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Phosphorus in Electroless Nickel Layers – Curse or Blessing?

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Abstract

The influence of co-deposited Phosphorous (P) (from low to high P) within an electroless Nickel layer, regarding the reliability of the solder joint integrity was investigated. The solder joint evaluation was carried, using solder mask defined BGAs as test vehicle and using the ball shear technique to establish the level of any “Brittle Fracture”.

The type and structure of the IMC created before and after thermal cycling was examined against the co-deposited P (from low to high P) within an electroless Nickel layer to determine if this has any influence on solder joint integrity.

Due to the nature of the electroless plating process, a high P-ENIG coating has a P content in the plated electroless Nickel layer of about 9.5 to 13 wt.%. This high P content leads to an amorphous structure, with no grain boundaries, which therefore influences the formation of the IMC between Nickel and solder. The high P content of the bulk electroless Nickel layer seems to control the diffusion rate of the Nickel into the solder, resulting into a dense and uniform IMC formation.

This paper describes the influence of co-deposited P (from low to high P) within an electroless Nickel layer, regarding “Brittle Fracture” and the reliability of the solder joint integrity, using solder mask defined BGAs as test vehicle.

The variation of the co-deposited P content did alter the characteristics of the ENIG surface, which impacts the yield at the assembler. It turns out that a high P content in the bulk Nickel layer increases the reliability of the solder joint.

ENIG Systems

In this paper Nickel / Gold surface finishes are investigated and correlated with their reliability during solder joint formation and bonding.

Solder joint formation of Nickel Gold surface finishes takes place by solving the Gold into the solder, and forming an intermetallic compound (IMC) between the Nickel and the Tin.

The kinetics of Ni/Sn IMC formation is well investigated and described already in several papers. The results show that the reaction mechanism with temperature as well as with time must be taken into account for a conclusive understanding of the IMC formation.

The parameters with relevance for reliability are electroless Nickel and immersion Gold thickness, and the P content in the bulk Nickel layer.

Experimental

BGA substrates were prepared with systematically varying ENIG layer thickness and varying bulk Phosphorus content.
The layers were characterized with X-ray fluorescence (XRF) and by scanning electron microscope (SEM) in an x-section.

Solderability was determined with a solder balance (Solderability Tester Multicore MUST II), comparing ENIG systems with different bulk Phosphorous content.

The following ball shear tests were done:
- BGA ball (SnPbAg) attachment on “as received” samples, comparing fracture behavior of ENIG systems with different bulk Phosphorous content.
- After BGA ball (SnAgCu) attachment the samples were exposed to thermo cycling (TC) (-55°C to 125°C / 900s – 3s – 900s) for 1000 cycles comparing fracture behavior of ENIG systems with different bulk Phosphorous content.

Solder joint integrity was determined by ball shear testing (Dage PC 2400) using solder mask defined and non solder mask defined pads.

Scanning Electron Microscope

Determination of the bulk Phosphorous (P) content of the ENIG layer is done by x-sectioning and SEM / EDX and is shown in wt.%.

XRF

The X-ray fluorescence intensity is proportional to the number of atoms within the probed volume (fraction of a mm^2, several µm depth). From this intensity, with the specific gravity of the layer entering as a proportional constant, the layer thickness is calculated. As the P content influences the composition of the probed volume, the P content analyzed from x-section / EDX was used.

When the instrument is properly calibrated, the measured Nickel layer thickness is correct for a known P content.

Solderability

As a control tool on site at the PCB producer, solderability tests as wetting balance tests are typically performed on a frequent base. Using either special coupons plated during production or taking the PCB itself. This test gives a good indication about overall quality of the final finishing plating process. As equipment runs automatic and results are numeric, they are operator independent.

The Multicore MUST II system performs each test with a fresh solder ball, avoiding any solder contamination, compared to using a solder pot. The tested samples as well as the solder ball are fluxed, before the sample is immersed into the solder ball. Results are given for wetting force and wetting time, additionally a time force diagram is plotted. Typical values shown are maximum wetting force (F_{max}), time to F_{max}, time to 2/3 F_{max}, force after 2 s (F_1) and after 5 s (F_2).
Pass / fail criteria within this paper is time to 2/3 F_{max} being smaller 1s.

Ball Shear Test

Manufacturers and assemblers of the BGA-laminate typically apply ball shear tests. As the individual pads are soldermask defined (SMD, Figure 1), the mechanical strength against a pad pull out is higher compared to a non-solder mask defined (NSMD, Figure 2) pad, as they are typically found on the board side. Higher strength against pad pull out will force the fracture to occur at the metallic layer, the IMC or the solder, or any interphase in between.

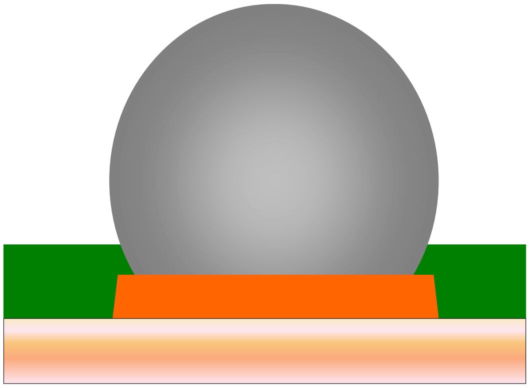


Figure 1 - Solder Mask Defined Pad (SMD)

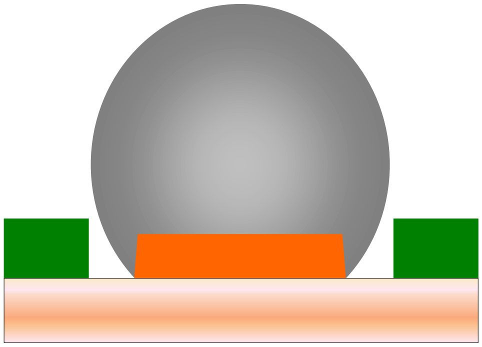


Figure 2 - Non Solder Mask Defined Pad (NSMD)

A BGA solder ball (760µm diameter) is soldered onto the SMD pad (600µm diameter opening) or NSMD pad (600µm diameter) and sheared off using a DAGE PC 2400 shear tester.

The surface of the remaining pad is analyzed and the fracture classified (Figure 4) as ductile (fracture in the solder / pad pull out) or brittle (fracture at the intermetallic layer).
Additionally force length diagrams are plotted. Diagrams with a steep descent after the maximum height represent the brittle interfacial fracture, while a flat descent represents the ductile plastic deformation of the solder (Figure 3).
In order to elucidate the solder joint integrity for the here tested ENIG layer systems, samples with 3µm to 6µm of electroless Nickel and 0.05µm to 0.15µm immersion Gold were assembled with SnPbAg solder balls (760 µm diameter) using Litton Kester 950 E3.5 (type F-SW33) as flux, in convection reflow oven.

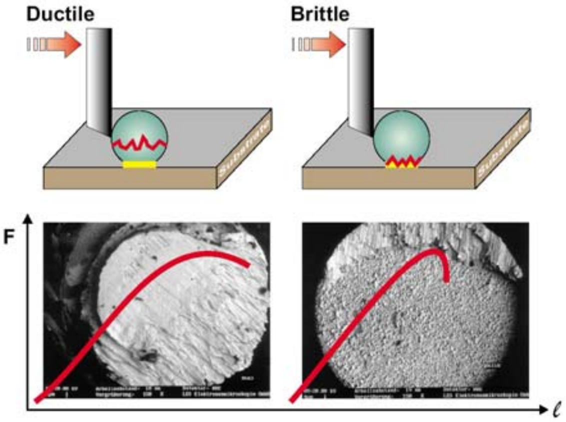
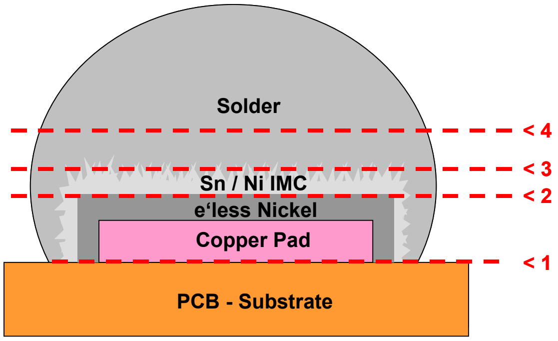


Figure 3 - Schematic Diagrams of Ball Shear Test and SEM Micrographs of Ductile and Brittle Fracture



Fracture mode:

1 pad pull out
2 between nickel and Sn / Ni IMC
3 between Sn / Ni IMC and solder
4 with in the solder

Figure 4 - Classification of Fracture Mode 1- 4 after Ball Shear Test

Fracture mode 4 (Figure 4) and 1 represent a ductile fracture, where the fracture occurs within the solder (mode 4) or in case of mode 1, the BGA pad is sheared of the PCB.

Fractures at the interphase between solder and Ni/Sn IMC represent a brittle fracture, same as a fracture between the e'less Nickel layer and the Ni/Sn IMC.

Results

Solderability – Multicore MUST II

As ENIG finishes are mostly used as solderable surface finish, solderability tests at the PCB producer site are common quality control tool. These tests are performed on a frequent base, collecting solderability data since many years. Data gained during assembly, compared to data gained by wetting balance resulted in pass / fail criteria for the Multicore MUST II system in time to 2/3 F_{max} to be smaller 1s.

As an example Figure 5 shows data for 156 measurements for each ENIG system. Altering bath age for the respective Nickel bath and for the Gold bath, none of the finishes exceeded the fail criteria for time to 2/3 F_{max} of 1s.
Average time to 2/3 F_{max}, for the 7- 9% P ENIG system was 0.36s, and for 9.5- 13% P ENIG system 0.30s.
Standard deviation for the 7- 9% P ENIG system was 0.18s, and for 9.5- 13% P ENIG system 0.15s.

This will result in "x + 3s" (for 99,73% of all expected times to 2/3 F_{max}) a maximum for the 7- 9% P ENIG system in 0.90s, and for 9.5- 13% P ENIG system in 0.75s.

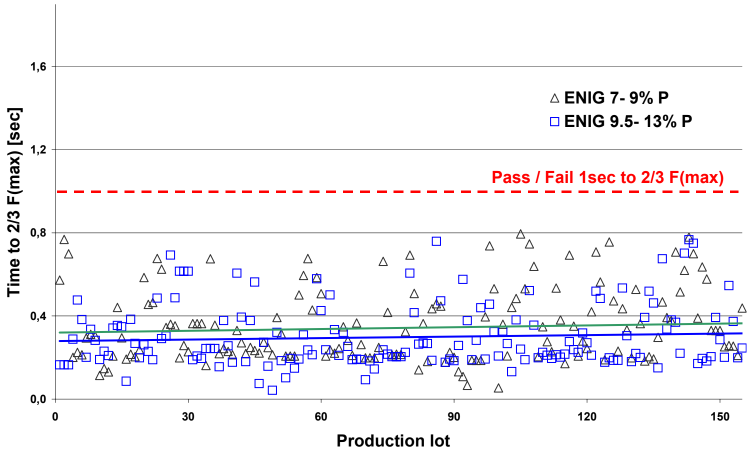


Figure 5 - Diagram for Time to 2/3 F_{max} Comparing a 7- 9% P ENIG System with a 9.5- 13% P ENIG System

Thickness of Nickel Gold Layers

The standard technique for the determination of the Nickel Gold, or Nickel Palladium Gold, layer thickness is X-ray fluorescence. The effective P content is considered as major sources of uncertainty.

Throughout these investigations, the P content was measured by x-section / EDX, implying that the P content constant in a series of samples.

Typical examples for the P determination with EDX (x-section) are given for samples used during this investigation. (See Figure 6.)

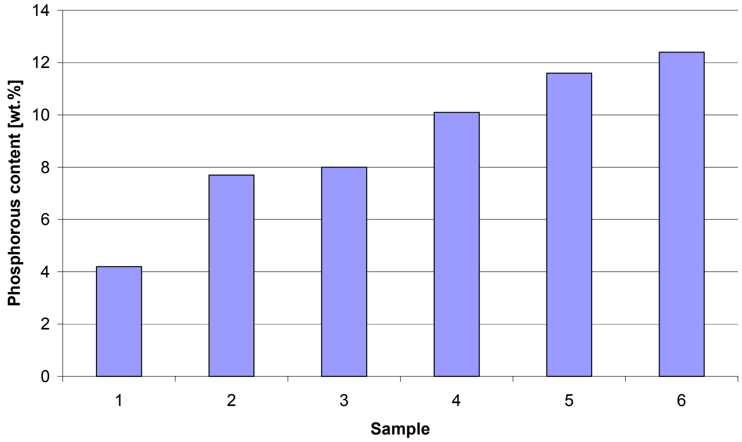


Figure 6 - Comparison of P Values of Samples during this Investigation, Measured by x-Section / EDX

Solder Joint Integrity of Nickel Gold Layers

It is well known that the formed Ni/Sn IMC influences the solder joint integrity. A uniform and dense IMC is essential for a ductile solder joint.

As an example, Figure 7 shows a series of ball shear with 600 µm SMD pads. Two ENIG systems are compared, one with a bulk P content of 7-9%, the other with 9.5-13% P. The plated ENIG thickness varied from 3.2µm to 6.1µm, and the Gold thickness from 0.06µm to 0.15µm. Solder balls were attached to samples directly after plating.

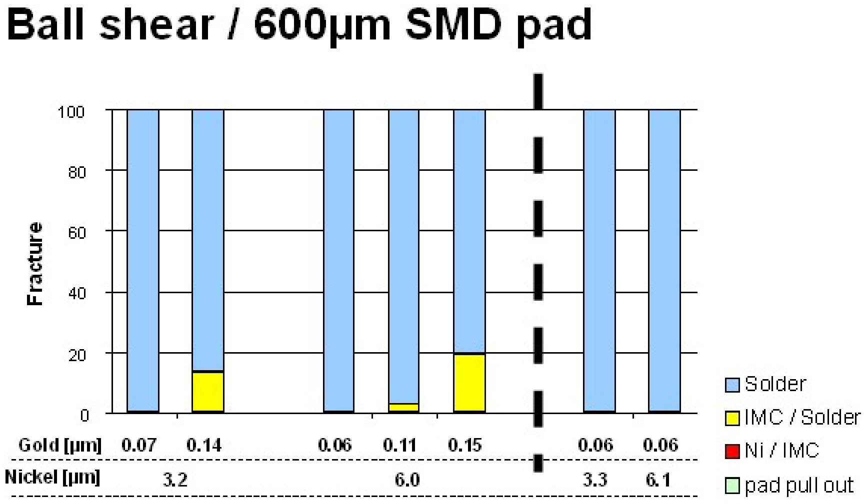


Figure 7 - Detected Fracture Modes of ENIG Layers on 600µm SMD Pads

Samples with a low Gold thickness (0.06µm and 0.07µm) layers fracture mostly within the solder (Mode 4). This fracture behavior is independent of P content.

Here tested samples with low Nickel thickness (3.2µm and 3.3µm) or / and high Gold thickness (> 0.14µm) show fractures at the interphase between Ni/Sn IMC and solder.

As an example, Figure 8 shows a series of ball shear with 750 µm SMD pads. Two ENIG systems are compared, one with a bulk P content of 7-9%, the other with 9.5-13% P. The plated ENIG thickness varied from 3.2µm to 6.1µm, and the Gold thickness from 0.06µm to 0.15µm. Solder balls were attached to samples directly after plating.

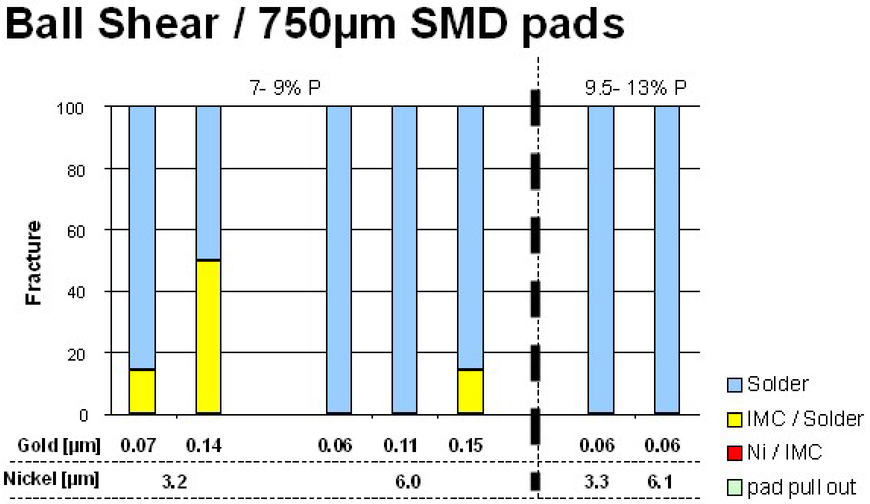


Figure 8 - Detected Fracture Modes of ENIG Layers on 750µm SMD Pads

Samples with low Nickel thickness (3.2µm) and a P content of 7-9% show fractures at the interphase between Ni/Sn IMC and solder, this is independent of the here tested Gold thickness (0.07µm and 0.14µm). Whereas low Nickel thickness (3.3µm) with 9.5-13% P have a ductile fracture mode within the solder.

Samples with a high Nickel thickness (6.0 µm and 6.1µm), regardless of the here tested P content and a Gold thickness smaller than 0.11µm fractures within the solder (Mode 4). Having a Gold thickness of 0.15µm on a 7-9% P Nickel layer with 6.0µm thickness, nearly 15 out of 100 fractures occurred at the interphase between Ni/Sn IMC and solder, as brittle fracture.

As an example, Figure 9 shows a series of ball shear with 600 µm NSMD pads. Two ENIG systems are compared, one with a bulk P content of 7-9%, the other with 9.5-13% P. The plated ENIG thickness varied from 3.2µm to 6.1µm, and the Gold thickness from 0.06µm to 0.15µm. Solder balls were attached to samples directly after plating.

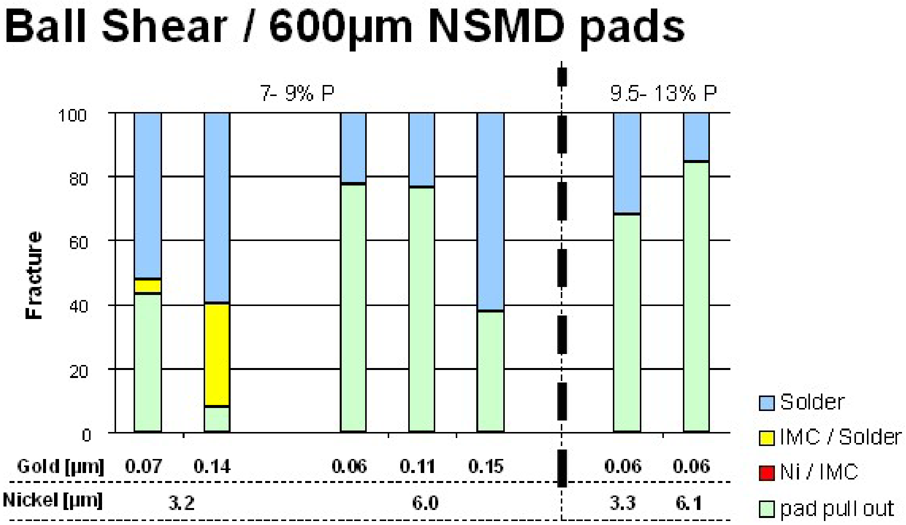


Figure 9 - Detected fracture modes of ENIG layers on 600µm NSMD pads.

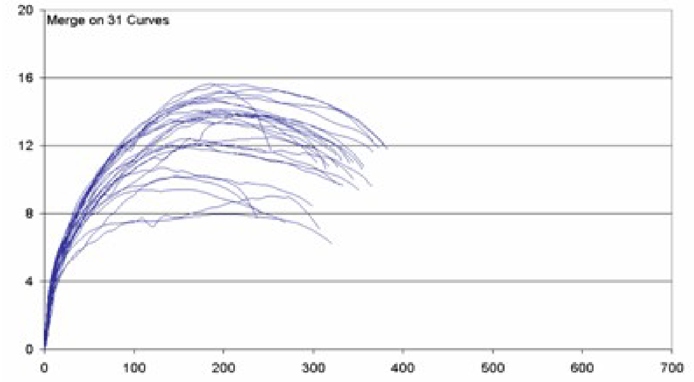
Only samples with P content of 7-9% in the Nickel layer and a Nickel thickness of 3.2µm showed brittle fracture (mode 3) at the interphase between Ni/Sn IMC and solder, regardless of the Gold thickness.

Throughout the testing only 600µm NSMD pads showed fracture mode 1 with pad pull out. All samples with a P content 9.5-13%, regardless of tested Nickel / Gold thickness, and Nickel layers with 7-9% P and 6.0µm thickness showed pad pull out or fracture within the solder ball.

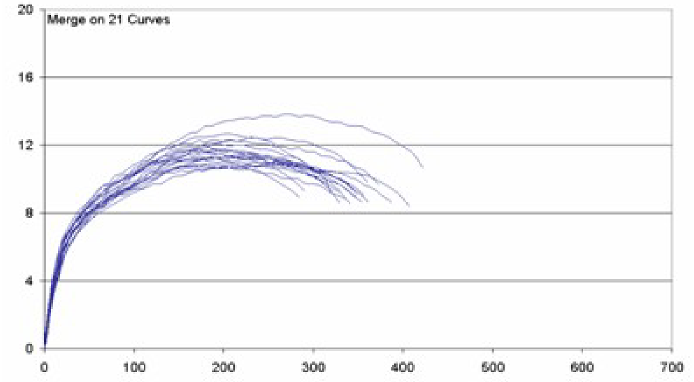
Nickel layers with 7-9% P, 6.0µm thickness and 0.15µm Gold thickness showed lowest amount of pad pull out (mode 1), less than 40%. Whereas high P Nickel layers with 6.1µm thickness and 0.06µm Gold had more than 80% of pad pull out (mode 1).

As an example Figure 10 shows a series of ball shear force length diagrams of test boards plated with 4.2% P, 8.0% P and 11.2% P in the bulk Nickel layer. The lead free (SnAgCu) solder balls were attached to samples directly after plating. The force length diagrams for 8.0% P and 11.2% P show a narrow shape of all curves, indicating similar force length strength for all tested SMD BGA pads. Whereas the Nickel layer with 4.2% P show a wide spread of force length curves, indicating a wider spread (10N – 16N) of total shear force for the tested SMD BGA pads.

Ball shear test after thermo cycling on 600 µm pads
As received



5µm NiP (4.2%) 0.08µm Gold



5µm NiP (8.0%) 0.08µm Gold

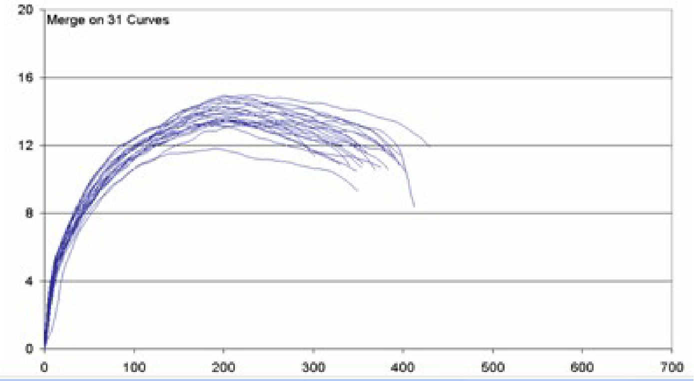
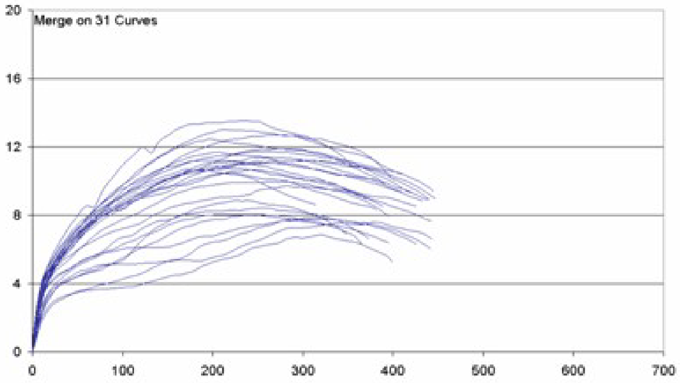


**Figure 10 - Comparison of Force Length Diagrams of 600µm SMD Pads, with Lead Free Solder Balls (SnAgCu) Determined with Three Different Bulk P Contents in the E'less Nickel Layers. **

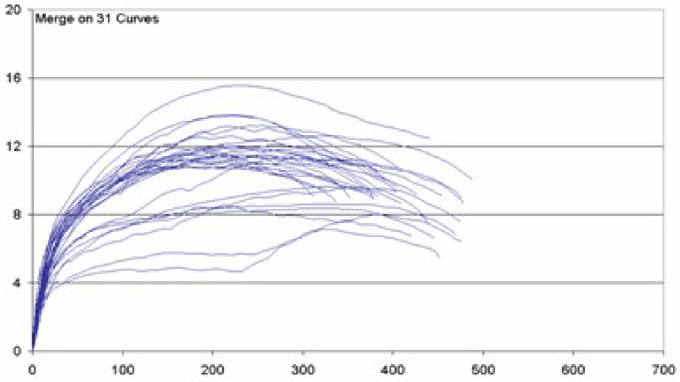
Note: The three Nickel systems show a flat descent after the maximum height representing a ductile plastic deformation of the solder.

As an example Figure 11 shows a series of ball shear force length diagrams of test boards plated with 4.2% P, 8.0% P and 11.2% P in the bulk Nickel layer, after 1000 TC. The lead free (SnAgCu) solder balls were attached to samples directly after plating, followed by 1000 TC (-55°C / +125°C). After 1000 TC only for 11.2% P in the bulk Nickel layer the force length diagrams show a narrow shape of all curves, indicating similar force length strength for all tested SMD BGA pads. Whereas the Nickel layer with 4.2% P and 8.0% P show a wide spread of force length curves, indicating a wider spread (8N – 13N for 4.2%P; 8N – 16N for 8.0% P) of total shear force for the tested SMD BGA pads.

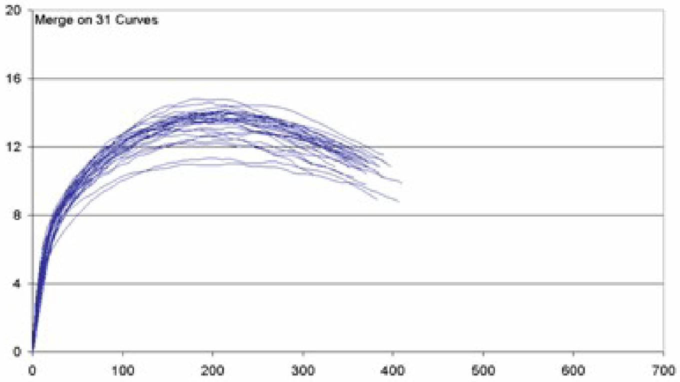
After 1000 thermo cycles –55°C / +125°C



5µm NiP (4.2%) 0.08µm Gold



5µm NiP (8.0%) 0.08µm Gold



5µm NiP (11.2%) 0.05µm Gold

Figure 11 - Comparison of Force Length Diagrams of 600µm SMD Pads, with Lead Free Solder Balls (SnAgCu) Determined with Three Different Bulk P Contents in the E'less Nickel Layers, after 1000 TC –55°C / +125°C

Note: The three Nickel systems show a flat descent after the maximum height representing a ductile plastic deformation of the solder.

The Nickel layer with 8% P showed a wider spread of total shear force compared to "as received" samples without TC. The Nickel layer with 11.2% P was not affected by TC.

In order to evaluate the differences in behavior of the here tested 8.0% P Nickel layer compared to the 11.2% P Nickel layer, the fractures occurred were examined by x-section and EDX.

As an example Figure 12 (8.0% P Nickel layer) and Figure 13 (11.2% P Nickel layer) are showing x-sections of a SMD BGA pad after ball attachment and ball shear testing. The belonging force length diagrams showed a flat descent after the maximum height representing a ductile plastic deformation of the solder for both bulk P contents.

Seen in Figure 14 and 15 are the NiSn IMCs formed with a SnAgCu alloy using a reflow profile recommended by lead free solder paste suppliers, shown in Figure 16.

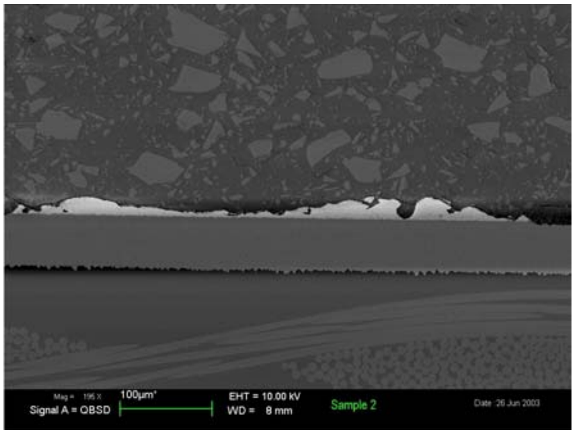


Figure 12 - SEM Image of a X-Section (195x mag.) of a SMD BGA Pad after Ball Shear Testing on an 8.0% P Nickel layer - Fracture within the Solder, nearby the Ni/Sn IMC

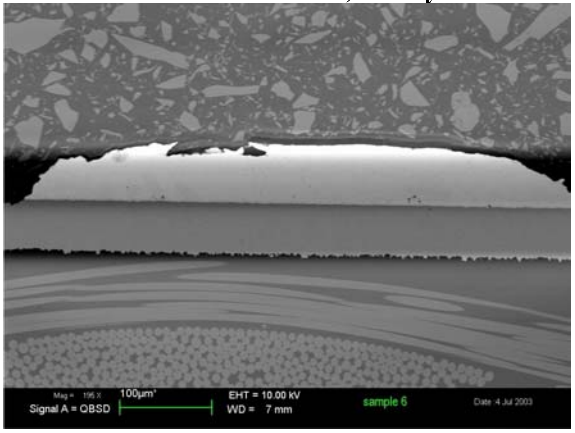


Figure 13 - SEM Image of a X -Section (195x mag.) of a SMD BGA Pad after Ball Shear Testing on an 11.2% P Nickel Layer - Fracture within the Solder

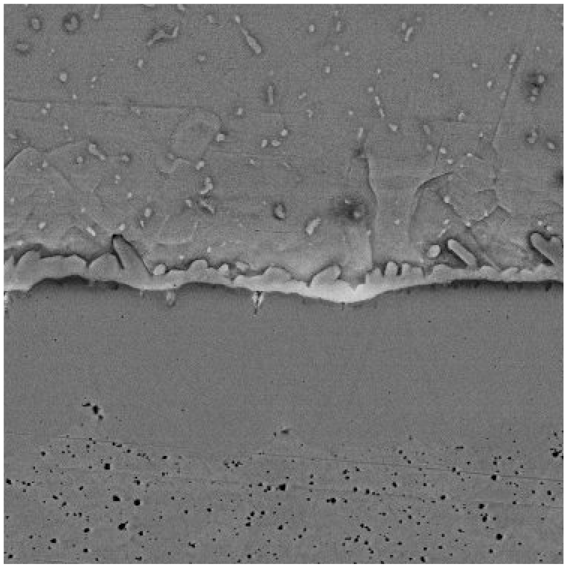


Figure 14 - SEM Image of a X-Section (2500x mag.) of the NiSn IMC on an 8.0% P Nickel Layer Using an SnAgCu BGA Solder Ball

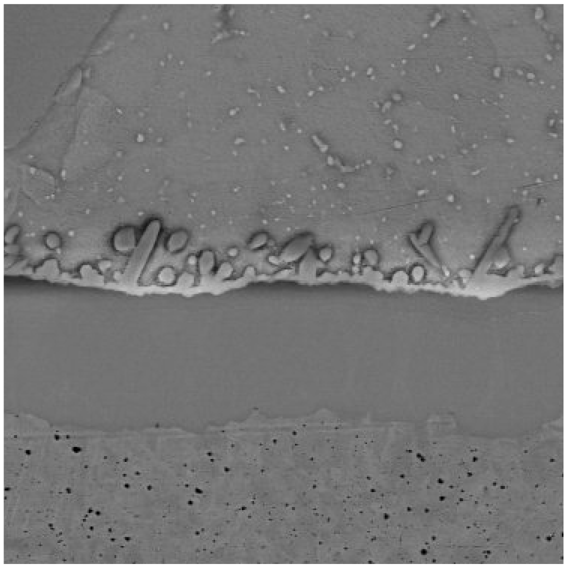


Figure 15 - SEM Image of a X-Section (2500x mag.) of the NiSn IMC on an 11.2% P Nickel Layer Using an SnAgCu BGA Solder Ball

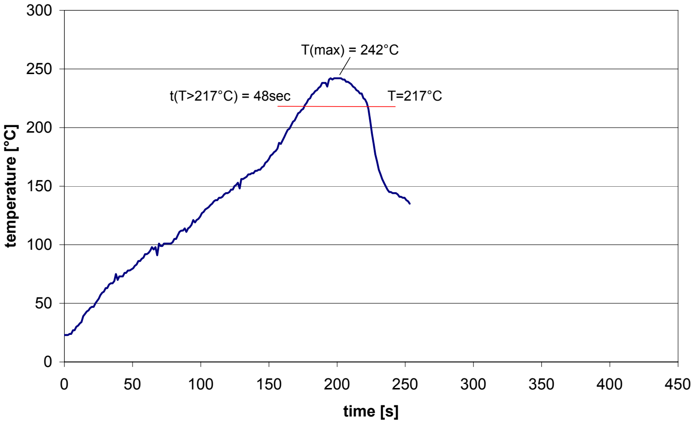


Figure 16 - Lead Free Reflow Profile with a Steady Temperature Increase to 180°C before Increasing to Peak Temperature of 242°C, Operating at Normal Atmosphere - Total Time above Liquid is 48s.

Obviously, both created IMCs (Figures 17 and 18) differ. Having a bulk P concentration of 8.0% the IMC thickness has a thickness range from 200nm to 600nm, indicating that the Nickel has not been solved equally over the entire surface, thus creating areas with a thicker and thinner IMC.

The question to be asked, is this the influence of Nickel “grain” (growth) boundaries, which are easier to solver / attack by the solder? Whereas the Nickel layer with 11.2% P has no evidence of these boundaries, or they are less strong marked (Figure 19).

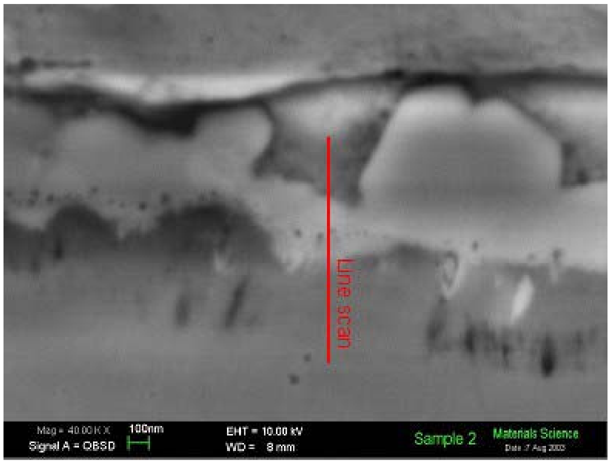


Figure 17 - Greater SEM Magnification of Image 3 (40 000x mag.) of the NiSn IMC on an 8.0% P Nickel Layer Using a SnAgCu BGA Solder Ball

Note: The red line indicates where a line scan was done, to gain information on the P concentration at the interphase e'less Nickel layer to NiSn IMC.

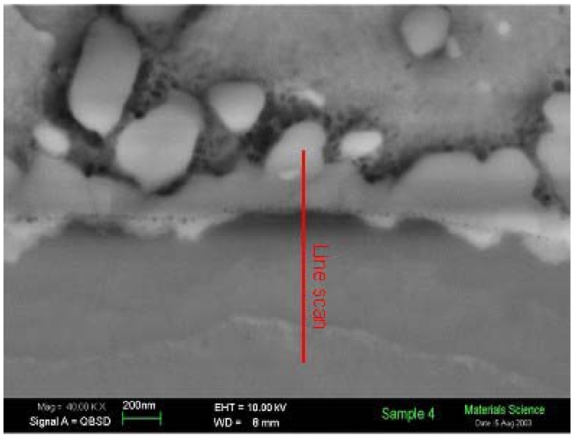


Figure 18 - Greater SEM Magnification of Image 4 (40 000x mag.) of the NiSn IMC on an 11.2% P Nickel Layer Using a SnAgCu BGA Solder Ball.

Note: The red line indicates where a line scan was done, to gain information on the P concentration at the interphase e'less Nickel layer to NiSn IMC.

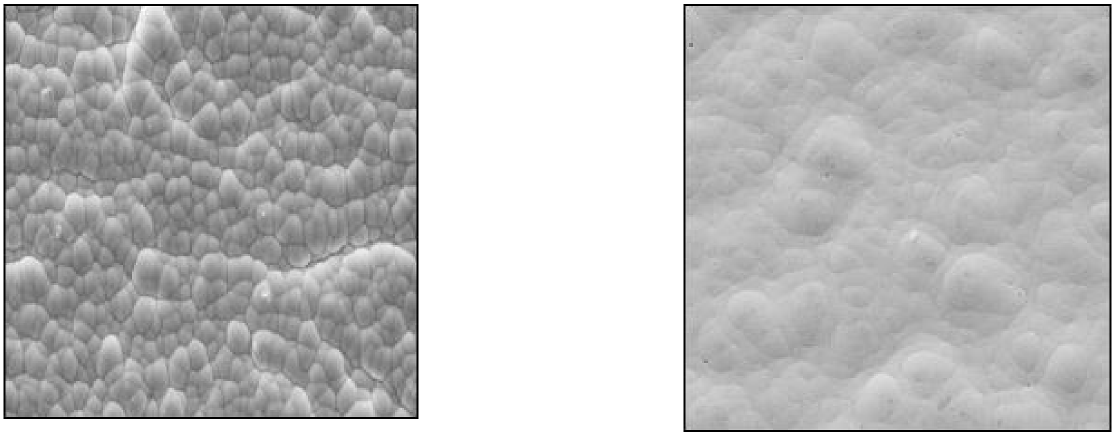


Figure 19 - Above Figures are Showing Typical SEM Images at 5000x mag. of Nickel P Surfaces having 8.0% P for the Top Image and 11.2%P for Below

Additionally a high P Nickel layer is more corrosion resistant, not only in corrosive environment like pollutant gas or wet-chemicals like immersion Gold, the attack of the molten solder alloy to the bulk metal is also understood as corrosion. The overall appearance of the IMC formed with the 11.2% P Nickel layer is denser with an average thickness of 150nm. Next to a denser IMC layer, needle shaped IMC "grow" from the IMC layer into the solder (Figure 15).

Typical examples for line scan (10KV C-sputtered) are shown in Figure 20 and Figure 21. The quantitative P measurement shows, for a bulk P content of 8.0%, an increase of P of 80% at the interphase between Nickel layer and NiSn IMC. Whereas the Nickel layer with 11.2% P shows only a P increase of 50% at the interphase.

For both Nickel layers two steps do the P increase. First, the immersion Gold reaction with the Nickel P according to:

$$\mathrm{Ni} + 2\mathrm{Au}^{-} \rightarrow \mathrm{Ni}^{2+} + 2\mathrm{Au}$$

Due to this reaction Nickel is solved and Gold is deposit, and the P gets enriched at the interphase between the e'less Nickel layer and the Gold layer.

Assuming that a corrosion resistant e'less Nickel layer is less attacked by the immersion Gold reaction, at same Gold bath parameters, the Gold thickness will be lower compared to a less corrosion resistant Nickel P layer.

As an example for immersion Gold thickness achieved during same immersion time on a medium / high P Nickel layer. Clearly seen is a higher Gold thickness, using a medium P Nickel layer. This also means, the medium P Nickel layer has a stronger P enrichment at the Nickel Gold interphase compared to a high P Nickel layer. (See Figure 22.)

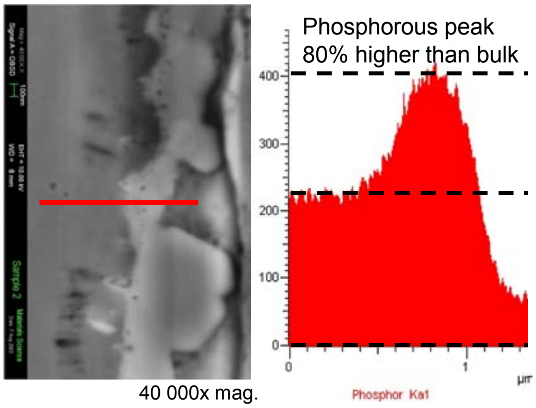


Figure 20 - SEM Image of a X-Section (40 000x mag.) of the NiSn IMC on an 8.0% P Nickel Layer Using a SnAgCu Solder Alloy

Note: The red line on the SEM image indicates the area for line scan. On the right hand side the quantitative P content is shown, for the investigated area.

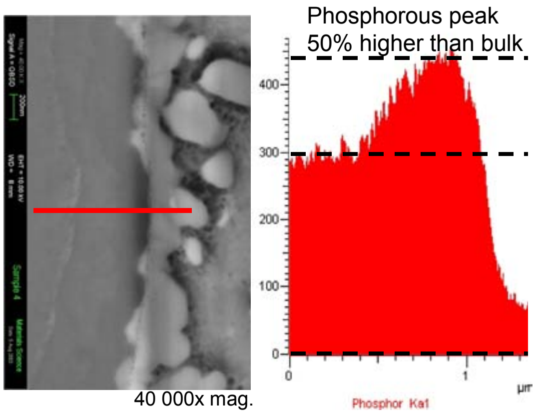


Figure 21 - SEM Image of a X-Section (40 000x mag.) of the NiSn IMC on an 11.2% P Nickel Layer Using a SnAgCu Solder Alloy

Note: The red line on the SEM image indicates the area for line scan. On the right hand side the quantitative P content is shown, for the investigated area.

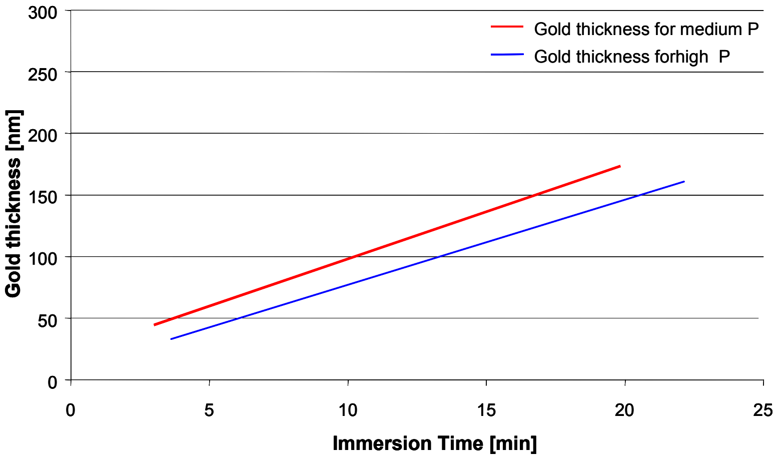


Figure 22 - Immersion Gold Thickness on Medium P (7-9%) Nickel Layers Compared two high P (9.5-13%) Nickel Layers, at Constant Immersion Gold Bath Parameters

The second P increase at the interphase occurs during soldering, when the molten solder solves Nickel and forms the NiSn IMC. Again P gets enriched at the surface of the e'less Nickel layer. The same corrosion resistance as for the immersion reaction is the driving force for more or less solving of Nickel and P enrichment at the interphase.

Coming back to the difference in ball shear behavior, force length diagrams, shown in Figure 10 compared to Figure11, the different behavior is based in the difference of the formed IMC. Where a higher bulk P in the e'less Nickel does not necessarily mean a higher P enrichment at the Nickel to NiSn interphase. In case of the here tested 11.2% P Nickel layer, the amount of P enrichment at the interphase had no impact to solder joint reliability.

Summary

- Plating a Gold thickness of average 0.05µm on high P ENIG the wettability / solderability is equivalent to 0.08µm Gold on a medium P ENIG system. This might be based on a denser, less porous Gold layer, covering the high P e'less Nickel layer, and the fact that high P Nickel layers are more corrosion resistant and therefore less prone to show oxide layers on the surface.
- A variation in e'less Nickel and immersion Gold thickness showed a clear indication to influence the brittle fracture behavior. The bulk phosphorous content showed for "as received" samples a minor effect (fig. 6 / 7 / 8 / 9) with a slight benefit for 9.5 – 13% phosphorous e'less Nickel.

  After solder ball attach and thermo cycling, inducing stress to the solder joint, a clear benefit for a high P e'less Nickel layer is seen. The stress induced after 1000 TC did not influence the strength of the solder joint for the high P e'less Nickel layer. The mid range P e'less Nickel layer showed a wide spread of all force length curves, and comparing to as received, 7-9% P layers were negatively influenced by 1000 TC.

- The SEM Figures 20 and 21 for the quantitative P distribution, after the immersion Gold reaction and soldering, is showing less P enrichment at the interphase e'less Nickel / NiSn IMC for using a high P ENIG system.

  This agrees with former studies that not the total amount of phosphorous at the interphase is critical; the difference between P of the bulk e'less Nickel layer and the enriched P zone (between Nickel and IMC) is the critical factor.

  At the tested high P ENIG system less Nickel is removed, therefore it shows a lower P enrichment and with the absence of "grain" boundaries a dense IMC formation. Due to the higher amount of Nickel which is removed by immersion Gold reaction and soldering, the typical P enrichment for low and mid P ENIG systems is therefore much stronger compared to their bulk P value. This enriched zone covers areas between Nickel and IMC, and does not react with the solder. Additionally the solder attack to the Nickel is uneven, based on the presence of "grain" boundaries, resulting in an uneven thickness of the IMC.

- Based on this investigation, an ENIG system with a bulk P concentration of 9.5- 13% P is showing advantages compared to a 7- 9% P ENIG system, whereas the solder joint reliability is much superior and the Gold wire bondability is unique for an ENIG system.

Based on this investigation, the recommended high P ENIG thickness * is as followed:

Electroless NiP: 5.5 (5 - 6) µm
Immersion Gold: 0.05 (0.03 – 0.07) µm
*Measured with XRF, using a 0.3 mm collimator on a 1- 2mm² pad

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