Studies on Ni-Sn Intermetallic Compound and P-rich Ni Layer at the Electroless Nickel UBM - Solder Interface and Their Effects on Flip Chip Solder Joint Reliability

Young-Doo Jeon and Kyung-Wook Paik
Micro-Electronic Packaging Laboratory,
Dept. of Mat. Sci. and Eng., Korea Advanced Institute of Science and Technology
373-1, Kusong-Dong, Yusong-Gu, Taejon, 305-701, Korea
E-mail doo@cais.kaist.ac.kr, Tel +82-42-869-3375, Fax +82-42-869-3310

Kyoung-Soon Bok, Woo-Suk Choi, and Chul-Lae Cho
Samsung Techwin co., LTD.
14 Nongseo-Ri, Kiheung-Eub, Youngin-Si, Kyounggi-Do, 449-712, Korea

Abstract

The electroless deposited Ni-P(Phosphorus) under bump metallurgy (UBM) layer was fabricated for Sn containing solder bumps. The amount of P in the electroless Ni film was optimized by controlling complexing agents and the pH of plating solution. And the interfacial reaction at the electroless Ni UBM/solder interface was investigated in this work. The intermetallic compound (IMC) formed at the interface during solder reflowing was mainly Ni$_3$Sn$_4$, and a P-rich Ni layer was also formed as a by-product of Ni-Sn reaction between the Ni-Sn IMC and the electroless Ni layer. A 1~4 μm of Ni$_3$Sn$_4$ IMC and a 1800~5000 Å of P-rich Ni layer were formed in less than 10 minutes of solder reflowing depending on solder materials and reflow temperatures. However, less than 1 μm thickness of the electroless Ni layer was consumed. It was found that the P-rich Ni layer contains Ni, P and a small amount of Sn (~7 at%). The atomic ratio of Ni:1P indicates that there is Ni$_3$P phase in the Ni-rich Ni layer which was verified by the X-ray analysis. No Sn was detected at the electroless Ni layer located just below the P-rich Ni layer. Therefore, the P-rich Ni layer formed as a by-product of Ni-Sn interfacial reaction, is not appropriate for a Sn diffusion barrier at the electroless Ni UBM and Sn containing solders.

Because of the fast diffusion of Sn into the P-rich Ni layer, series of Kirkendall voids were found in the Ni$_3$Sn$_4$ IMC, just above the P-rich Ni layer during extended solder reflowing. The amount of the Kirkendall voids appeared to be proportional to the growth of the P-rich Ni layer determined by solder reflowing and subsequent annealing processes. Because the Kirkendall voids are considered to be the main cause of the brittle fracture, it is recommended to restrict the growth of the P-rich Ni layer by choosing proper processing conditions. The growth kinetics of Ni-Sn IMC and P-rich Ni layer followed 3 steps: there was a rapid initial growth during the first minute of solder reflow followed by a reduced growth step, and finally a diffusion controlled growth. During the diffusion process, there was a linear dependence between the IMC and P-rich Ni layer thickness and $\sqrt{time}$.

Flip chip bump shear test was performed to measure the effects of the IMC and P-rich Ni layers on bump adhesion property. Most failure occurred at the inside of soft solder and partly at the Ni$_3$Sn$_4$ IMC. Exposed portion of the Ni$_3$Sn$_4$ IMC area after shearing bump surface increased, as solder reflow time increased. The brittle characteristics of the Ni-Sn IMC and the Kirkendall voids at the electroless Ni UBM-Sn containing solder system cause brittle bump failure which result in a decreased bump adhesion strength.

Introduction

Recently, in micro-electronic packaging applications, electroless Ni plating has been applied for flip chip bumps and under bump metallurgies (UBM) because of its many advantages, such as maskless selective metal deposition, low cost processing, good solder wettability, and good solder diffusion barrier compared with the conventional solder bumping and UBM processes [1,2,3,4]. However, issues like improvement of the reliability of the electroless Ni and studies of the interactions with solders have to be investigated in order to apply the electroless Ni extensively. Unlike the Ni layer prepared by vacuum deposition, the electroless Ni plated by hypophosphite (H$_2$PO$_2^-$) has been known that phosphorus (P) in the electroless Ni greatly influences the interfacial reactions with solders. And solder joint reliability must be also closely related to the P in the electroless Ni [5,6,7,8]. Consequently, the behavior of P at the electroless Ni/solder interface has to be investigated.

In the case of electroless Ni, not only IMCs but also P rich Ni layer was detected during the solder reflows [5,8]. This P rich Ni layer forms because of the phosphorus accumulated at the interface between the electroless Ni and the IMC layer. Jang reported that P rich Ni layer was composed of Ni$_3$P phase by TEM (Transmission electron microscopy) analysis [5]. Apparently, solder joint failure is closely related to the growth of these products at the electroless Ni/solder interface. Ni-Sn IMCs are very brittle and P rich Ni layer is also considered to have poor solderability [1,2,4,8]. In present study, interfacial reactions between the electroless Ni and solders (96.5 Sn-3.5Ag and 62.5 Sn-37.5Pb) and the shear strength of the solder bumps was measured. The P rich Ni layer was also investigated in detail: its composition, growth, and phenomena at adjacent layers due to the generation of the P rich Ni layer.
Experimental

Electroless Ni-P UBM fabrication

Test chips which have 100 µm×100 µm area Al pad and 400 µm pitch were fabricated after a 1 µm Al sputtering on Si wafer. Table 1 shows the process flow of the electroless Ni plating. Before the electroless Ni plating, double zincate process was performed to remove the Al₂O₃ layer and to activate the Al surface. Zincate solution was made of NaOH and ZnO, whose ratio was optimized to create fine and numerous Zn particles on Al pad [2,3]. After the double zincate process, a 5 µm electroless Ni UBMs were formed.

Table 1. Electroless Ni deposition processes on an Al surface

<table>
<thead>
<tr>
<th>Process</th>
<th>Solution</th>
<th>Time</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning</td>
<td>HNO₃ 50%</td>
<td>20 sec</td>
<td>N/A</td>
</tr>
<tr>
<td>Zincate pretreatment</td>
<td>ZnO, NaOH</td>
<td>20 sec</td>
<td>N/A</td>
</tr>
<tr>
<td>Acid dipping</td>
<td>HNO₃ 50%</td>
<td>5 sec</td>
<td>N/A</td>
</tr>
<tr>
<td>Double Zincate</td>
<td>ZnO, NaOH</td>
<td>20 sec</td>
<td>N/A</td>
</tr>
<tr>
<td>Electroless Ni plating</td>
<td>NiSO₄·6H₂O, NaPH₄O₂·6H₂O, CH₃COONa, Lactic acid, Thiourea</td>
<td>20min</td>
<td>5 µm</td>
</tr>
<tr>
<td>Immersion Au plating</td>
<td>Immersion Au solution</td>
<td>20min</td>
<td>0.2 µm</td>
</tr>
</tbody>
</table>

The temperature of the plating bath was controlled at 90 ± 0.5 °C. Then, a 0.2 µm Au, which prevents Ni oxidation and increases initial solderability, was plated on the electroless Ni UBM. Eutectic 62.5 Sn-37.5 Pb and eutectic 96.5 Sn-3.5 Ag were selected as solder materials. Using screen-printing method, solder bumps were fabricated on the Ni/Au UBMs. Reflowing steps were classified in 3 stages: flux activation zone at 150 °C for 1 minute, dwell zone at 210 °C and 250 °C, respectively, and cooling zone for 90 second.

Results and Discussions

Fabrication of Electroless Ni UBM

When hypophosphite (NaH₂PO₂·H₂O) is used as a reducing agent, phosphorus must be involved in electroless Ni because of the reaction in equation 1.

\[ H_2PO_2^- + H \rightarrow P + OH^- + H_2O \] (Equation 1)

Electroless Ni is divided into 3-types according to the P content in it. (less than 4 wt%, more than 10 wt%, and intermediate region) It was reported that properties and structure at each region are apparently different [3,11]. Therefore, if electroless Ni is applied to the UBMs, P content must be seriously considered. It has been known that the low P electroless Ni, whose structure is crystalline, has many defects such as high stress, high hardness and magnetic moment [11]. Therefore, almost electroless Ni used in micro-electronic packaging application has more than 4 wt % P content. However, when more P is included in electroless Ni, P acts like an impurity and it generates various unexpected effects on the electroless Ni. Therefore, an electroless Ni with medium P content (4 wt%~10 wt%) would be suggested in our work, and also taken the reasonable plating speed into consideration when the electroless Ni was fabricated.

To control these two crucial variables, additives in the electroless Ni plating solution and pH of the solution changed. Generally, NiSO₄ and NaH₂PO₂ are used as a Ni source and a reducing agent, respectively. However, various chemicals are used as complexing agents and properties of the electroless Ni are seriously dependent on them. Two kinds of complexing agents were selected: sodium acetate (CH₃COONa) and lactic acid (CH₃CH(OH)COOH). Also, thiorea (H₂NCSNH₂) was used as a stabilizer. Figure 1 represents the effects of complexing agents on P content and plating speed. As the concentration of the complexing agents increases, the plating rate, which is related to surface roughness, decreases abruptly and there is also a small increase in P contents. The reason why the complexing agent affects these properties is due to its tendency to reduce the concentration of free Ni ions in plating solution [3]. From figure 1, the concentration of the complexing agent to obtain the optimum surface roughness and plating rate can be decided.

Fig. 1. The effects of complexing agent on P content and plating speed.

Another variable, which can control plating speed and P content, is the pH of the plating solution. Figure 2 shows the relationships of the plating speed and P content as a function of pH. Figure 2 indicates that P content is very sensitive to pH. To obtain the intermediate range of P content (4~10 wt%), pH should be adjusted below 5. Therefore, the plating rate and surface roughness of the electroless Ni can be determined by concentration of the complexing agent and P content can be controlled by pH of the solution.

Finally, the electroless Ni which showed 12.55 ± 0.40 at% (7.05 wt%) P content, and 437±174Å average surface roughness (Peak to peak valley was 4201±1774Å and root mean square of roughness was 554±218Å) was obtained. At this plating condition, plating rate was 0.25 µm/min.
Resistivity and hardness of the electroless Ni were 70 ± 10 µΩ-cm, 500 ± 50 HV (Vickers hardness), respectively.

**Fig. 2.** Variations of plating speed and P content as a function of pH.

**Analysis of the Electroless Ni-Solder Interface**

To investigate the reactions at the electroless Ni/solder interface, all samples were cross-sectioned to reveal the growth of IMC and other products. Figure 3 shows the typical interface between the electroless Ni and the eutectic 96.5 Sn-3.5 Ag solder after reflowing at 250 °C for 1 minute. Ni-Sn IMCs, shown as layer II in figure 3, had an irregular shape and were easy to find. Besides the Ni-Sn IMCs, a dark layer, shown as layer III, was also observed between the IMC layer and electroless Ni layer. Using energy dispersive X-ray spectroscopy (EDS), the IMCs (layer II) were analyzed that they were composed of 43 at% Ni and 57 at% Sn, indicating Ni₃Sn₄ phase. There are three IMCs in the Ni-Sn binary system, all stable at room temperature: Ni₃Sn₄, Ni₃Sn₂, Ni₃Sn. Most early works reported that only Ni₃Sn₄ phase was present in liquid Sn-electroless Ni interaction [5,6,7,8,9,10,12,13].

When the dark layer and the electroless Ni were investigated, diffusion behavior of P atoms during the reflowing process can be estimated. The electroless Ni (layer IV) was composed of 91.3 at% Ni and 8.7 at% P. The P content, which was 12.6 at% before soldering, decreases by 8.7 at% after soldering due to the diffusion of P atoms into the interface or solder. And the dark layer (layer III) appeared as a thin continuous layer was composed of 73.6 at% Ni, 19.1 at% P and 7.3 at% Sn. However, besides continuous layer, discontinuous “dot” phase were observed in the dark layer after reflowed longer time. This “dot” phase was shown in figure 4-(c) (region I). Most portion of the dark layer in figure 4-(c) was a thin continuous layer, and only small portion of discontinuous “dot” phase was distributed in the P rich Ni layer. And the composition of this “dot” phase was 75.0 at% Ni and 25.0 at% P, exactly 3 Ni : 1 P ratio. Because of consumption of Ni with Sn, P was accumulated at the electroless Ni/IMCs interface resulting in a P rich Ni layer. Previously, it was reported that the P rich Ni layer was made of Ni₃P crystalline phase by TEM analysis [5].

However, in this study, 7.30 at% Sn atom was observed in the P rich Ni layer and, simultaneously, the discontinuous “dot” phase known as Ni₃P is distributed in the P rich Ni layer. Therefore, it is concluded that the discontinuous “dot” phase is Ni₃P crystalline phase, and the thin continuous dark layer is a Sn containing metastable Ni-P phase. Moreover, this discontinuous Ni₃P phase only appears during severe reflow conditions such as high temperature soldering and long-time reflowing.

Existence of the Sn atoms in the P rich Ni layer is a very interesting phenomenon. Another evidence of Sn diffusion into the P rich Ni layer is the Kirkendall voids in the Ni₃Sn₄ IMC layer, just above the P rich Ni layer. The Kirkendall voids in the Ni₃Sn₄ IMC are shown in figure 4 and figure 5. Figure 4 shows how the Kirkendall voids grow as reflow time increases during solder reflow at 250 °C. And figure 5 shows magnified view of the Kirkendall voids in two typical cases. First, in Sn-Pb solder bump reflowed at 250 °C for 4 minutes, there are series of tiny Kirkendall voids in Ni₃Sn₄ IMC. (Figure 5-(a)) However, in Sn-Ag solder bumps reflowed at 250 °C for 256 minute, larger Kirkendall voids which have about 1 µm diameter are observed.
Fig. 4. Interfacial reactions at the electroless Ni/Sn-Pb solder interface as a function of reflow time

(a) 250 °C, 1 minute
(b) 250 °C, 16 minutes
(c) 250 °C, 256 minutes

shows the amount of the Kirkendall voids at each soldering case

The Kirkendall voids are usually considered to be developed at the inside of solder, above IMC phase, due to the Sn diffusion into the IMC layer. However, these Kirkendall voids are different from those reported in other solder joint system because they appeared at the inside of Ni₃Sn₄ IMC. The Kirkendall voids in Ni₃Sn₄ IMC represent that Sn atom is the faster diffusion element than Ni or P during soldering reaction. Sn atoms were detected up to the bottom of the P rich Ni layer, and then disappeared at the electroless Ni layer. Therefore, electroless Ni layer behaves as a good Sn diffusion barrier.

The above results show that the amount of the Kirkendall voids was proportional to the thickness of the P rich Ni layer because diffusion of Sn atoms occurred through the P rich Ni layer. The thicker P rich Ni layer grows, the more Kirkendall voids would be generated. From the practical point of view, the Kirkendall voids may cause brittle fracture at the solder joint. Therefore, it is important to be able to restrict undesirable growth of the P rich Ni layer.

Growth of the IMC and the P rich Ni Layer

It has been known that the formation of certain IMCs and the P rich Ni layer can have an undesirable effect resulting in a serious degradation of solder joint reliability, as described before [1,2,4,8]. Therefore, the growth rates of these products and their growth mechanism have to be understood. The variables were the composition of the solder alloy and reflow time. Eutectic Sn-Pb solder and eutectic Sn-Ag solder were selected as solder materials, and their reflow temperature were 210 °C and 250 °C, respectively. The growth of these products in eutectic Sn-Pb solder bump was shown in figure 4. And figure 6 shows measured thickness of IMC and P rich Ni layer as a function of reflow time. The reflow time varied from 1 minute up to 256 minutes. In fact, though soldering over 10 minutes could be not performed in real situation, severe conditions like 256 minutes reflowing were investigated to reveal growth kinetics of the each product. All reflowed samples were mounted and cross-sectioned. The samples were analyzed by backscattered electron image and EDS.

Regardless of solder materials, consumption of the electroless Ni, whose initial thickness is 5 µm, did not occur seriously. Therefore, the electroless Ni was very good for UBM material because of low reactivity with solders. However, the thickness of the IMC layer was much larger in comparison with the consumption of Ni layer. In the eutectic Sn-Pb solder bumps, the IMC layer and the P rich Ni layer were 1.02 µm, 1800 Å in thickness in early 1 minute, and 1.47 µm, 2380 Å in thickness after 8 minutes of reflowing, respectively. And, In the eutectic Sn-Ag solder bumps, the IMCs layer and the P rich Ni layer had a thickness of 1.38 µm, 2030 Å in the early 1 minute, and 3.73 µm, 5010 Å after 8 minutes of reflowing, respectively. The growth rates for the IMCs and the P rich Ni layer in the eutectic Sn-Ag solder bumps were much greater than those for the eutectic Sn-Pb solder bumps because eutectic Sn-Ag solder had more Sn content and, above all, because reflow temperature was 40 °C higher.

As reflow time increases, the IMCs and the P rich Ni layer grow gradually. However, growth rate after 1 minute is very slow rather than that before 1 minute. A number of theories about the growth of IMCs have been proposed. Most of them were based on diffusion controlled growth mechanism. That
means that there is a linear dependence of the thickness of products on (time)$^{1/2}$. Many works reported that the growth of IMCs in the Ni/solder interface followed the ideal diffusion controlled mechanism [5,6,10]. However, Lee and Lin proposed the two-step diffusion controlled growth mechanism consisting of rapid initial growth and later a diffusion controlled growth [7,12]. And Kang and Ramachandran reported the 3-stage growth mechanism characterized by rapid initial growth (t<30second), followed by a “hold”, and then diffusion controlled growth (t>30minutes) [9].

Figure 7 represents the results above in terms of thickness versus time$^{1/2}$. The result in figure 7 is quite consistent with the 3-stage growth mechanism reported by Kang and Ramachandran. The growth in figure 7 can be divided into 3-stage: Rapid growth within 1minute, reduced growth until about 30 minutes, and a linear relationship after 30 minutes. However, the exact time, which divides each step, is not well defined and the growth rate of the IMC is slower than the values obtained in Kang’s work. This discrepancy is due to the specific conditions of the experiment: their work involved pure Ni and liquid Sn instead of electroless Ni and eutectic solders. Moreover, it has been known that the reaction rate at the electroless Ni/solder interface is much slower than that of the pure Ni [14].

From the results above, the total amount of the IMC and the P rich Ni layer at the electroless Ni/solder interface can be estimated. And initial reflowing step is very important to control the thickness of the IMCs and the P rich Ni layer because the total amount of each layer is mostly determined within less than 1 minute of reflowing.

**Fracture Mode Investigation**

After solder bumps were fabricated as shown in figure 8, ball shear strength and fracture mode were investigated using a ball shear tester and SEM. The ball shear strength was measured at the 15 µm stylus height. Reflow times vary from 1minute to 16minutes. Shear strength at each condition ranged from 80 to 100 MPa, and there was no certain dependence of reflow time on shear strength, because initial fracture occurred inside of solders in all conditions. However, detailed fracture surface analysis using SEM shown in figure 9 shows interesting behavior.

From the shear direction of the solder bumps, it is obvious that every fracture initiated inside of soft solder. As reflow time increased, outer exposed regions changed gradually from smooth surface to rough and coarse surface. (figure 9-(b), 9-(c)) Ni$_3$Sn$_4$ IMC was detected on this surface. Figure 10-(a) shows a brittle fractured surface treated for a 16-minute reflowing. Trace of the Kirkendall voids at the exposed Ni$_3$Sn$_4$ IMC was also found. The size and shape of these traces were very similar to those of Kirkendall voids shown in figure 5. Figure 10-(b) represents the top view of Ni$_3$Sn$_4$ IMC after the sample was reflowed for 16 minutes at 250 °C, followed by solder bump etching. Compared fractured surface (Figure 10-(a)) with etched surface (Figure 10-(b)), they are quite different even though they are the same Ni$_3$Sn$_4$ phase.
of Ni$_3$Sn$_4$ IMC reflowed at 250 °C for 16 minutes (after solder bump was etched).

This means that the brittle fracture must occur along the inside of Ni$_3$Sn$_4$ IMC and trace of the Kirkendall voids.

From the above results, two fracture mechanisms in electroless Ni/solder joint can be proposed: the brittle property of Ni$_3$Sn$_4$ IMC and the presence of the Kirkendall voids. As reflow time increased, more brittle fracture was observed because of the growth of both IMC and Kirkendall voids.

Conclusions

The electroless Ni plating process has been developed for flip chip bumps and UBM applications. Ni$_3$Sn$_4$ intermetallic compound and Pb-rich Ni layer were observed at the electroless Ni/solder interface. The Pb-rich Ni layer consisted of mostly a metastable continuous layer, including Sn atoms, and discontinuous Ni$_3$P crystalline phase. Because of fast diffusion of Sn atoms into the Pb-rich Ni layer, Kirkendall voids were generated in the Ni$_3$Sn$_4$ IMC, just above the Pb-rich Ni layer. And the amount of the Kirkendall voids was proportional to the thickness of Pb-rich Ni layer. The growth of the IMCs followed the 3-stage diffusion-controlled mechanism characterized by rapid initial growth, followed by a reduced growth step, and then the diffusion controlled growth. The growth of the IMCs and the Pb-rich Ni layer within a 1 minute reflowing was much higher than that after a 1 minute reflowing. From the ball shear test, most solder bumps were sheared inside of solder. However, brittle fracture occurred at Ni$_3$Sn$_4$ IMC region when the solder bumps were reflowed for a longer time. And the Kirkendall voids were also found at the fractured Ni$_3$Sn$_4$ surface. Therefore, the brittle property of the Ni$_3$Sn$_4$ IMC and the growth of the Kirkendall voids may induce brittle fracture at the electroless Ni UBM system. And the growth of the IMCs and the Pb-rich Ni layer, and the Kirkendall voids must be restricted to prevent the brittle fracture at the electroless Ni/solder joint.

Acknowledgments

The authors would like to acknowledge financial support provided by the Samsung Techwin Co., Ltd., KOREA.

References