FAILURE ANALYSIS OF DISCOLORED ENIG PADS IN THE MANUFACTURING ENVIRONMENT

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Abstract

Manufacturing of electronic assemblies using printed circuit boards (PCBs) with electroless nickel/immersion gold (ENIG) surface finishes requires front-end PCB evaluation that will guarantee that good quality product enters the assembly line. The most common is an IPC-4552 mandated plating thicknesses verification of 3-6µm and a minimum of 0.05µm for nickel and gold, respectively. Coupled with visual examination, this verification method suffices for general PCB acceptance but may not be robust enough in cases where ENIG plating in PCBs is compromised. That poses challenges in the manufacturing environment, where resulting latent defects are detected in downstream processes but not at upfront incoming inspection.

Manifestation of such latent anomaly was observed in the form of ENIG pad discoloration with variations from yellow, red or grey discolored surfaces to a more pronounced plating degradation, such as corrosive pitting. The launched failure analysis involved evaluation of manufacturing processes suspected to contribute to the cause of the condition. Effects of thermal processes, cleaning methods, soldering, parylene deposition and factory cleanliness were examined thoroughly. Concurrently, metallurgical analysis of ENIG pads was performed, where samples were subjected to scanning electron microscopic/energy dispersive x-ray spectroscopic (SEM/EDX) cross section analysis, Auger electron spectroscopy (AES) and gold (Au) and electroless nickel (Ni) surface examination. The resulting analysis revealed a highly porous electroless nickel coating with deep crevasses and fissures penetrating down to the base copper (Cu) layer. These open nickel boundaries were attributed to the corrosive environment within ENIG plating, which resulted in the pad surface discoloration. The root cause of ENIG pad discoloration and pitting was traced back to poor ENIG line process controls. Subsequent introduction of a nickel controller into the ENIG line were the implemented countermeasures. To mitigate the effects of discoloration at the electronic assembly level, a tinning process was implemented to prevent nickel plating oxidation and to ensure that good wettability for reliable solder joints was maintained.

Key words

Microelectronic assemblies, manufacturing processes, PCB ENIG plating, discoloration

I. INTRODUCTION

ENIG-based PCBs have been implemented as a response to the Pb-free mandate by the Restriction of Hazardous Substances (RoHS) directive, effective 2006. Since then, ENIG has become popular in the electronics industry as a surface finish for fine pitch surface mount and ball grid array (BGA) packaged devices [1]. Manufacturers choose PCBs with ENIG plating due to their long-term solderability, wear resistance, conductivity and surface planarity [2]-[4]. Our PCB-based electronic assemblies are used in medical implantable devices, thus their manufacturing, including raw materials and components must meet industry accepted IPC standards for commercial product and also comply with ISO 13485 to ensure quality and durability of the assembly. ENIG board consists of a base Cu layer that is plated with 3-6µm (120-240 µin) thick electroless Ni, and then with a 0.05-0.127 µm (2-5µin) layer of immersion Au to protect the Ni from oxidation. Plating defects have been reported in the past [1], [5] – [6] including pad discoloration [4]. While there can be multiple factors contributing to the latent defect manifestation, an underyling root cause is typically traced to the ENIG plating line and its processes that have deviated from the control limits.

II. BACKGROUND

Front end production of our electronic assemblies (EAs) is preceded by a screening of the raw PCBs at an Incoming Quality Assurance (IQA) inspection point. The incoming PCB is evaluated whether its fabrication meets Class III Acceptability Criteria in accordance with the *IPC-600* and *IPC-6012* standards. Plating thicknesses are verified against *IPC-4552, The Specification for ENIG Plating for PCBs*. Once the raw material is accepted, it is released into the production for the microelectronics assembly.

The IQA inspection does not include any ENIG structure examination, as it is understood that adequate process controls are in place at the supplier's fabrication site to ensure good plating. When the quality of ENIG is compromised and microstructural defects not identified early in the supply chain process, the seemingly benign anomalies get compounded with each subsequent manufacturing step of the assembly. Recently, numerous PCBs with acceptable plating thicknesses exhibited ENIG pad problems in our factory. The pads on the secondary side of the PCBs showed varying degrees of surface discoloration ranging from light yellow and orange through dark red and grey (Fig. 1a-d). Some boards also showed corrosive pitting (Fig. 1e).

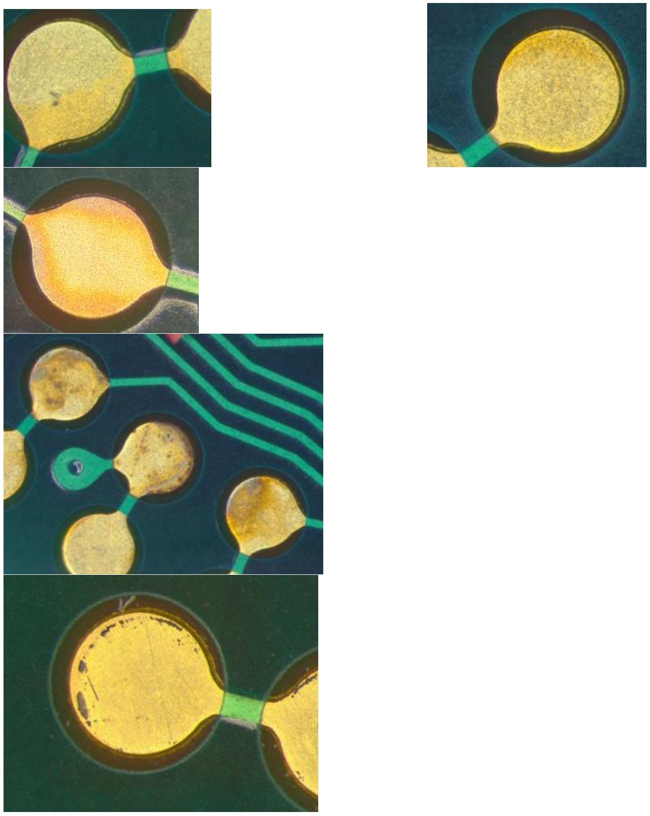

Figure 1: ENIG pad surface discoloration a) yellow, b) orange, c) red, d) grey, e) pitting.

Out of concern that these anomalies could lead to latent failures in implantable devices, any form of surface anomalies or contamination was considered unacceptable and devices showing discoloration were rejected. A formal, cross-functional failure investigation was launched to identify the root cause of the pad discoloration.

This paper describes a systemic approach to problem solving of ENIG pad discoloration.

IIIA. Failure Investigation – Manufacturing Processes Evaluation

First, an evaluation of assembly processes with any factors that could potentially effect pad appearance was performed.

A general process map is shown Fig 2. After 100% of visual PCB inspection upon receipt, components go through the surface mount technology (SMT) line using an SnPb water soluble solder paste. After cleaning and two thermal processes, EAs are moved through 3 hand soldering operations, again, using SbPb solder and water soluble liquid flux. An aqueous cleaning follows each soldering step. The parts are then sent outplant to be parylene coated on the top side of the assembly.

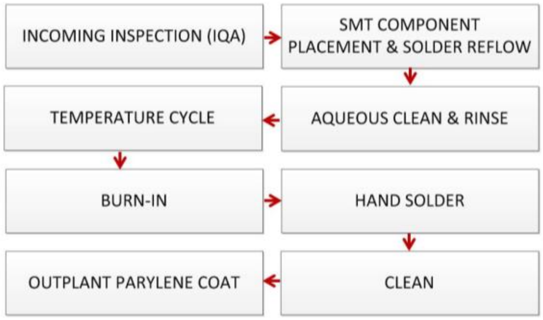

Figure 2: Electronic assembly (EA) process map for some operations.

A. Accelerated Thermal Aging – Air Bake

We tested the effects of thermal treatment on the ENIG pads using an accelerated aging test. Five randomly selected complete assemblies were subjected to a 36 hour air bake at 150°C. Some pads exhibited a darkening of a pre-existing discoloration (Fig. 3), while new discoloration appeared on other previously clean pads (Fig. 4).

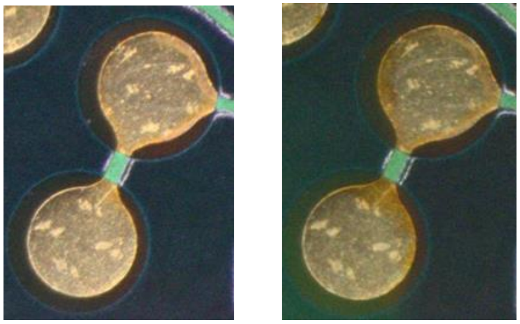

Figure 3: Pads before and after thermal aging (16x).

These results indicate that exposure of the ENIG pads to elevated temperatures may result in changes to the pads' surface appearance.

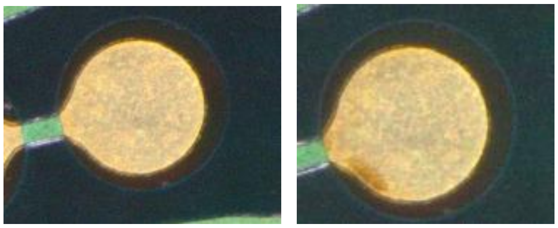

Figure 4: Pad before and after thermal aging (16x).

B. Soldering

Another experiment was set up to simulate exposure of the ENIG pads to the water soluble flux used during soldering of the pads on primary side. Solder flux was dispensed onto part of the board, which was then placed on a hotplate at 150°C for 5 minutes to activate the flux, then spray-cleaned with deionized water, followed by air baking at 125°C for 24 hours. When inspected with a microsope at 60x, no discoloration was observed, however cross sections of these same solder pads showed Ni etching with some of the etched locations exhibiting gold spikes (Fig. 5).

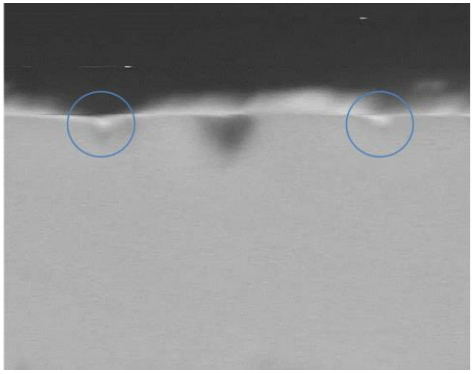

Figure 5: Cross-section of flux-cleaned sample with Ni etching (dark spot) and Au spikes (circled).

C. Aqueous Cleaning

An experiment was performed to evaluate the effects of extended exposure of cleaning chemistry on the solder pads. We used an ethanolamine-based saponifier, a highly basic (~11pH) organic aqueous cleaning agent designed to remove water soluble flux and solder paste residues. The sample was soaked at room temperature for 2 hours in a 90% cleaning agent/10% DI water solution. This was intentionally chosen to represent a much higher concentration and much longer time than experienced during production. The sample was spray-cleaned with DI water to remove the cleaning chemistry and then air baked at 125°C. When inspected at 60x with a microsope, no discoloration was observed. Metallurgical SEM cross sections showed no evidence of Ni etching.

D. Outplant Parylene Process

Discoloration was observed to be worse after an outplant parylene process, which led to the hypothesis that the parylene process was causing the condition. Standard parylene coat protocol requires a masking material to be applied to the entire secondary side or backside of the assembly in order to restrict parylene coverage to the primary side only. The mask is later removed leaving the secondary side parylene-free. The chosen masking material is known to react with Cu by turning it red. Unfortunately, a detailed examination of the maskant material could not be performed due to the proprietary nature of its chemistry. Instead, a reference FTIR spectrum of masking material was used to compare against the FTIR spectrum taken from discolored pads. Comparison of the two FTIR spectra showed no peak overlapping, which excluded the association of the masking material with the discolored material on the pad surface as a root cause.

E. Factory Environment

The factory environment was investigated to determine if there were any sources of contamination that could cause the solder pads to become discolored. A total of eight different processing areas and equipment were wiped with lint-free wipes to collect residues, which were then submitted for an FTIR and EDS analyses. The EDS samples were taken from inside of four ovens used during the electronic assembly process: 1) RTV cure, 2) underfill cure, 3) burn-in and 4) solder reflow. A solvent extraction method was applied to four additional samples: 5) a metal transport tray used for carrying EAs, 6) a burn-in board used as a fixture and bias for the EAs during the week-long burn-in, 7) a solder reflow pallet used to transport the part through an SMT line and 8) a plastic separator sheet used for keeping raw PCB panels separated during shipment from supplier.

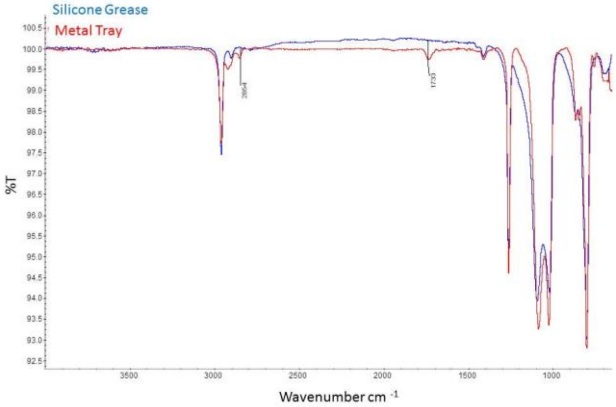

Figure 6: FTIR results comparing the material on the metal transport tray to a silicone residue profile.

The EDS found particles containing elements used in stainless steel and aluminum fixturing such as Fe, Cr, Mn, Ni and Al. Particles containing elements common to electronic assemblies such as C, O, Sn, Pb, Ag, Si and Cu silicon were also detected. The FTIR found materials such as silicones attributed to an RTV material (Fig 6), organic acids (fluxes/plastics), and polyamide (polymers/plastics) materials, all common to an electronics manufacturing facility.

F. Main Assembly Process

To understand and quantify escalation of discoloration through the assembly process, a monitored build of 66 EAs was processed following standard production processes but with additional inspection and photo documentation steps. Photos were taken in four quadrants for each EA resulting in 264 opportunities for discoloration. The largest percent of defect accumulation was observed at steps involving soldering and cleaning operations, followed by parylene coating, the incoming inspection and burn-in (Fig. 7).

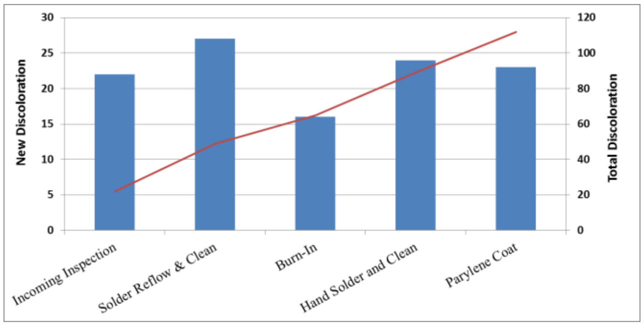

Figure 7: Accumulation of pad discoloration throughout the assembly process.

Discoloration intensity varied at different assembly steps but was most pronounced after the parylene outplant processing step. An example of the process-dependent pad surface changes is shown in Fig. 8.

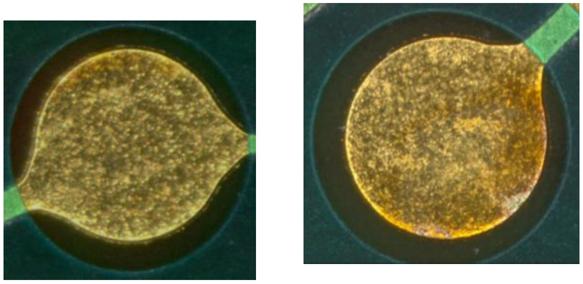

Figure 8: Typical discoloration after hand solder (left) and after parylene coating step (right).

IIIB. Failure Investigation – ENIG Surface and Metallurgical Analysis

In order to understand the nature and source of the pad discoloration, surface and metallurgical materials characterization of samples with discolored and non-discolored pads was performed.

A. Auger Surface Analysis

Surface of the pads was analyzed with an Auger Electron Spectroscopy (AES), where all elements in the periodic table, except hydrogen and helium, were simultaneously detected from the top 20-40Å thick layer of the sample. A subsurface analysis down to ~2500Å thickness, well within Ni layer, was performed by depth profiling at an Argon sputter etch rate of 50Å/minute. AES spectrum of a discolored Sample 1 (Fig. 9) shows a significant amount of O and Cu detected on top of the Au layer and seemingly inside the Au coat. High levels of Cu and O are also detected inside the profile for Ni, indicating substantial amounts of NiO associated with with the Ni coating. Oxygen can be associated with Cu in the form of CuO as well.

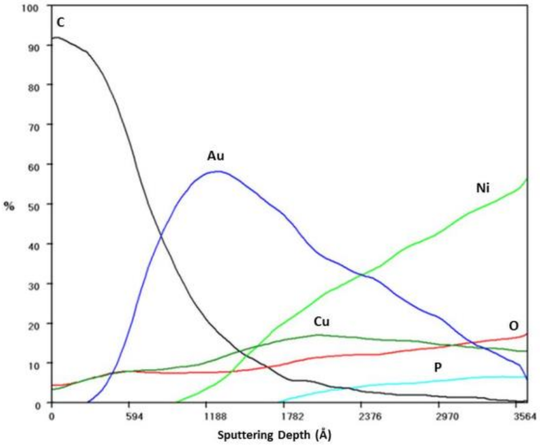

Figure 9: AES of a discolored Sample 1.

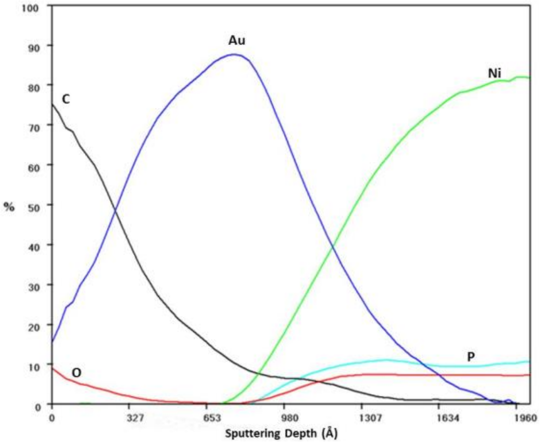

Figure 10: AES of a non-discolored Sample 2.

The non-discolored Sample 2 has Ni and O species but not Cu. (Fig. 10) The Au coverage on or at the sub-surface is scattered (maximum 40-60% in Sample 1 and 50-90% in Sample 2), instead of having an expected 100% surface coverage. The Au and Ni interface should be well defined and square in profile (similarly to profile in Fig. 11), which would indicate uniform and distinct ENIG layers, but instead it is broad and substantially overlapping in both discolored and non-discolored

Samples 1 and 2, respectively. The profile of a second non-discolored Sample 3 (Fig. 11) is the closest to the expected Auger spectra for ENIG plating, where Au covers 100% of the surface (~300-800Å; 1-3µin) and has a more condensed profile that is distinguishable from the clearly defined Ni peak. The presence of a carbonaceous layer on top of the Au coating in all samples, or Zn and S in Sample 3 is assumed to be from handling or other surface contamination.

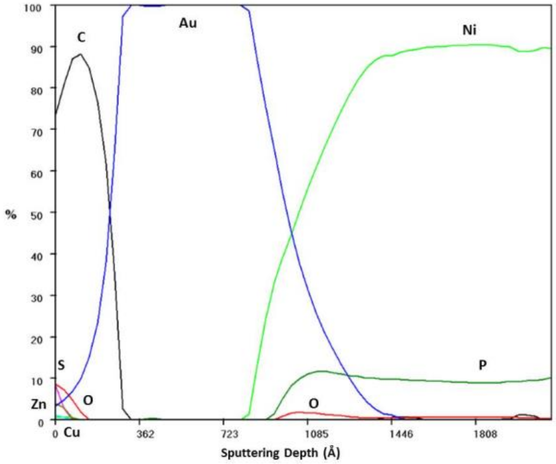

Figure 11: AES of a non-discolored (exemplar) Sample 3.

B. *Metallurgical microscopy of a cross-section and SEM imaging*

The three samples were cross-sectioned at pad locations of interest and imaged with an optical and then scanning electron microscope. The micrographs and SEM cross-sections clearly show crevasses and wide open Ni nodule boundaries in the Ni coating.

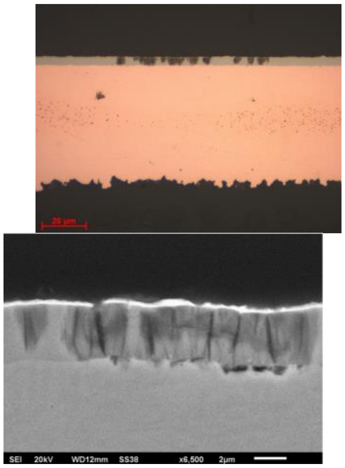

Figure 12: Cross-section of a discolored Sample 1: a) micrograph, b) SEM .

The fissures in the discolored Sample 1 (Fig. 12) were found to span the entire Ni coating thickness, which was just under 3.7 µm (~140 µin), while the fissure density in the non-discolored Samples 2 and 3 was a little lower (Fig. 13, 14). Defective structure in the Ni layer, was to a varying degree found in all tested samples. Moreover, the base Cu appeared to be disturbed in its upper section in a discolored Sample 1. In addtion, Au showed variation, including gaps, exposing bare Ni and its nodule boundaries.

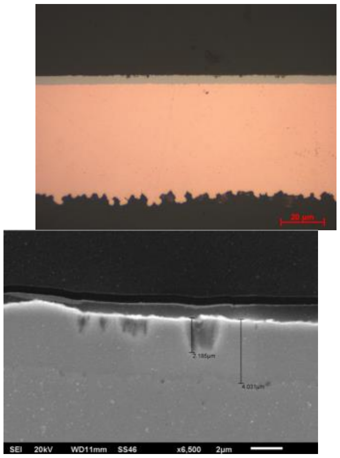

Figure 13: Cross-section of a non-discolored Sample 2: a) micrograph, b) SEM.

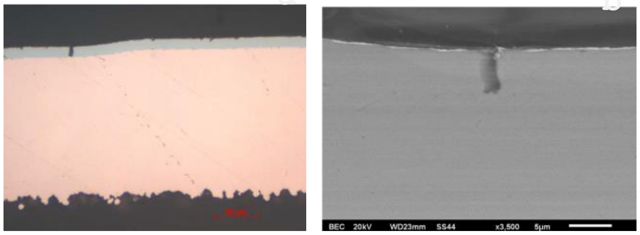

Figure 14: Cross-section of a non-discolored Sample 3: a) micrograph and b) SEM.

C. *SEM imaging of the Nickel surface, after Gold removal*

To assess the quality of the electroless Ni and enable a microstructure examination, the Au layer was removed using a proprietary gold strip solution that does not attack the Ni coating. Two new samples (discolored sample 4 and non-discolored sample 5) and one sample used in earlier AES and SEM analysis (non-discolored sample 3) were selected for this purpose. The results were considered representatives of the pad conditions equivalent to those seen in Auger and cross-sectional analysis. Several pad locations were inspected using SEM and the results were consistent with those shown below. Fig. 15 shows SEM micrographs with mixed-size Ni grains, pad topography and flawed open Ni nodule boundary structures. This correlates to the SEM micrographs of cross-sections that show deep crevasses along the Ni nodules. The wide open Ni boundaries are visible not only in the discolored Sample 4 (Fig. 15a) , but also in the non-discolored Samples 5 and 3 (Fig. 15 b, c). All samples exhibit a defective Ni coating, regardless of the visual color of the pad’s surface.

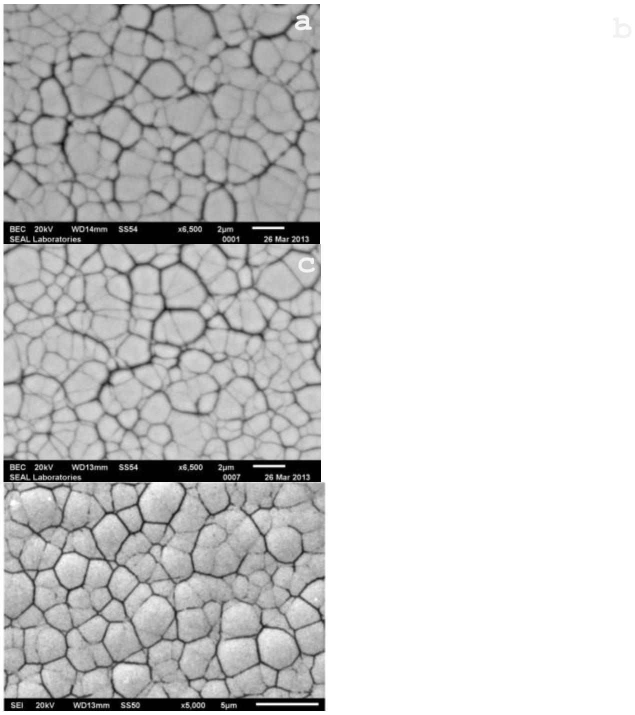

Figure 15: a) discolored Sample 4, b) non-discolored Sample 5, c) non-discolored Sample 3.

IV. Discussion

Root Cause

The Auger surface analysis was validated by comparing it with the results of SEM pad cross sections and with surface analysis of the Ni layer. The AES showed the presence of O throughout the Au coating in the discolored and one non-discolored sample. Also, inside the profile of the Ni coating there were high levels of O and Cu, which implies the existence of a substantial amounts of NiO, which is associated with the Ni coating, as well as CuO, which is associated with Cu from base layer. Cu and Ni diffusion through Ni nodule boundaries and their subsequential oxidation is postulated based on the evidence seen in cross-sectional micrographs and Ni surface SEM images that show large open Ni nodule boundaries with deep crevasses penetrating into the Ni coating. In many locations, the long fissures reach through the Ni layer down to Cu base layer.

The Cu diffuses from the bulk material through the wide and deep open Ni nodule boundary sidewalls. Ni serves as an oxidation and diffusion barrier for Cu species, but in the presence of open Ni boundaries and long fissures both Ni and Cu diffuse onto the crevasses walls and onto the pad surface while being oxidized by atmospheric exposure. The Au-stripped Ni surface analysis revealed areas of the ENIG pad that had defective Ni nodule boundries, a phenomena that was noticeably larger in the samples that exhibited discoloration.

Ultimately, the changes in pad color were a result of the presence of Cu and Ni oxides on the surface and along the Ni boundary crevices. The appearance of colors spanning from yellow, orange, through red and grey are due to the optical interference. The increase in observed discoloration after thermal exposure is due to an increased migration rate of Ni and Cu to surface and the increased rate of oxidation of those metals. If the Ni nodule boundaries were closed, then Au would protect the underlying Ni and the Cu would not have an avenue for diffusion to the surface of the Au. The pad surface in multiple samples showed areas of missing Au plating, which when present, served to protect Ni from oxidation. Without the protective top layer of Au, even tight Ni nodule boundaries would not prevent Ni from being oxidized. The broad and diffuse AES profiles for Au and Ni, along with an identified presence of O and Cu on the surface of the Au layer suggest an anomalous structure and the network of defective Ni nodule boundaries suggests an "out of control" ENIG process.

When the raw incoming PCBs were accepted into production, they showed little surface discoloration. Once they entered the assembly line and were exposed to manufacturing processes, various degrees of surface discoloration began to manifest itself on the ENIG pads. Accelerated thermal aging showed that prolonged exposure to elevated temperature contributed to creating new or worsening existing discoloration on pads. This occurs because the increased temperature causes an increased rate of diffusion of the Ni and Cu to the surface.

Exposure to the flux used in the soldering process did not appear to cause discoloration since no further discoloration was seen after this step. While cross sections showed Ni etching, the presence of Au spikes indicated that etching had occurred in the Au plating bath. Since Ni etching was present before the part was flux-exposed and it is not possible to cross section the pad before exposure, it was not possible to determine if the flux also etched the Ni. Similarly to soldering flux, cleaning was not the cause of discoloration because no discoloration was seen after exposure to the cleaning chemistry.

The FTIR comparison of the masking material and discolored pads ruled out discoloration as coming from the masking material. The FTIR and EDS evaluation of the factory's cleanliness yielded a list of elements and materials, all common to electronics manufacturing facility but not causing pad discoloration.

Countermeasures

Ni Controller: To address the concerns with electroless Ni deposition process, improved process controls were implemented at the PCB manufacturing site. The major improvement was an introduction of an automated Ni bath controller into the ENIG line. The controller automatically adds the chemicals to the Ni bath in response to measured changes in the bath composition every four minutes. Previously, the bath chemistry was manually adjusted by an operator every four hours.

Pad Tinning: To mitigate the effects of discoloration at the electronic assembly level, a tinning process was implemented to prevent nickel plating oxidation. First, the discoloration (Fig. 16a) was removed by cleaning the pads with flux to remove the oxides (Fig. 16b). The pads were then immediately tinned with solder Sn63 to prevent re-oxidation of the surface (Fig. 16c). The solder pads were then visually inspected for wetting of the solder to the ENIG pad. This verified the integrity of the nickel to solder layer.

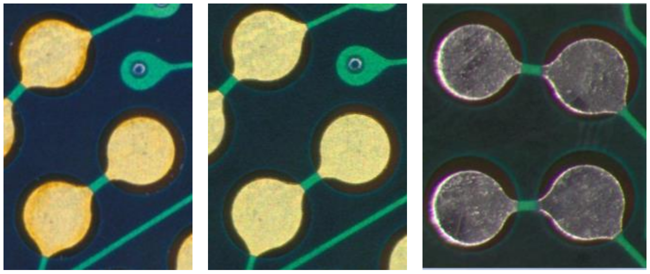

Figure 16: a) Pads before, b) after flux clean, c) after tinning.

Soldered Wire Pull Test: The reliability of the solder joints was verified by a mechanical pull test of soldered wires on a representative set of samples. The discolored ENIG pads were cleaned, tinned and stabilized by baking for 24 hours at 125°C. The samples were then submitted to 100 temperature cycles per MIL-STD-883 TM 1010.8. The soldered wires were then pulled per IPC-TM-560 until failure occurred. The results exceeded the minimum pull values for all wires as defined by MIL-STD-883, TM 2004.6 "Lead Integrity."

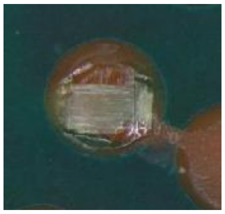

Figure 17: Wire pull failing at the pad metallization to laminate layer, an indicator of a strong solder to pad interface.

None of the solder connections separated at the ENIG pad surface to solder interface, with the majority of the separations occurring at the PCB pad metallization to laminate layer. A representative image (Fig. 17) shows a strong solder joint connection that when pulled, delaminates deep from the PCB metallization-to-pad layer (pad separated from laminate). If the pad contained severe corrosion and its reliability was compromised, the separation would have occurred between the SnPb solder and the electroless Ni.

V. Conclusions

Processes involved with microelectronics manufacturing place a high demand on the assemblies and components through repetitive thermal exposures and cleaning treatments. Thus, marginal quality ENIG in PCBs will not withstand the manufacturing processes for microelectronics without revealing surface anomalies at the production stage. It is a requirement that the end product does not exhibit any surface defects or discoloration. We learned that it cannot be assumed that ENIG plating meets our incoming quality standards solely on a visual inspection or Au, Ni plating thicknesses verification. If at any stage of the assembly process a pad exhibits surface discoloration, it can be inferred that the plating ***may*** be compromised to a certain degree and that a microstructural analysis of the ENIG coatings and solder joint reliability testing should be performed.

Acknowledgment

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