Interfacial Reactions between Sn-3.8 Ag-0.7Cu Solder and Ni-W Alloy Films

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Abstract (IEMT2012-P003)

In this study, interfacial reactions between Ni-W alloy films and Sn-3.8Ag-0.7Cu solder have been investigated. Ni-W alloys films with tungsten content in the range of 5.0 – 18.0 at.% was prepared on copper substrate by electrodeposition in ammonia citrate bath. Solder joints were prepared on the Ni-W coated substrate at a reflow temperature of 250 °C. The solder joint interface was investigated by cross-sectional scanning electron microscopy, energy dispersive X-ray spectroscopy and electron back scatter diffraction. It has been observed that a (Cu,Ni)5Sn3 layer formed on the Ni-W alloy film after reflow. The thickness of the (Cu,Ni)5Sn3 layer was found to decrease with increase of tungsten content in the Ni-W film. An additional layer with a bright appearance was also found to form below the (Cu,Ni)5Sn3 layer. The bright layer was identified to be a ternary phase containing Sn, Cu, W and Ni. The bright layer is found to be amorphous and is suggested to have formed through solid state amorphization caused by anomalously fast diffusion of Sn into Ni-W film.

1. Introduction

In recent year, the electronic packaging industries have been putting lots of efforts in replacing lead solders to lead free solders. Because the usage of lead has shown negative impact on the human body and the environment, many countries have banned the use of lead solder. In conjunction to replace lead solder, Sn based solders have received the most attention. Tin fulfills several requirements such as good metallurgical, environment friendly, low material cost, and acceptable melting temperature [1, 2]. Researchers have been investigating on binary and ternary tin based alloys over the past few years, which included Sn-Ag, Sn-Cu and Sn-Ag-Cu, just to name a few.

Haseeb et. al. [3] studied the interfacial reactions between Sn-3.5Ag (SA) and Ni-W alloy films at different reflow cycles. In addition to the formation of Ni3Sn4, a ternary phase containing Ni, W and Sn was found to form between Ni3Sn4 and Ni-W film. The ternary layer, bright in the appearance, was found to be an amorphous layer. Based on the experimental results, we suggest that the ternary layer is formed through solid state amorphization. It is similar with the case found between Ni-V alloy film and tin reaction [4]. It is generally believed that the amorphous film can be effective barrier as it exhibits low diffusivity. However, the thickness of Ni3Sn4 intermetallic compound (IMC) showed a gradually decrease in trend with an increasing of W content of its film. From the view point of Ni-W alloy distribution, Detor et. al. [5] found that strong segregation of Ni-W was observed in grain boundaries at high concentration of W atoms. Tungsten atoms are thought to act as “pinning agent” at grain boundaries and have reduced the growth of Ni3Sn4 IMC between SA and Ni-18 at.% W. With the amorphous ternary layer and higher W content alloy film, it is therefore expected that presence of W would add some credits to reduce the thickness of IMC layer.

To have a better understanding on the formation of ternary layer, Sn-3.8Ag-0.7Cu (SAC) lead free solder was selected in this work. Studies have shown that decreasing of melting temperature of Sn-Ag lead free solder with small amount of Cu addition [6]. Meanwhile, experimental results have shown that Sn-Ag-Cu lead free solder has better mechanical properties and microstructural stability [7-13]. The main aim of this work is to investigate the interfacial reactions between SAC and Ni-W alloys. The effect of W content in alloy film has also been evaluated.

2. Experimental procedures

Nickel tungsten alloy films were electroplated on copper substrates with the dimension of 0.3 mm x 30 mm x 30 mm. The Cu substrate was cleaned with detergent and dipped in 10 vol. % H2SO4 to get rid of the oxide layer before plating. It was rinsed with distilled water followed by drying with acetone. Electrodeposition of Ni-W alloys films was carried out in an ammonia citrate baths maintained at 80 °C ± 2 °C. Table 1 shows the bath composition and parameters for electrodeposition. The bath pH was adjusted to 8.5 by sulphuric acid or ammonia solution at room temperature. Deposition current density was 10 mA/cm2 and Ni-W alloy films were deposited to a thickness about 2.0-2.5 µm. Before soldering, the Ni-W alloy films were cleaned with detergent and rinsed thoroughly in deionized water and dried with acetone. Sn-3.8Ag-0.7Cu (SAC) solder paste (Indium Corporation) was placed on electrodeposited substrate through a stencil with 6.5 mm opening and 1.24 mm height. After reflow process at a peak temperature of 250 °C, the flux residue on the top of the solder was cleaned with acetone. Multiple reflow were performed in a reflow oven ( Forced convection, FT 02). Samples were prepared for cross sectional examination by standard metallographic technique. The samples were examined by backscattered electron detector is a field emission scanning electron microscope (Gemini FE-SEM, Zeiss). The average thickness of the interfacial IMC layer was measured by dividing the area covered by the layer by
its length. The area measurements were done using Adobe Photoshop CS4 by employing the Magnetic Lesso Tools. For each experimental condition, the average thickness was calculated from at least four micrographs taken at randomly selected position on the cross sectional samples. The elemental analysis of different phases was carried out by energy dispersive X-ray spectroscopy (EDX). Electron probe microanalysis (EPMA, Cameca SX 100) with wavelength dispersive spectroscope (WDS) was used for elemental mapping. Electron back scatter diffraction (EBSD, EDAX) analysis was used to identify the channeling pattern of the phase. For EBSD analysis, the sample was further polished with colloidal silica to produce a cleaner surface topography for revealing better Kikuchi pattern.

Table 1: Composition of electrolytic solution of Ni-W alloy electrodeposition.

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel (II) sulphate hexahydrate, NiSO₄·6H₂O</td>
<td>0.06-0.33</td>
</tr>
<tr>
<td>Sodium citrate dihydrate, Na₂C₄H₆O₇·2H₂O</td>
<td>0.50</td>
</tr>
<tr>
<td>Sodium Dihydrate, Na₂WO₄·2H₂O</td>
<td>0.01-0.14</td>
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<tr>
<td>Ammonium Chloride, NH₄Cl</td>
<td>0.5</td>
</tr>
<tr>
<td>Sodium Bromide, NaBr</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 2: Composition of electrolytic solution of Ni-W alloy electrodeposition.

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.33</td>
</tr>
<tr>
<td>Na₂WO₄·2H₂O</td>
<td>0.01</td>
</tr>
<tr>
<td>Deposit W content at. %</td>
<td>5.0</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.22</td>
</tr>
<tr>
<td>Na₂WO₄·2H₂O</td>
<td>0.07</td>
</tr>
<tr>
<td>Deposit W content at. %</td>
<td>11.3</td>
</tr>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.06</td>
</tr>
<tr>
<td>Na₂WO₄·2H₂O</td>
<td>0.14</td>
</tr>
<tr>
<td>Deposit W content at. %</td>
<td>18.0</td>
</tr>
</tbody>
</table>

3. Results and Discussion

Table 2 shows the EDX analyses of the Ni-W alloy films deposited from three different baths. Three different W contents viz., 5.0, 11.3, and 18.0 at.% W were obtained in various nickel and tungsten contents of the baths. It indicates that higher W content is obtained with lower nickel to tungsten ratio in the electrodeposition bath [3].

The surface morphologies of deposits obtained at various W contents are shown in Fig. 1. At Ni-5 at.% W, the surface morphology forms by elongated and globular structures. The morphology becomes globular at Ni-11.3 at.% W. A smoother surface can be seen at higher tungsten content which is Ni-18 at.% W. Haseeb [14] revealed that larger grain size is due to lower W content of the deposit. A smaller grain size, 2.4-6.8 nm in their Ni-W alloy with 22.5-17.7 at.% W obtained by Yamasaki et al. [15]. In this study, all samples were deposited at a current density of 10 mA/cm². Early studies show that the average grans size of samples deposited at 10 mA/cm² is about 20 nm [16, 17].

Fig 1: Morphology of the deposits obtained at different W content: a) Ni-5 at.% W, b) Ni-11.3 at.% W and c) Ni-18 at.% W.

Fig. 2 shows cross sectional FE-SEM micrographs of the interface between SAC and Ni-W alloy films after first time reflow. Two layers form at the interface between SAC and Ni-W alloy films. The outer layer, darker in appearance, is uniform and chunky type formed at the interface between SAC and Ni-5 at.% W. Elemental ratio obtained from EDX result suggested that darker layer is (Cu,Ni)₆Sn₅ IMC. The second layer which is much thinner and brighter in appearance formed below (Cu,Ni)₆Sn₅ layer. EDX analysis showed that the bright layer contains Sn, Cu, Ni and W.

It can be seen that a continuous and compact (Cu,Ni)₆Sn₅ layer formed at the interface between SAC and Ni-11.3 at.% W. In contrast, a non-uniform and discontinuous (Cu,Ni)₆Sn₅ layer formed on Ni-18 at.% W interface. It has shown that the thickness of (Cu,Ni)₆Sn₅ layer decreases with increasing of W content. However, the thickness of the bright layer remains insensitive to W content.

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Fig. 2. Cross-sectional back scattered electron image of interface between SAC and Ni-W barrier film with different W content after 1 x reflow for different barrier films: a) Ni-5 at.% W, b) Ni-11.3 at.% W, and c) Ni-18 at.% W.

Cross-sectional micrographs of the interface after twelve reflow cycles are shown in Fig. 3. The thickness of (Cu,Ni)_6Sn_5 layer increases after twelve reflow cycles. An agglomerated chunky type of (Cu,Ni)_6Sn_5 layer is observed at Ni-5 at.% W and Ni-11.3 at.% W interface with a bright layer formed below each (Cu,Ni)_6Sn_5 layer. A non-uniform and discontinuous (Cu,Ni)_6Sn_5 can be seen at Ni-18 at.% W interface after twelve reflow cycles, as shown in Fig. 3c. A thicker bright layer is observed at the interface between SAC and Ni-18 at.% W. The thickness of (Cu,Ni)_6Sn_5 layer decreases with increasing of W content in the film. This observation is similar to the case of first reflow.

Table 3: Composition of bright layer (Sn-Cu-Ni-W) on different Ni-W barrier film after 12 x reflows.

Fig. 4. Variation of the thickness of (Cu,Ni)_6Sn_5 IMC and bright layer (Sn-Cu-Ni-W) as a function of tungsten content of Ni-W film for 1 x and 12 x reflows.

Fig. 5. Elemental mapping at interface between SAC and Ni-11.3 at.% W after twelve reflows by EPMA.

Figure 5 shows the EMPA elemental mapping at interface between SAC and Ni-11at.% W after twelve reflows. Nickel content diffused to solder area to form (Cu,Ni)_6Sn_5 IMC, while tin atoms diffuse toward alloy film. It can be seen that tungsten atoms remain in Ni-W film and no tungsten is found in copper substrate. Tungsten content is high in areas between the substrate and (Cu,Ni)_6Sn_5 layer.

with the increase of W content in the barrier film. This trend is similar to our previous study of Ni_3Sn_4 layer thickness that found to decrease with increasing of W content at SA and Ni-W alloy films interface [3].
Previous study between Sn-3.5Ag (SA) and Ni-W alloy films has shown that solid state amorphization occurs at the interface is characterized by inward diffusion of Sn atoms into barrier layer [3]. However, the amorphous layer is a ternary layer (Sn-Ni-W), with the additional of Cu element in SAC solder, a quaternary layer is found in the present case. The amorphization reactions on Ni-W alloy films are now caused by the influx of tin and copper atoms into it. EPMA data reflected that tin and copper atoms have moved into the barrier film, whereas W atoms are relatively immobile. It is thus believed that the anomalously fast diffusion of tin and copper atoms into Ni-W film has contributed to the solid state amorphization leading to the formation of the amorphous quaternary Sn-Cu-Ni-W layer. It may be noted that amorphous layer formation was also observed by Chen et. al. between Sn-0.7Cu and Ni-V barrier films [20]. They found that the bright layer formed when vanadium content of the Ni-V layer was more than 7 wt.% at 250°C for 5 min reaction time [20]. Analysis showed that the bright layer contains Sn, Cu, Ni and V. They termed this quaternary phase as Q phase. As in previous discussion, a similar unknown phase denoted ‘T’ phase has been found between Sn and Ni-V barrier film [4]. The difference between ‘Q’ and ‘T’ phase is that the two phases are found in quaternary and ternary, respectively. These quaternary and ternary system is in good agreements with the experimental observations in case studies at SA [3] and SAC interface.

Table 3 shows the average composition of the bright layer (Sn-Cu-Ni-W) that formed after twelve reflows on different Ni-W films. It is seen that tin is the major constituent in the bright layer accounting for about half of its content. The amount of nickel in the bright layer is far smaller compared with the original nickel content of the Ni-W film.

<table>
<thead>
<tr>
<th>Barrier film</th>
<th>Composition of Bright layer, at.%</th>
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<tbody>
<tr>
<td>Ni-5 at.% W</td>
<td>Ni 30.95 Cu 18.33 W 9.60 Sn 41.13</td>
</tr>
<tr>
<td>Ni-11.3 at.% W</td>
<td>Ni 26.31 Cu 4.84 W 23.89 Sn 44.97</td>
</tr>
<tr>
<td>Ni-18 at.% W</td>
<td>Ni 23.06 Cu 6.59 W 24.46 Sn 45.89</td>
</tr>
</tbody>
</table>

From the above results, the (Cu,Ni)₆Sn₃ layer decreases in following order after first reflow and twelve reflow cycles: Ni-5 at.% W > Ni-11 at.% W > Ni-18 at.% W. The phenomenon is significantly related to the W content in electrodeposited films. It can be seen that with highest W content which is Ni-18 at.% W, the lowest (Cu,Ni)₆Sn₃ layer was formed. The decrease of (Cu,Ni)₆Sn₃ layer at Ni-18 at.% W interface might due to decreasing of crystallinity of the film [14, 17, 19]. From the view point of Ni-W alloy distribution, strong segregation of Ni-W was found in grain boundaries at high concentration of W atoms [5]. Thus, tungsten atoms are thought to act as ‘pinning agent’ at grain boundaries and have reduced the growth of (Cu,Ni)₆Sn₃ between SAC and Ni-18 at.% W. This is in a good experimental agreements in SA/Ni-18 at.% W study, which lowest Ni₃Sn₃ is found at Ni-18 at.% W [3].

Previous SA/Ni-W study has indicated that the thickness of Sn-Ni-W ternary layer is in range of 1 to 2 μm [3]. The thickness of Sn-Cu-Ni-W quaternary layer is however lower than the ternary layer which is below 1 μm. Figure 7 shows the schematic drawing of different IMCs formed in SA/Ni-18 at.% W and SAC/Ni-18 at.% W reaction couples. A continuous and compact Ni₃Sn₄ layer formed in SAC/Ni-18 at.% W and the ternary layer (Sn-Ni-W) formed below Ni₃Sn₄ in Fig 7a. In contrast, a discontinues and non-uniform (Cu,Ni)₆Sn₃ layer formed in SAC/Ni-18 at.% W and the quaternary (Sn-Cu-Ni-W) formed below (Cu,Ni)₆Sn₃ layer. The thickness of Ni₃Sn₄ formed between SA and Ni-18 at.% W is (2.55 ± 0.23) μm and Sn-Ni-W IMC layer is (1.82 ± 0.04) μm [3]. However, the thickness of (Cu,Ni)₆Sn₃ layer that formed between SAC and Ni-18 at.% W is (2.25 ± 0.24) μm and Sn-Cu-Ni-W layer is (0.72 ± 0.04) μm. Higher IMC thickness that was found between SA and Ni-18 at.% W is suggested to relate to the standard Gibbs energy of the formation of Ni₃Sn₄ IMC, which is -24.1 kJ/mol [21]. The continuous and larger thickness of IMC are observed at SA interface, because Ni₃Sn₄ phase is easier to form and more stable. While, the Gibbs energy of (Cu,Ni)₆Sn₃ IMC is -16.0 kJ/mol of atoms [21]. This may
due to lower Gibbs free energy of the formation of (Cu, Ni)$_5$Sn$_3$ IMC resulting in less thickness of (Cu, Ni)$_5$Sn$_3$.

Based on interfacial reactions between Ni-V alloy films and Sn-Ag-Cu solder, after ten reflow cycles at 250°C, a spalling of IMC was found [12, 20]. It is worth to note that thin and discontinuous (Cu, Ni)$_5$Sn$_3$ layer was formed at SAC/Ni-18 at.% W interface in our case. Ni-18 at.% W film is suggested to possess a good barrier layer as having these two components. The first component is lower IMC thickness formed at the interface after twelve reflow cycles. This means that the film is capable to perform at long period of time. The second component is the quaternary amorphous layer was formed below the (Cu, Ni)$_5$Sn$_3$ layer. It is generally implying that amorphous barrier layer exhibits low diffusivity. Ni-8 at.% W alloy film has the potential to provide long term barrier properties. The mechanical properties of the Ni-18 at.% W are necessary to investigate for implication on the long term reliability of solder joint.

Fig. 7. Schematic drawing of the interface of (a) SA and Ni-18 at.% W, (b) SAC and Ni-18 at.% W.

4. Conclusions
The interfacial reactions between Sn-3.8Ag-0.7Cu solder and Ni-W alloy films with W contents of 5.0, 11.3 and 18.0 at.% W were investigated. Besides (Cu, Ni)$_5$Sn$_3$ layer formed on the solder side, a quaternary Sn-Cu-Ni-W layer formed below the (Cu, Ni)$_5$Sn$_3$ layer. The thickness of the (Cu, Ni)$_5$Sn$_3$ layer was found to decrease with the increase of W contents in the Ni-W films. However, the quaternary Sn-Cu-Ni-W layer contains no W and did not depend significantly on the W contents of the Ni-W films. It is suggested that the quaternary Sn-Cu-Ni-W layer formed through solid state amorphization caused by anomalously fast diffusion of Sn and Cu into Ni-W. Therefore, extensive studies of the quaternary layer are required in the future.

Acknowledgments

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