000, wavelength 808 nm, power 300 W) was carried out whose irradiation time was 100, 300, 500 or 1000 ms (Table 2).

The plated surfaces during laser irradiation were observed using a high-speed video camera. In the following sentences, the specimen without laser irradiation is expressed as ‘as-plated’, and that with laser irradiation as ‘100 ms’, ‘300 ms’, ‘500 ms’ or ‘1000 ms’ according to irradiation time.

Appearance of the plated surfaces was optically observed, and the two-dimensional surface shape was measured using a non-contact scanning white light interferometer (Zygo New View 5032). A focused ion beam was used for observation of copper-tin intermetallic compounds which developed at the interface between plated films and substrate. A microtome

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was used in the sample preparation for cross-sectional observation and analysis, where rough sectioning was performed by glass knife, followed by sectioning with diamond knife (blade angle 45°, final feed 50 nm, sectioning speed 0.1 mm/s).

A field emission electron probe microanalyzer was used for observation of generation and growth of whiskers on plated films. A microfocus X-ray diffractometer with two-dimensional detector was used for measuring residual stress of plated films. Strain tensor was calculated by measuring the distortion of diffraction intensities in reciprocal space, then, stress tensor was evaluated6–9 by setting Young’s modulus and Poisson ratio as $E = 41.4$ GPa and $\nu = 0.3$, respectively. The diffraction peak of $(321)_{\text{Sn}}$ ($\theta = 105.109$ deg.), which showed the weakest texture, was used for the above calculation.

3. Experimental Results and Discussion

3.1 Formation of compounds by laser irradiation

Figure 1 shows optical images of the plated surfaces after laser irradiation. The laser-irradiated areas showed changes in color which increased with irradiation time. In the cases of 500 and 1000 ms, the central parts in the color-changed areas were smooth as to exhibit metallic luster. The high-speed video showed that the above color-changed areas were formed by melting of the tin films during laser irradiation. In addition to melting, evaporation of the plated films was observed in the cases of 500 and 1000 ms. Here, oxidation of surface by laser irradiation was negligible from the viewpoint of packaging, since wettability of the laser-irradiated area with solder was almost the same as that of as-deposited surface.

Figure 2 shows the two-dimensional shape of the plated surfaces measured using a non-contact scanning white light interferometer. The averaged roughness Ra was $\sim 1$ μm in the case of the as-plated surface, which corresponds to the grain size of tin. In the case of 100 ms, the laser-irradiated surface became partly smooth, and the other area was almost the same as the as-plated specimen. As irradiation time was increased to 500 ms, the surface became smooth as the surface of substrate, which completely lost the initial surface state observed on the as-plated specimen. In the case of 1000 ms, smoothness was rather decreased by evaporation of tin and resulting formation of a number of undulations, which had not been observed on the initial surface of copper substrate.

Table 2 Laser treated conditions.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>808 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focusing distance</td>
<td>100 mm</td>
</tr>
<tr>
<td>Spot diameter</td>
<td>600 μm</td>
</tr>
<tr>
<td>Exposure mode</td>
<td>pulse (N = 1)</td>
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<tr>
<td>Defocusing distance</td>
<td>12 mm</td>
</tr>
<tr>
<td>Laser power</td>
<td>300 W</td>
</tr>
<tr>
<td>Exposure time</td>
<td>100, 300, 500 or 1000 ms</td>
</tr>
<tr>
<td>Exposure atmosphere</td>
<td>in air</td>
</tr>
</tbody>
</table>

Figure 3 shows X-ray diffraction patterns of the laser-irradiated surfaces. While the as-plated specimen showed only the diffraction peaks of tin and copper, Cu$_6$Sn$_5$ was identified in the laser-irradiated specimens. As the irradiation time was increased, the peak intensities of Cu$_6$Sn$_5$ became higher, then, Cu$_5$Sn began to be identified. Here, elongated laser irradiation should be avoided from the viewpoint of the loss of plated film, decrease in wettability and softening of substrate. Regarding the change in the texture by laser irradiation, the initially (200)-oriented tin showed strong (101) diffraction peak after laser irradiation for any conditions. The initial (200) texture became weaker as laser irradiation was elongated, and the film showed isotropy in the cases of 500 and 1000 ms.

Figure 4 shows cross-sectional scanning ion micrographs of electroplated film and substrate. Here, cross-sectional observation was made within 3.6–7.2 ks after laser irradiation. While the as-plated specimen showed no meaningful diffraction peaks of Cu$_6$Sn$_5$ (Fig. 3(a)), small grains of Cu$_6$Sn$_5$ can be observed at the interface between the plated film and the substrate in Fig. 4(a). From the point that the Cu$_6$Sn$_5$ grains are on the grain boundaries of tin, the lines are considered to be preferable nucleation sites of Cu$_6$Sn$_5$, where grain boundaries of tin meet the interface between tin and copper. On the other hand, the whole interface was covered with the layer of Cu$_6$Sn$_5$. Thickness of Cu$_6$Sn$_5$ was increased as irradiation time was elongated, and the continuous layer of Cu$_6$Sn$_5$ lied at the interface for any irradiation conditions.

Thus, laser irradiation is hopefully used as a rapid heat treatment by which nonuniformity in the morphology of Cu$_6$Sn$_5$ and resulting growth of whisker can be suppressed. In the case of as-plated specimen, Cu$_6$Sn$_5$ develops on the grain boundaries of tin under ambient conditions.\textsuperscript{3,10} Residual stress of tin might promote nucleation of Cu$_6$Sn$_5$ on grain boundaries of tin, which brings about nonuniform development of Cu$_6$Sn$_5$ grains.\textsuperscript{3,4,10}

In contrast to the above solid-solid reaction to form nonuniform Cu$_6$Sn$_5$, laser-irradiated volume consists of
liquid tin and solid substrate, where uniform nucleation and growth of Cu$_6$Sn$_5$ occur. Heat treatment by laser irradiation is different from the conventional heating by furnace in the points that the top surface is tin which assures good wettability with solder and that intermetallic compound of Cu$_6$Sn$_5$ is formed as a uniform layer instead of Cu$_3$Sn.

### 3.2 Generation of whiskers, development of compound and changes in residual stress

Figure 5 shows secondary electron images of the surfaces of the specimens kept in ambient conditions for 10.4 Ms after electroplating and laser irradiation. In the case of as-plated film, whiskers were generated on the electroplated tin film within 432 ks. Whiskers and nodules were observed on the surface of as-plated specimen (Fig. 5(a)), some of which were ~100 µm in length. On the other hand, the laser-irradiated areas (Fig. 5(b)(c)) showed no whiskers as well as nodules for any irradiation conditions.

Here, no whiskers were found in the cases of 300 ms and 1000 ms as in the case of 100 ms and 500 ms.

Figure 6 shows X-ray diffraction patterns of the specimens kept in ambient conditions for 2.59 Ms after electroplating and laser irradiation. Diffraction peaks of Cu$_6$Sn$_5$ were identified in the as-plated specimen (Fig. 6(a)), while any of them was not confirmed immediately after electroplating (Fig. 3(a)). Development of Cu$_6$Sn$_5$ is caused by diffusion of copper atoms from the substrate into the electroplated film of tin.$^{11}$ In the cases of the laser-irradiated specimens, diffraction intensities or the amount of Cu$_6$Sn$_5$ did not show meaningful change (Fig. 6(b)(c)).

Figure 7 shows cross-sectional scanning ion images of Fig. 5. In the case of the as-plated specimen, Cu$_6$Sn$_5$ developed nonuniformly between the electroplated film and the substrate, some of which reached the surface. The fixed-point observation for 10.4 Ms showed growth of Cu$_6$Sn$_5$ grains which seemed to have nucleated on the grain boundaries of tin. The nonuniform development of Cu$_6$Sn$_5$ is thought to form nonuniform stress field in the electroplated film of tin which generates the driving force for growth of whiskers.$^{3,4}$ Changes in the brightness of SIM images at the substrate adjacent to the electroplated film of tin (Fig. 7(a)) indicate that the areas were deformed by formation of Cu$_6$Sn$_5$, since the brightness change in the substrate can not
be observed in the as-plated specimen (Fig. 4(a)). On the other hand, deformations of tin cannot be found in the SIM images. Although tin is considered to be deformed as Cu$_6$Sn$_5$ grows, its plastic and elastic strains might be released by recovery, recrystallization, or cross sectioning.

In the laser-irradiated areas, change in the thickness of Cu$_6$Sn$_5$ layer was little after 10.4 Ms. This means that diffusion rate of copper in Cu$_6$Sn$_5$, which determines the growth rate of Cu$_6$Sn$_5$, is quite low under ambient conditions. Since the substrate near Cu$_6$Sn$_5$ in the laser-irradiated areas shows no brightness change in Scanning Ion Microscope (SIM) images as Fig. 7(b), nonuniformity in strain field is thought to be small in the laser-irradiated specimens. Uniformity in the morphology of Cu$_6$Sn$_5$ and relaxation of stress are supposedly achieved by appropriate laser irradiation or rapid heat treatment.

Figure 8 shows residual stress in the electroplated films of tin obtained by X-ray diffraction. In the case of as-plated specimen, residual stress of the tin film was compressive immediately after electroplating, as previously reported. On the other hand, the laser-irradiated specimens of 100 ms and 500 ms showed tensile residual stress of 9 and 2 MPa, respectively. The initial compressive residual stress in the as-plated specimen is canceled by laser irradiation for 500 ms, since tin atoms are arranged in elastically stable state during solidification. For shorter irradiation time as 100 ms, a part of tin is thought to stay in a solid state and be affected by the surrounding Cu$_6$Sn$_5$, whose residual stress remains compressive after laser irradiation.

In the case of the as-plated specimen, the absolute value of residual stress increased with the lapse of time, since development of Cu$_6$Sn$_5$ is accompanied by an increase in volume. On the other hand, the small changes of residual stress in the laser-irradiated specimens are due to the quite slow growth of Cu$_6$Sn$_5$.

From these results, heat treatment of electroplated film of tin on copper substrate by laser irradiation is a hopeful method for suppression of whiskers. While a layer of another intermetallic compound (Cu$_3$Sn) at the interface between electroplated film and substrate has been reported to suppress whiskers, a uniform layer of Cu$_6$Sn$_5$ is shown to have a similar effect in this research. The intervenient layer of Cu$_3$Sn has been reported to be effective as a barrier layer, supposedly because the phase can be formed when the system is heated by conventional furnace. Since laser irradiation can rapidly heat-treat the surface to form uniform layer of Cu$_6$Sn$_5$ without loss of wettability and mechanical properties of terminals, it is one of the most ideal solutions for suppression of whiskers from the viewpoints of energy saving and throughput.

Fig. 4  Cross-sectional scanning ion images of tin plating on rolled surface. (a) As-plated, (b) Laser exposure time-100 ms, (c) 500 ms.
Figure 9 shows a schematic illustration of the above experimental results and discussions. In the case of the as-plated specimen, Cu$_6$Sn$_5$ nucleates on the grain boundaries of tin which contact the copper substrate, then, the nuclei grow along grain boundaries of tin under ambient conditions (Fig. 9(a)). The residual stress in the as-plated specimen immediately after electroplating means elastically strained or unstable state of tin, which is supposedly caused by a large amount of additives in the solution. Since the additives caught in the electroplated film of tin have been reported to have influence on the growth mode of whiskers, nucleation of Cu$_6$Sn$_5$ is also possibly affected by the additives. As Cu$_6$Sn$_5$ nonuniformly develops along the grain boundary of tin, the nonuniformity in the strain field of tin may induce migration of tin atoms into certain grains from which whiskers grow (Fig. 9(b)).

On the other hand, uniform layer of Cu$_6$Sn$_5$ can be formed by laser irradiation at the interface between molten tin and solid copper. If the solidified tin film loses the nonuniform compressive strain and tin atoms are rearranged to be elastically stable, growth of whiskers by strain-induced diffusion can be further suppressed. Here, evaporation of the additives in tin may promote uniform nucleation and growth of Cu$_6$Sn$_5$ (Fig. 9(d)).

4. Summary

In this research, electroplated films of tin on copper substrate were subjected to rapid heat treatment by laser irradiation. Growth of whiskers, development of copper-tin intermetallic compound, and changes in residual stress are summarized as follows.

1. In the case of the as-plated specimen, Cu$_6$Sn$_5$ preferentially nucleates and grows along grain boundaries of tin under ambient conditions. However, uniform layers of Cu$_6$Sn$_5$ are formed in the laser-irradiated specimens by rapid reaction at the liquid-solid interface. Thickness of the layers does not meaningfully increase supposedly because the diffusion rate of
copper atoms in Cu₆Sn₅ is quite low under ambient conditions.

(2) Residual stress of the as-plated specimen immediately after electroplating and those of laser-irradiated ones are compressive and tensile, respectively. Since formation of Cu₆Sn₅ is accompanied by increase in volume, residual stress of tin in the as-plated specimen becomes further compressive under ambient conditions. The laser-irradiated specimens, where meaningful growth of Cu₆Sn₅ is not observed, show little changes in residual stress.

(3) While many nodules and whiskers were observed on the surface of the as-plated specimen, the laser-irradiated areas showed neither nodules nor whiskers after keeping for 10.4 Ms under ambient conditions. Formation of a uniform layer of Cu₆Sn₅ by laser irradiation was confirmed to be effective for suppression of whiskers as that of Cu₃Sn formed by furnace heating.

REFERENCES