Interfacial reactions on electrolytic Ni and electroless Ni(P) metallization with Sn–In–Ag–Cu solder

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Abstract
In this study, interfacial reactions of electrolytic Ni and electroless Ni(P) metallization of the ball-grid-array (BGA) substrate with the molten Sn–9In–3.5Ag–0.5Cu (wt.%) solder alloy were investigated, focusing on identification of the intermetallic compound (IMC) phases and the IMC growth rates at various reflowing times. A fixed volume of BGA solder ball (760 μm diameter) was used on a substrate metallization pad with a diameter of 650 μm. The peak reflow temperature was fixed at 240 °C while the reflow time was varied between 1 and 120 min. The intermetallic compounds thickness was lower on the electroless Ni(P)/solder interface. The consumption of the electroless Ni(P) in Sn–9In–3.5Ag–0.5Cu was also lower than that of the electrolytic Ni. The appearance of a P-rich Ni layer at the interface played a major role in inhibiting the overall interfacial reaction in the soldering reaction with the electroless Ni(P) metallization. The stable IMC initially formed at the interface was the (Cu, Ni)₆(Sn, In)₅ phase. During further reflowing, the (Cu, Ni)₃(Sn, In)₄ IMC started forming because of the limited Cu content in the solder. These bright low-Cu IMCs appeared earlier at the interface of the Ni/solder system than the Ni(P)/solder system. Bulk of the Sn–9In–3.5Ag–0.5Cu solder contained Cu₆(Sn, In)₅, Au–In–Sn and Au–In–Sn precipitates embedded in the Sn-rich matrix.

Keywords: Indium containing solder alloy; Electrolytic Ni; Electroless Ni(P); Intermetallic compounds

1. Introduction
The demand for lead-free solders and high-density input–output interconnection technology is rapidly developing for advanced electronic assemblies. Based on increasing pressures to achieve environmentally friendly electronic materials and processes, and indeed, growing governmental regulations around the world, the drive has highlighted the fact that the industry has not yet arrived at a consensus for lead-free solders [1–3]. Owing to several advantages, the Sn–Ag–Cu alloy has been recommended by the National Electronic Manufacturing Initiative (NEMI) to replace the eutectic Sn–Pb solder in reflow processing [4]. However, the high melting point of this alloy (217 °C) as compared to the traditional Sn–37Pb solders (183 °C) is an issue in electronic packaging. An attractive approach to lower its melting temperature is to use an additive such as indium. In application, indium added solder has high ductility, improved fatigue resistance and good wettability [5,6]. Some large Ag₃Sn intermetallic plates use to appear in the Sn–Ag–Cu solder matrix. It is reported that large plate-like Ag₃Sn structures can grow rapidly within the liquid phase, during cooling, before the final solidification of solder joints [7]. The appearance of such large compounds in the solder can be detrimental to the mechanical properties of the solder joints [8,9]. The formation of Ag₃Sn is suppressed by the presence of indium in Sn-rich solder and Ag₂In appears in the solder matrix [10]. It is also reported that the addition of indium into Sn-based solders facilitates the formation of AuIn₃ intermetallics at the solder/pad interface, capable of inhibiting Au dissolution into solder matrix to generate the brittle AuSn₄ phase [10]. It is also found that the failure in In–Sn solder joints caused by Au embrittlement can be curtailed because of the lower solubility of Au in In–Sn alloys [11]. Unlike tin, indium has a much lower affinity for precious metals and dissolves gold.
at a rate 13–14 times slower than tin [12]. Also, in devices with operational temperature below 125 °C, the intermetallic that forms between In and Au is of a much more compliant and ductile nature and is not susceptible to embrittlement [12]. There already exist some well-developed solders (e.g. Sn–2.8Ag–0.5Cu, Sn–20In–2Ag–0.5Cu) from the Sn–Ag–In system with a melting temperature range close to that of the eutectic Pb–Sn [10,13]. Unfortunately, the cost of the In content within these solders is notably high. It is also recommended that these high indium containing solders should not be used over 100 °C due to the formation of a low temperature eutectic phase at 118 °C [12]. A compromise may be reached by consolidating the features of high In-containing solder and Sn–Ag–Cu alloys with the Sn–9In–3.5Ag–0.5Cu solder as a substitute for the traditional Sn–37Pb solder.

The most common surface finishes on BGA pads are electrolytic Ni/Au and electroless Ni(P)/Au plated over the Cu pad of the flexible substrate. The electrolytic Ni/electroless Ni(P) acts as a diffusion barrier layer and Au acts as an oxidation barrier layer. The use of new materials will necessitate high standards for reliable, high-density, assembly. Especially a flip chip under bump metallurgy (UBM) comprising few micron thick metal or alloy layers which requires precise designing so that adequate diffusion barriers and good adhesion functions can be fulfilled [14]. At the same time, the UBM layers should not dissolve too strongly into liquid solders and react excessively with them. It is of great importance to control the metalurgical compatibility of solders with different metallization materials. Therefore, the present study was carried out to investigate the interfacial reactions of the electrolytic Ni and the electroless Ni(P) metallization with the Sn–In–Ag–Cu solder.

2. Experimental procedures

The solder mask defined copper bond pad of a substrate of the BGA package was used as a base for electrodeposition of Ni and electroless deposition of Ni(P). The P content in the Ni(P) layer was around 16 at.%. The thickness of Ni(P) and electrolytic Ni plating was about 3.5 and 7.5 μm, respectively. Au plating was immediately layered on top of the electrolytic Ni and electroless Ni–P to avoid oxidation of the nickel surface. In both the cases, Au plating thickness on the surface finish was about 0.5 μm. Differential scanning calorimetry analysis showed the solidus and liquidus temperatures of the Sn–9In–3.5Ag–0.5Cu solder at 203 and 208 °C, respectively. Lead-free 87%Sn–9%In–3.5%Ag–0.5%Cu (wt.%) solder balls with a diameter of 0.76 mm, were placed on the pad of the substrates as shown in Fig. 1 and then soldered at 240 °C for times (t) of 1 (as-reflow), 5, 30, 60 and 120 min in a convection reflow oven. The flux used in this work was a commercial no-clean flux.

To investigate the microstructure, the as-reflowed and extended reflowed samples were mounted with resin, cured at room temperature, mechanically ground and then polished in order to obtain the cross-sections of the solder/UBM interfaces. The chemical and microstructural analyses of the gold-coated cross-sectioned samples were obtained by using a Philips XL 40 FEG scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDX). The accuracy of the compositional measurement was about ±5%.

3. Results and discussion

During reflow, the molten solder absorbs the entire Au layer in to solution, allowing the solder to react with the metallization material and to form different types of intermetallic compound at the interface as well as within the solder. Fig. 2 shows the microstructure of the as-reflowed interface between the substrate metallization and the indium containing lead-free solder. The IMCs thickness on the Ni metallization is relatively higher than that on the Ni(P) metallization. The difference in IMCs formation is more pronounced after 5 min of reflow (Fig. 3). The growth rate of IMCs is high for electrolytic Ni layer. According to EDX analysis, the IMCs composition is more or less similar for both
the metallization layers and is composed of Cu–Ni–Sn–In, i.e. (Cu,Ni)$_{1-x}$Sn$_{y}$In$_{1-y}$, and is based on Cu$_6$Sn$_5$. The amount of indium in the IMCs is small. The atomic percentage of Ni in the Cu–Ni–Sn–In quaternary compounds (QIMCs) is higher for the electrolytic Ni than for the Ni(P) layer. The EDX analysis shows that the composition (at.%) of the intermetallics at the interface between solder and Au/ Ni/Cu pads is Cu:Ni:Sn:In = 31:2:7:3, which corresponds to (Cu$_{0.58}$Ni$_{0.42}$)$_6$(Sn$_{0.94}$In$_{0.06}$)$_5$. Cheng et al. found that (Cu$_{0.76}$Ni$_{0.24}$)$_6$(Sn$_{0.86}$In$_{0.14}$)$_5$, Ag$_2$In and AuIn$_2$ were the stable phases in the Sn–20In–2Ag–0.5Cu soldering reaction on Au/Ni surface finish[10]. In the present study, as the indium content in the solder is less, the indium content in the interfacial IMCs is also less. A thin dark layer is observed between the interfacial IMCs and Ni(P) layer from the SEM images. EDX analysis shows that the phosphorous percentage of this dark P-rich Ni layer is about 25 at.%. This observation implies that the dark layer is composed of Ni$_3$P compound. Jang et al. [15] confirmed a crystalline Ni$_3$P compound at the interfaces through TEM studies, and proposed that amorphous electroless Ni(P) underwent crystallization during soldering with the Sn–Pb solder alloys. This kind of crystallization process is referred to as solder-reaction-assisted crystallization. The bulk of the Sn–9In–3.5Ag–0.5Cu solder contains Cu$_6$(Sn$_{0.86}$In$_{0.14}$), Au–In–Sn and Au–In–Sn precipitates embedded in the Sn-rich matrix. No Ag$_3$In or Ag$_3$Sn IMCs are observed in the In-containing solder. On the other hand, the composition (at.%) of the Au–In–Sn IMCs is Ag:In:Sn = 75:1:13:9, which corresponds to the Ag$_3$(In$_{0.65}$Sn$_{0.35}$) phase. Also no AuIn$_2$ IMC is observed in the solder matrix. The composition of the Au–In–Sn IMCs is Au:In:Sn = 33:2:68:20, which corresponds to the Au$_3$(In$_{0.65}$Sn$_{0.35}$). The formation of Au–In–Sn IMCs prevents the formation of more brittle AuSn$_4$ IMCs. It is already proven that subsequent aging treatments cause the AuSn$_4$ intermetallics in the solder matrix to migrate to solder ball/pad interfaces leading to the formation of a continuous (Au, Ni)Sn$_4$ intermetallic in the Sn–Pb solder balls [16–18]. The existence of a brittle (Au, Ni)Sn$_4$ layer is the reason for the lower reliability of the solder joint [19]. An interesting point to be noted is that according to the EDX analysis the Sn-rich solution phase contains around 7 at.% of In. For this high solubility of indium in Sn, small amounts of In have the chance to be involved in the interfacial IMCs formation. The average thickness of intermetallic compounds at the solder-substrate metallization interface after reflow for different durations is shown in Fig. 4. The initial growth rate of the IMCs is high for both the solder systems. With the prolonged isothermal reflow at 240 °C, the thickness of IMCs for both of these metallization layers increases at a distinctly different rate. It is also evident that the Cu–Ni–Sn–In IMCs in the Ni/solder system grow much faster than in the Ni(P)/solder system during extended reflow. The presence of P-rich Ni layer acts as a diffusion barrier layer between the solder and the substrate metallization. The formation of IMCs on the electrolytic Ni layer is quite straightforward. During extended reflow, the presence of thick intermetallics at the Ni/solder interface ultimately slows down both the Ni layer consumption and the growth rate of the intermetallics.

Fig. 2. SEM micrographs showing the interface after soldering for 1 min at 240 °C on (a) electrolytic Ni and (b) electroless Ni(P) layer.

Fig. 3. SEM micrographs showing the interface after soldering for 5 min at 240 °C on (a) electrolytic Ni and (b) electroless Ni(P) layer.
Fig. 4. Growth of intermetallic compound layers at 240 °C on different substrate layers.

Fig. 5. The consumed thickness of metallization layer vs. reflow time at 240 °C.

By measuring the remaining metallization thickness from the SEM micrograph and by subtracting it from the initial thickness, the consumed metallization thickness is deduced. Fig. 5 shows a comparison between the two metallization layers as regards thickness reduction due to dissolution in the Sn–9In–3.5Ag–0.5Cu solder. The initial consumption rate is high for both the metallization system. It is seen that the consumption of the electroless Ni is lower in the Sn–9In–3.5Ag–0.5Cu solder than that of the electrolytic Ni during extended reflow. The high growth rate of the IMCs with little bit of more Ni is the main reason for the high consumption of the electrolytic Ni layer in the indium containing solder.

During long time molten reaction, bright low-Cu quaternary IMC (QIMC) appears earlier at the interface of the Ni/solder system than the Ni(P)/solder system (Fig. 6). Here, the BGA solder ball of 0.23 mm contains a limited amount of Cu; it can be exhausted soon. Due to the long time molten reaction, these bright IMCs grow beneath the relatively dark high-Cu Cu–Ni–Sn–In IMCs layer, as most of the Cu in the bulk solder has been consumed and is incorporated in the upper quaternary IMCs. As the interfacial reactions are faster in the case of Ni layer, the exhaustion of Cu is also quicker. From the curve of the growth rate of IMCs (Fig. 4), the growth kinetics of IMCs slows down after 30 and 60 min for electrolytic Ni and electroless Ni(P) layer, respectively. It is concluded that low-Cu-containing QIMCs starts to form after the above mentioned periods and thus the IMCs growth rate slows down.

Another important point to be noted that in the case of Ni/solder system, the interface between the solder and the IMCs are more or less planner, i.e. the IMCs formation is uniform throughout the interface. Islam et al. also found the same phenomenon with the Sn–Ag–Cu solder[20]. In electroless Ni(P)/solder system, the formation of Ni3P along the interface may lead to a less uniform formation of the IMCs. With Sn–Ag–Cu solder, the high-Cu ternary IMCs show spalling with the appearance of low-Cu ternary IMCs along the interface[20]. For the addition of 9% indium in the solder, even with the appearance of low-Cu QIMCs, no spalling is observed after 120 min of reflow. That means even though the percentage of indium in the IMCs is low, it reduces spalling.

Fig. 7 illustrates the backscattered electron micrographs of the interface after reflow for 2 h at 240 °C. For the Ni layer, a high dissolution (around 3.2 μm) of the surface metallization is observed. On average, around 2.2 μm of Ni(P) layer is consumed with 120 min in molten condition. The consumption of the electroless Ni layer is not uniform throughout the interface. In some places more Ni(P) layer consumption is observed like an uneven etching phenomenon. At this stage, a layer type spalling is observed in those particular places with no more original Ni(P) layer below the P-rich Ni layer (Fig. 8a). It may be stated that when the supply of Ni from the pad is ended, spalling of the more Cu-containing QIMCs...
from the low-Cu-containing QIMCs starts to occur at the interface of the solder/Ni(P) system. With higher magnification (Fig. 8b), another compound layer is also observed between the low-Cu QIMCs and the P-rich Ni layer. The composition of this compound layer is Ni:Sn:In:P = 35.6:22.7:9.7:32. For long time reflow, a high amount of Kirkendall voids may be generated at the P-rich Ni layer during the diffusion process and some channels may also be created by the coalescence of these Kirkendall voids [20]. Due to this, a high dissolution of the electroless Ni layer is observed in those specific places. Through these channels, molten metal comes into contact with the Cu layer underneath the electroless Ni layer. Below the P-rich Ni layer, a bright layer is also detected at this stage (Fig. 9). This layer is determined to be Cu$_3$Sn phase through EDX. The existing layer of compounds limits the supply of Sn from the solder more than Cu from the substrate, so Cu$_3$Sn forms beneath the P-rich Ni layer.

Though the initial growth rate of IMCs formation is higher for the Ni layer, the rate is reduced after 30 min of reflow. It is already stated that the growth rate is related to the formation of low-Cu interfacial IMCs. The Ni layer consumption in the molten solder does not decrease too much even with such a lower IMCs growth rate. In the initial high-Cu IMCs, around 22 at.% of Ni is present, whereas in the bright low-Cu IMCs, the atomic percentage of Ni is around 33. Thus, the consumption of Ni from the substrate to produce a 1 μm thick low-Cu IMCs layer is much higher than to produce the same thickness of high-Cu IMCs. Though the growth rate of IMCs is reduced in the later stage, the overall consumption of Ni remains high.

It is important to note that according to EDX analysis, a high amount of Ni is also present in the P-rich Ni layer. So the consumption of electroless Ni in Sn–9%In–3.5%Ag–0.5%Cu is also attributed to the growth of the P-rich Ni layer whereas the IMCs growth is relatively less. The average thickness of the P-rich Ni layer is around 970 nm after 120 min of reflow. At this stage the percentage of P in this layer is around 37. For such a long time of molten condition, different types of Ni–P compound may crystallize. According to the composition of the P-rich Ni layer, it seems that Ni$_3$P$_x$ and Ni$_2$P may also have formed. Fig. 10 shows a plot of the P-rich Ni layer thickness versus time at 240°C.

The plot displays a linear relationship, so it can be assumed that the growth of the P-rich Ni layer in the Sn–In–Ag–Cu
solder is controlled by a diffusion process. The formation of the P-rich Ni layer in Pb–Sn solder is also proven to be diffusion controlled [15].

4. Conclusion

The effects of reflow on the interfacial reactions of the substrate metallization with Sn–9%In–3.5%Ag–0.5%Cu BGA solder ball are presented in this paper. Electroless Ni(P) layer shows less dissolution than the electrolytic Ni layer during the long time reflow condition. Less than 2.3 μm of the electroless Ni layer is consumed by the indium containing solder with 120 min molten reaction at 240 °C. However, a more than 3 μm thick electrolytic Ni layer is consumed by the same solder within the same reported period. The P-rich Ni layer acts as a good diffusion barrier layer, which deceases the dissolution rate of the Ni(P) layer. With the straightforward reactions, the interfacial IMCs formation on the Ni layer is higher and is more uniform throughout the interface. With the addition of 9% indium in the solder, the formation of Ag3Sn and AuSn4 compounds is suppressed. Ag11(In0.6Sn0.4) and Au0.58Sn0.42 compounds appear in the bulk solder. Electroless Ni(P) layer has lower dissolution and is more protective for the Cu layer during extended times of reflow.

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