Interfacial Reactions between Ni-Zn Alloy Films and Lead-free Solders

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Abstract

Because of the miniaturization trend in electronic devices in recent years, semiconductor industry is striving hard to produce smaller and thinner devices while improving the performance and processing speed. The issue of reliability of solder joints in these miniaturized devices becomes very critical. In this study zinc is incorporated into the nickel barrier film in the form of Ni-Zn alloy by electrodeposition. The effects of the presence of Zn on the interfacial reactions between nickel barrier film and Sn-3.8Ag-0.7Cu and Sn-3.5Ag solders are investigated. Ni-Zn alloy films 1.73wt%Zn were prepared from ammoniacal diphosphate baths. Elemental composition of the alloy film was determined by energy dispersive x-ray spectroscopy (EDX) while x-ray diffraction method (XRD) was used to determine the phases present in the alloy film. Spreading rate was characterized with the use of optical microscope. Reflows were done for 1 and 12 cycles to investigate the effect of multiple reflows on the IMC growth and morphology. Results have shown that the IMC formed at the interface of SAC/Ni and SA/Ni was (Cu,Ni)₃Sn₅ and Ni₅Sn₄ respectively. (Ni,Cu)₂Sn₄ IMC was formed at the interface of SA/Ni-Zn alloy film. No spalling was detected at the SA/Ni-Zn solder joint. On the other hand, it has been observed that (Ni,Cu)₂Sn₄ and (Cu,Ni)₃Sn₅ layer with continuous non-uniform morphology were formed on the SAC/Ni-Zn alloy film after 1x reflow. As the number of reflow increased, (Cu,Ni)₃Sn₅ layer spalled from the interface leaving only (Ni,Cu)₂Sn₄ IMC at the interfacial region.

1. Introduction

A demand for higher performance and multi-functional electronics products have led to miniaturization of the products. This in turn has set a challenge for the electronic industry to incorporate more powerful functions into smaller and thinner products. Hence, it is important to have better understanding of the reliability issue at the solder joint interface between the solder and the component.

Solder plays a very crucial role in the assembly and packaging of chips in the electronic industry [1]. It is a fusible metal alloy which acts as joint material between the chip and the metallization lines on the PCB board. Up to year 2002, lead solder has been used in the industry due to their outstanding properties such as good mechanical and excellent wetting properties. However, lead is very hazardous to both human health and the environment. In 2002, the European Union Waste Electrical and Electronic Equipment Directive (WEEE) and Restriction of Hazardous Substances Directive (RoHS) have banned all consumer products containing lead due to health and environmental concerns. Thus, the electronics industry has shifted to lead free solder in response to the concern over lead.

However, Sn-based solders will react with the Cu substrate to form a thick layer of Cu-Sn IMCs such as Cu₅Sn₃ and Cu₅Sn₆. Cu₅Sn₃ has been found to grow substantially during operation of electronic devices [2]. A great deal of research has been done to reduce the growth of IMCs formed at the solder joints. One of the ways is to introduce a thin layer of barrier film between the Cu substrate and the Sn-based solder to hinder the diffusion of Sn and Cu. Studies have shown that a thin layer of Ni is effective in reducing the interfacial IMC growth between Cu and Sn-based solder. This is because it has been reported that the reaction kinetics of Ni-Sn compounds are much slower than that of Cu-Sn IMCs [1].

However, Sharif and Chan has shown that Ni alone may not be adequate for high temperature applications [3]. This has led to the investigation of Ni based alloys barrier films such as Ni-P [1, 4-5], Ni-B [6] and Ni-W [7]. Results have shown that alloying elements such as P, B and W in the Ni based barrier films can influence the thickness of the Ni₅Sn₃ IMC. Thus, much research has been done to study the interfacial reactions between Ni and Cu. Cho et al. has done a study on the liquid state interfacial reaction between Cu-Zn substrate and SAC solder [8]. With increasing amounts of Zn alloying element in Cu, results have shown that Zn is incorporated into the Cu₅Sn₃ IMC. Also, there seems to be suppression of Cu₅Sn IMC formation as the driving force of Cu₅Sn formation decreases with increasing Zn content in the Cu substrate [9]. Kim et al., on the other hand, did investigations on the solid state interfacial reactions between SAC solder and Cu-Zn alloys [10]. They also found that with 10wt.% of Zn in Cu, Cu₅Sn IMC is completely suppressed after 2000 hour aging at 120°C and 150°C. Apart from Cu-Zn substrate, researchers are also experimenting on Ni-Zn substrate. Cho et al. has done studies on the interfacial reactions between DC magnetron sputtered Ni-Zn thin film and Sn solder [11]. Results showed that with Zn alloying element in Ni, there is a decrease in the thickness of Ni₅Sn₃ IMC after 1000 hour aging at 150°C. However, data available in the literature are very limited and does not allow understanding in the reactions between Sn and Ni in the presence of Zn.

In this study, the main objective is to investigate the interfacial reactions between Ni-Zn thin films and two types of lead free solder, namely Sn-3.5Ag (SA) and Sn-3.8Ag-0.7Cu (SAC). Two types of solder are used to investigate the effect of Cu in the bulk solder towards the formation of interfacial intermetallic compounds (IMC) layers.
2. Experimental procedures

In this study, both Ni and Ni-Zn barrier films were prepared on Cu substrate by electrodeposition. Electrodeposition using Watts bath was carried out to plate Ni alloy films while ammoniacal diphosphate bath was used for plating Ni-Zn alloy films [12].

The bath pH was adjusted to 7.5 by using sodium hydroxide solution and 3.5 by using sulphuric acid for the ammoniacal diphosphate and watts bath, respectively. Stirring condition was set at 60rpm for both baths. Deposition current density was 5mA/cm² and 20mA/cm² for ammoniacal diphosphate and watts bath, respectively.

The alloy films were deposited to around 2.0-2.5µm with the deposition time set at 14 minutes and 120 minutes for plating Ni and Ni-Zn films, respectively. Energy dispersive X-ray spectroscopy (EDX) was used to determine the composition of the electrodeposited Ni-Zn thin films. The phases of the Ni-Zn thin films was investigated by X-ray Diffraction Method using Bruker D8 Advance diffractometer with Cu Kα radiation which has a wavelength, λ, of 1.5418 Å. After that, the peaks shown in the XRD pattern was identified by using the Powder Diffraction File card (JCPDS).

Zn thin films was investigated by X-ray Diffraction Method using Bruker D8 Advance diffractometer with Cu Kα radiation which has a wavelength, λ, of 1.5418 Å. After that, the peaks shown in the XRD pattern was identified by using the Powder Diffraction File card (JCPDS). SAC/SA solder by Indium Corporation was placed on top of the deposited substrates by using a jig with an opening of 6.5mm and a height of 1.24mm. The samples were then reflowed in a reflow oven (Forced convection, FT 02) at 250°C for approximately 45 seconds. Reflows are done for 1 cycle and 12 cycles to study the effect of reflow cycle on the IMC formation. Top-view samples were prepared by immersing the samples into an etching solution consisting of 93% methanol, 2% HCl and 5% H₂SO₄ for 18 hours. The spreading rate (SR) of the solder is calculated by the equation stated in the Japanese Industrial Standard-JIS Z 3197-1896.

Zeiss Gemini Field-emission Scanning Electron Microscope (FESEM) was used to examine the interfacial IMCs between SA/SAC solder and the Ni/Ni-Zn alloy films. 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 CS5 by employing the Magnetic Lesso Tools. The average thickness was calculated from at least four micrographs taken at randomly selected position on the cross sectional samples.

3. Results and Discussions

3.1 EDX analysis and XRD characterisation on Ni-Zn alloy films

EDX analyses were done on the Ni-Zn alloy films electrodeposited in this study to determine the composition of each element in the alloy films. The composition of the Ni and Zn element from the electrodeposited Ni-Zn alloy film is shown in Table I. It was found that there was an average of 1.73wt%Zn in the alloy films. Thus, Ni-1.73wt%Zn would be designated as Ni-1.73Zn in this study.

XRD analysis was done on the Ni-Zn alloy film to determine the phases present in the deposited Ni-Zn alloy films. The XRD pattern obtained is shown in Fig. 1. The phases from the XRD patterns were identified with the powder diffraction file card (JCPDS).

According to the Ni-Zn phase diagram, Ni and Zn can form several phases. In alloys containing 0-27at%Zn, face-centered cubic (fcc) α-NiZn can be found while body-centered tetragonal (bct) β-NiZn is found in alloys containing approximately 50%Zn. For 74-85at%Zn, the body-centered cubic (bcc) γ-NiZn can be obtained [13].

From Fig. 1, it could be seen that for Ni-1.73Zn, Zn exists as solid solution in Ni as only Ni peaks were detected.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zn content (wt%)</th>
<th>Ni content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.81</td>
<td>98.19</td>
</tr>
<tr>
<td>2</td>
<td>1.14</td>
<td>98.86</td>
</tr>
<tr>
<td>3</td>
<td>2.23</td>
<td>97.77</td>
</tr>
<tr>
<td>Average</td>
<td>1.73</td>
<td>98.27</td>
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3.2 Spreading rate of solder on Ni-Zn film

Figure 2 shows the spreading rate of SAC and SA solder on Ni and Ni-Zn film substrates, respectively.

Spreading rate was calculated using the Japanese Industrial Standard-JIS Z 3197-1896. From the calculation, the spreading rate for Ni/SAC is 91.68 ± 3.036 while that of Ni-1.73Zn/SAC is 90.195 ± 1.025. Spreading rate for Ni/SA and Ni-1.73Zn/SA were found to be 85.78° ± 4.456 and 85.67 ± 2.002, respectively, which show no significant change.

Thus, according to the calculated spreading rates, with the addition of Zn in the alloy film, it can be safe to suggest that Zn did not significantly influence the spreading rate.

3.3 Interfacial reactions between SA and Ni-1.73Zn alloy films

Figure 3 shows the cross sectioned micrographs for SA/Ni and SA/Ni-1.73Zn interfaces after 1x and 12x
reflows. Interface reaction between SA/Ni is shown in comparison. From Fig. 3(a), it can be seen that the

corresponding to previous studies [15]. However, some studies showed the presence of (Ni,Cu)₅Sn₆ IMC [6, 16] but
this type of IMC was not found in this study. According to Ho et al., the intermetallics formed during soldering were
reported to be dependent on the Cu concentration in the solder. If the Cu concentration in the solder is less than 0.4
wt.%, (Ni,Cu)₅Sn₆ IMC forms at the interface. On the other hand, if the Cu concentration is higher than 0.6 wt.%, only
(Cu,Ni)₅Sn₆ IMC forms at the interface. As discussed in the study done by Ho et al., reactions at small solder joints with
limited Cu supply shall produce both (Ni,Cu)₅Sn₆ and (Cu,Ni)₅Sn₆ IMC while using a large solder joints shall
only produce only (Cu,Ni)₅Sn₆ IMC. This corresponds to the studies done by Yoon and Liu where in both cases,
small solder balls with diameter of 500µm and 2.4mm were used while in this study solder paste were placed upon the
substrate using a jig with an opening of 6.5mm. Thus, the sole formation of (Cu,Ni)₅Sn₆ IMC in this study can be
corresponded to the large solder joint used. When Zn content is added into the Ni thin film, an additional
(Ni,Cu)₅Sn₆ IMC is formed between the SAC solder and the (Cu,Ni)₅Sn₆ IMC. From the results, it could be noted that
there was no trace of Zn in the IMC formed. This corresponds to the study done by Tai et al. where no Zn was
traced from the interfacial reaction products formed between Sn-3Ag-0.5Cu/Ni-8Zn-8P due to the slow growing rate of Ni-Zn IMC [18].

Figure 5 and 6 show the line scans done on the cross section interfacial region in the SAC/Ni and SAC/Ni-
1.73Zn samples, respectively. It can be seen clearly that the line scans for SAC/Ni corresponds well to the spot EDX that
is previously done on the IMC layer. There is only one type of IMC shown in the line scan, which is the
(Cu,Ni)₅Sn₆ IMC for the SA/Ni joint.. The line scan for Ni-
1.73Zn, on the other hand, shows two types of IMC as there are clearly different intensities shown in the graph. When
approaching the Ni/solder interface at a distance of ~25µm, it can be seen that the intensity for Sn is higher than the
intensity of Sn at a distance of 3-6µm. Thus, the IMC formed in the solder should be that of (Ni,Cu)₅Sn₆ while those
near the Ni interface should be (Ni,Cu)₅Sn₆ corresponding to the spot EDX done previously.

Figure 7 shows topview micrograph for SAC/Ni-1.73Zn after etching in a 93% methanol, 2% HCl and 5% H₂SO₄ solution for 18 hours. EDX analysis was done on the top surface IMCs. In correspondence to the results above, two types of IMC morphology were shown in Fig. 7, one of the needle type and the other of the bulky type. The bulky type morphology corresponds to the (Cu,Ni)₅Sn₆ IMC while the needle-like type IMC was of the (Ni,Cu)₅Sn₆ IMC. It can be seen clearly from the micrograph that the needle-like
(Ni,Cu)₅Sn₆ are embedded below the plate-like (Cu,Ni)₅Sn₆ IMC.

**Fig. 2.** Spreading rates for SA and SAC solder on Ni or Ni-
Zn alloy films.

**3.4 Interfacial reactions between SAC and Ni-1.73Zn
alloy film**

Figure 4 shows the cross sectional micrographs for solder joints formed between SAC and Ni, and SAC and
Ni-1.73Zn alloy films. It is observed that there was a change in the morphology of the IMCs formed. Without
any Zn addition in the barrier thin film, it was observed that the IMC formed is of the irregular needle shaped structure for both the 1x and 12x reflow samples. The only difference was that after 12x reflow, a few chunks of (Cu,Ni)₅Sn₆ IMCs were detached from the continuous layer of faceted
(Cu,Ni)₅Sn₆ at the Ni/SAC interface.

However, interfacial IMC between SAC and Ni-1.73Zn alloy film is observed to be continuous, although non-
uniform, for both 1x and 12x reflow samples. After 12x reflow, massive spalling occurred to the (Cu,Ni)₅Sn₆ phase as seen in Fig. 4(d).

After 1x reflow, it can be seen that the Ni/SAC solder joint interface only exhibited (Cu,Ni)₅Sn₆ phase, which is in
good agreement to previous studies [15]. However, some studies showed the presence of (Ni,Cu)₅Sn₆ IMC [6, 16] but
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Fig. 3. FESEM micrographs showing cross-sectional images of interfacial reactions at SA/Ni (a,b) and SA/Ni-1.73Zn (c,d) solder joint after 1x and 12x reflow at 2000x magnification.

Fig. 4. FESEM micrographs showing cross-sectional images of interfacial reactions at SAC/Ni (a,b) and SAC/Ni-1.73Zn (c,d) solder joint after 1x and 12x reflow at 2000x magnification.
Fig. 5. FESEM micrograph of the interfacial region in the SAC/Ni sample after 1x reflow and the concentration profiles across the interface by line scan marked by the line.

Fig. 6. FESEM micrograph of the interfacial region in the SAC/Ni-1.73Zn sample after 1x reflow and the concentration profiles across the interface by line scan marked by the line.

Fig. 7. Top view FESEM micrographs of SAC/Ni-1.73Zn after 1x reflow at 4000x magnification.

The presence of Zn in the Ni barrier layer is seen to cause massive spalling after the 12x reflow in SAC. Similar detachment phenomenons were found in previous studies. According to Wang and Chen who did a study on the interfacial reactions of Sn-Cu solder and Ni film, the reason for the detachment of Cu₆Sn₅ IMC was due to the formation of a fine-grain layer above the large grain layer. The difference in the grain sizes caused stress build up and thus initiates fracture at the weakest point. Cracks will become more significant as the reaction time increases and eventually, detachment will occur [19].

Another reason proposed for the massive spalling phenomenon was discussed by Ho [15]. In the study, it had been reported that both the solder volume and the concentration of Cu in the solder will influence the type of IMC formed. It has been reported that Ni₃Sn₄ IMC will form when the Cu concentration in the solder was less than 0.5wt%. This corresponds to the Cu-Sn-Ni phase diagram at 240°C. Thus, the change of Cu concentration is a solder joint may cause a change in the interfacial reaction products where single layer (Cu,Ni)₆Sn₅ IMC may transform into two-layers (Cu,Ni)₆Sn₅ and (Ni,Cu)₃Sn₄ IMCs. Since Cu is a minor constituent in lead-free solder, its supply is limited. Hence, a reduction in the Cu concentration at the interface would cause (Cu,Ni)₆Sn₅ to spall massively from the interface as the layer was destabilized.

In this study, it was shown that only (Cu,Ni)₆Sn₅ IMC was formed when Zn is not added in the Ni barrier film. This result was in good agreement to previous study [19]. But when Ni-1.73Zn alloy film was used as the barrier film, (Ni,Cu)₃Sn₄ IMC was formed in between the alloy film and (Cu,Ni)₆Sn₅ layer. Thus, Cu in the solder would be consumed in the reaction and the Cu concentration near the interface would gradually decrease. Eventually, Cu concentration would be too low to remain stable with the (Cu,Ni)₆Sn₅ IMC causing the whole layer to be detached from the interface.

4. Conclusions
(a) The addition of Zn in the Ni alloy film did not significantly affect the spreading rate of the SA and SAC solder on the Ni-Zn film.
(b) One type of IMC formed at the interface of both the SA/Ni and SAC/Ni-1.73Zn solder joint after 1x and 12x refloows e.g., Ni$_3$Sn$_4$ and (Ni,Cu)$_5$Sn$_6$, respectively. After 12x reflow, the IMC morphology changed from the faceted, scallop type structure to a large columnar faceted structure when Zn was added to the barrier film. Cu may have diffused pass the barrier film and reacted to form (Ni,Cu)$_5$Sn$_6$, IMC after Zn was added in the barrier film.

c) There was only one type of IMC formed at the interface of SAC/Ni solder joint after 1x and 12x refloows e.g., (Cu,Ni)$_5$Sn$_6$. At the SAC/Ni-1.56Zn interface, two types of IMCs formed after 1x and 12x refloows e.g., (Cu,Ni)$_5$Sn$_6$ and (Ni,Cu)$_5$Sn$_6$. The morphology of the interfacial IMCs changed from the faceted structure to a continuous non uniform type when Zn was added to the barrier film. Massive spalling was observed at the SAC/Ni-1.56Zn solder joint after 12x reflow. Reason for massive spalling to occur was due to limited Cu supply at the interfacial region.

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References