



High performance Cyanide-free Immersion Gold

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ABSTRACT

Printed circuit board requires surface finishes to be applied to functional areas prior to assembly operations. There are a number of final finishing technologies available in the market. Electroless Nickel Immersion Gold (ENIG) is a widely used surface finish which is suitable for use as a solderable and aluminum wire-bondable finish, and also a contact surface for metal contact switches. It is because of its excellent solderability and ability to resist corrosion. Conventionally, cyanide containing gold salt for example potassium gold cyanide, is used as gold source in the immersion gold bath. It is well known to have excellent bath stability, easy bath control and high repeatability performance. However, environmental, health and safety (EHS) concerns arose on this process. Potassium gold cyanide is well-known as a highly toxic substance. It may be fatal if swallowed, contacted or inhaled. It is also highly toxic to environment especially to aquatic life. Mishandling of the gold salt or the gold bath may lead to release of cyanide gas which causes environmental issues.

As green material and process safety are the future trend in the industry, development of cyanide free immersion gold process is one of remarkable research topics. However, up to now, there is only limited amount of cyanide free immersion gold bath available in the market. The challenge is to maintain good bath stability during continuous operation when getting rid of cyanide to complex the gold ions.

In this paper, a novel cyanide free immersion gold bath will be described which can be applied in ENIG process for continuous operation. Beside free of cyanide, the bath can be operated at about 45°C and neutral pH. This operating temperature is much lower than traditional cyanide containing immersion gold bath which operated at about 80°C. This bath can solve the EHS concerns and serve for energy saving as well. The bath was stable with no significant change in plating rate after long time idling. Most importantly, the plating performance is equivalent to conventional immersion gold bath.

INTRODUCTION

Electroless nickel and immersion gold (ENIG) is one of the most common final finishes used in Printed Circuit Boards (PCBs). A key advantage of ENIG is that it offers excellent corrosion resistance, solderability and bondability and its high electrical and thermal conductivity. Conventionally, potassium gold cyanide is commonly used as gold source for immersion gold bath due to its excellent stability. However, it will release toxic substance, cyanide ion. Mishandling of a cyanide containing immersion gold bath may lead to health and environmental issue.

Cyanide free immersion gold can serve as solution for the environmental and safety concerns. A number of literatures and patents [1-4] reported several cyanide-free immersion gold developments. Different kinds of gold ligands were tried including sulfite, thiosulfate, thiourea, halide and thiocyanate to replace cyanide. However, poor bath stability and deposit properties are the key barriers for extensive application.

In this paper, a high performance cyanide free immersion gold bath was reported for PCB application. Proper selection of the stabilizer and complexing agent system for the gold bath leads to outstanding performance. It has excellent bath stability which can survive under long term heat idling and aging through panel plating. The cyanide-free immersion gold bath was operating with conventional medium-high phosphorous EN (8 – 10 wt. %) in the development.

The characteristics of the novel cyanide free IG system will be presented. It included thickness distribution, corrosion resistance, Au layer composition and solder joint reliability. Similar performance for fresh and aged bath was obtained and the performance was compared to conventional cyanide containing IG.

EXPERIMENTAL

Sample Preparation

A standard test panel designed by DOW Electronic Materials with pads, through holes and ball grid array (BGA) pads features was used for plating rate, thickness distribution, corrosion resistance and solder



joint reliability analysis. The size of pads was ranging from 10 mm x 10 mm to 2 mm x 0.4 mm, diameters of through holes were ranging from 1.9 mm to 2.1 mm and diameter of BGA pad was 0.47 mm.

All the chemicals used for preparing the ENIG deposits were Dow Electronic Materials products. Prior to EN plating, standard copper surface cleaning and surface activation steps appropriate for ENIG were carried out. A typical EN with 8 – 10 wt% phosphorous content was freshly prepared prior to IG plating.

The thicknesses of the electroless nickel and immersion gold layers were 4 – 5 μm and 0.04 – 0.07 μm , respectively. Gold and nickel thickness were measured by X-ray fluorescence (XRF) spectroscopy.

To examine the structure of the interfacial region between EN and IG, the IG layer was first stripped off from the ENIG deposits, using a proprietary cyanide-based room temperature gold stripper.

Corrosion Resistance Analysis

For selective ENIG application, the effects of the OSP (Organic Solderability Preservatives) process on the ENIG surface should be considered. To simulate OSP process in laboratory, the ENIG deposits were immersed into an SPS (Sodium Persulfate) microetch and then a 5 vol. % sulfuric acid dip. The copper etch amount on a copper clad panel after 1 cycle of this process was about 0.75 μm .

Corrosion resistance performance was then investigated by two techniques, a) plan-view Scanning Electron Microscope (SEM) after gold stripping and b) Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) with an ultrathin sputtered platinum deposit over the IG layer.

Au layer components Analysis

The composition of the IG layer was investigated by X-ray Photoelectron Spectroscopy (XPS) with depth profiling.

Solder Joint Strength

The strength of solder joints formed on the ENIG deposits was evaluated using normal speed ball shear test.

The Restriction of Hazardous Substances Directive (RoHS) has led to the replacement of tin-lead solders with lead-free solders for most applications. Amongst the available lead-free solder alloys, SAC305 (tin 96.5% / silver 3% / copper 0.5%) is most commonly used. The solder joint tests reported in this paper are based on SAC305 solder.

Prior to attachment of 0.63 mm diameter SAC305¹ lead-free solder balls, a soluble non-activated flux² was applied to the pad surfaces. The test panels were then processed through a reflow oven with a profile peak temperature of 260°C. In addition to the as-plated condition, other parts with either after 1 cycle of OSP simulation or after heat treatment at 150°C for 4 hours were tested too.

A Dage 4000 bond tester was used to evaluate solder ball shear performance. The test speed and shear height for ball shear test were set at 200 $\mu\text{m/s}$ and 100 μm respectively.

Data checkpoint

In this paper, bath aging from 0 to 2 MTO was conducted by cycling with panels plating and made necessary replenishment such as gold and bath components to the bath at 0.25 MTO intervals. For data larger than 2 MTO, the data was collected from simulated aged bath which Cu and Ni ion contaminants were added to a freshly prepared bath. For 6 MTO, the simulated aged bath contained 3ppm Cu and 300ppm Ni. For 12 MTO, the simulated aged bath contained 6ppm Cu and 700ppm Ni.

RESULTS AND DISCUSSION

Operation condition

One of the features of this cyanide-free immersion gold chemistry is its pleasant operation condition. The operating temperature of this gold bath is 45°C which can achieve around 2 μm in 10 minutes. For conventional cyanide containing gold bath, it needs to operate at 80°C for achieving similar plating rate. With this plating rate at low operating temperature, energy saving became advantage for production. Besides, the operating pH of this bath is neutral which provides a more favorable condition for soldermask on PCB when compared with alkaline bath.

Plating Rate

This Cyanide-free immersion gold bath is capable of depositing about 2 μm with a process cycle of 10 – 12 min at 45°C. The deposition rate was maintained after bath aging (Fig. 1). The deposition rate was also maintained after heat idling at 50°C for 28 days (Fig. 2). The variation in immersion gold thickness between different pad sizes (pads with sizes of 1 mm x 3.5 mm and 8 mm x 8 mm) was found to be small and comparable with conventional cyanide containing gold bath throughout the bath life study (Table 1).

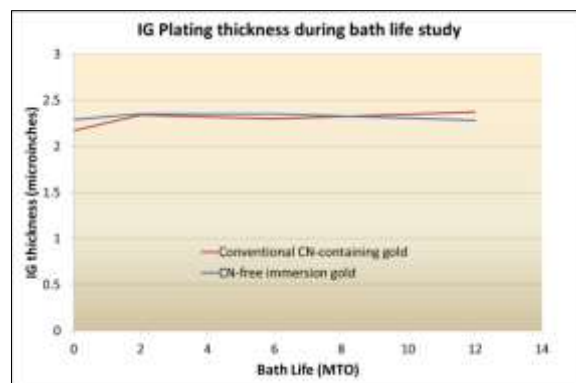


Figure 1: Comparison of IG plating thickness for the CN-free immersion gold bath (45°C, 11 min) and Conventional CN-containing gold bath (84°C, 8 min) as a function of bath life.

¹ Sharemate Technology (Dongguan) Co. Ltd.

² Cookson Electronics

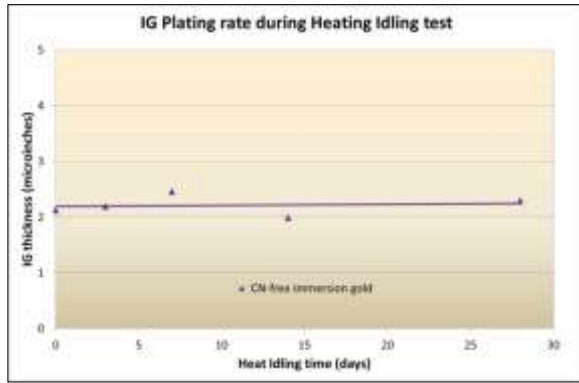


Figure 2: IG plating thickness for the CN-free immersion gold bath (45°C, 11 min) as a function of time of heat idling at 50°C.

CN-free Immersion Gold bath			
MTO	Standard Deviation	Means	Coefficient of Variance
0	0.11 μ''	2.29 μ''	0.05
2	0.14 μ''	2.35 μ''	0.06
6 ³	0.14 μ''	2.35 μ''	0.06
12 ³	0.11 μ''	2.28 μ''	0.05

Conventional CN-containing Gold bath			
MTO	Standard Deviation	Means	Coefficient of Variance
0	0.16 μ''	2.17 μ''	0.07
2	0.21 μ''	2.34 μ''	0.09
6 ³	0.25 μ''	2.30 μ''	0.11
12 ³	0.25 μ''	2.37 μ''	0.11

Table 1: Comparison of IG plating thickness distribution for the CN-free immersion gold bath and Conventional CN-containing gold bath as a function of bath life.

Corrosion Resistance Analysis

Corrosion resistance on EN surface of as-plated samples and samples after 1x OSP prepared by OSP simulation were investigated. Samples prepared with the newly developed immersion gold were investigated using plain view SEM after gold stripping (Fig. 3). No corrosion on the as-plated samples and only small pits on surface for samples after OSP simulation were observed.

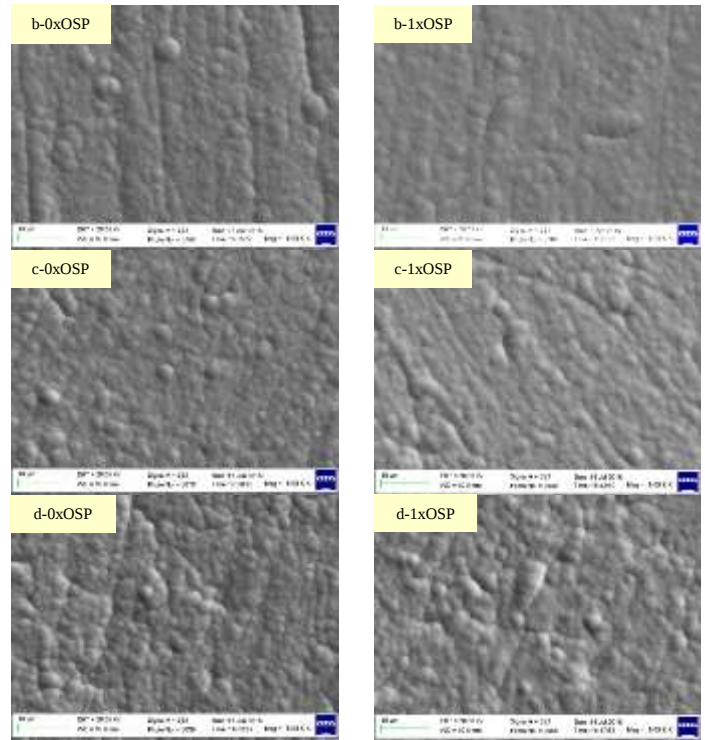
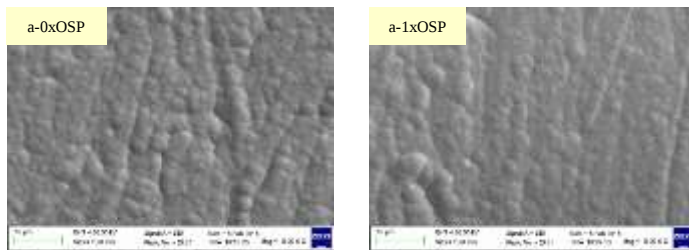


Figure 3: SEM images of EN surface for as-plated (0 x OSP) and after OSP simulation (1 x OSP; copper etch 0.75μm) of ENIG after gold stripping; (a) 0 MTO (b) 2 MTO (c) 6 MTO and (d) 12 MTO.

Investigation was also conducted on as-plated sample with cross-sectional FIB SEM (Fig. 4). Cross-sections were milled with a focused ion beam, and SEM photos recorded on the samples. These results show that the ENIG deposit was free of abnormal local corrosion during immersion gold deposition.

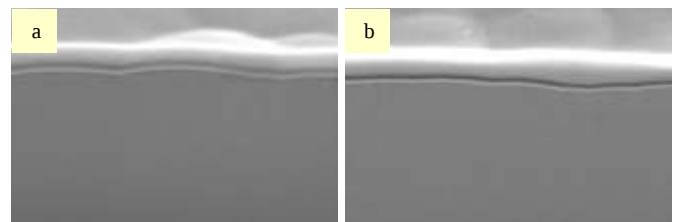


Figure 4: Cross section FIB-SEM images of ENIG deposit for (a) fresh bath and (b) aged bath from Cyanide-free immersion gold chemistry.

Au layer composition study

IG layer composition is piece of important information for electronic industry. Changes in composition of gold layer may affect the capability in resistance to corrosion, electrical conductivity, ductility and stability. The composition of the IG deposits was evaluated by XPS.

Survey scan and elemental scan (C, N, O, Au, Cu, Ni, P and S) was conducted during depth profiling. No Cu or S or other foreign element was detected which was indicated in Fig. 5 where Au was dominated in the IG layer. No chemical state changes during depth profile which

³ Simulated aged bath



was shown in Fig. 6. Both evidences indicated the IG layer formed was a pure Au layer even bath was aged with Ni ion was built up to 700ppm and Cu ion was built up to 6ppm.

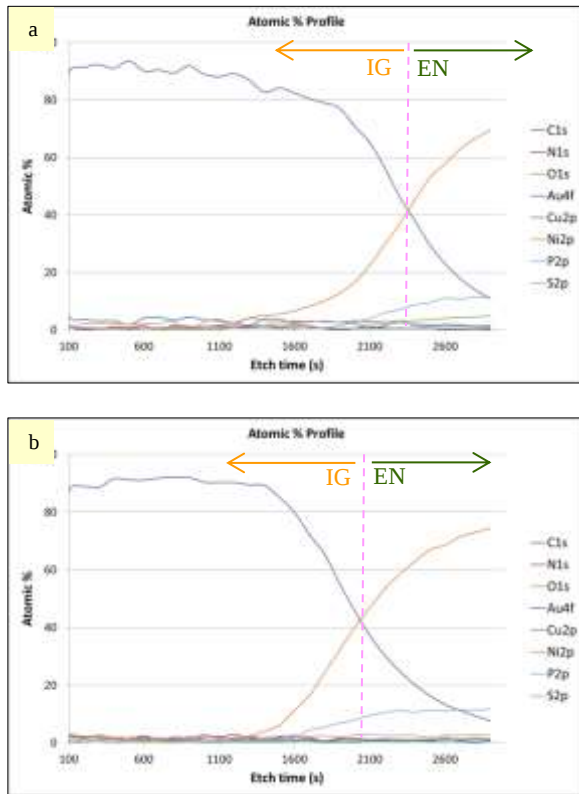


Figure 5: Atomic % depth profile of IG layer to ENIG interface for the as-plated sample of (a) the fresh CN free immersion gold bath and (b) aged CN-free immersion gold bath with 700ppm Ni and 6ppm Cu.

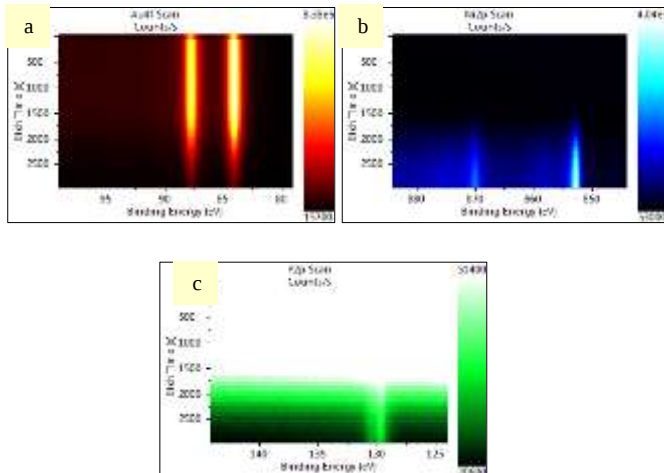
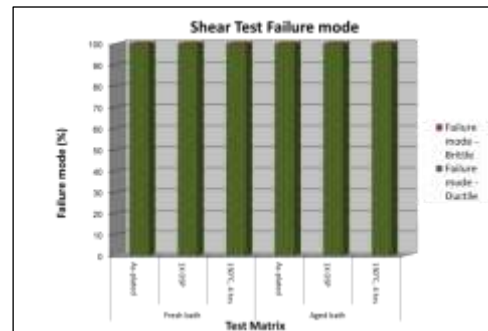
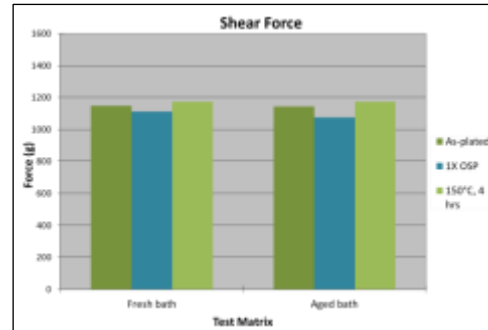


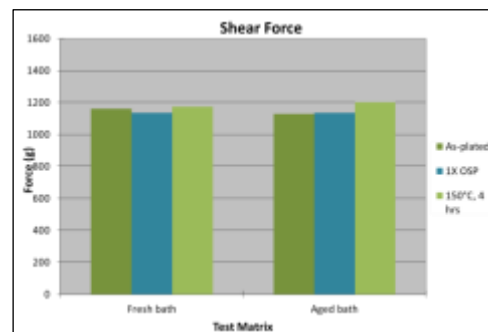
Figure 6: Elemental scan during depth profile of IG layer to ENIG interface (a) Au scan (b) Ni scan and (c) P scan of aged CN-free immersion gold bath with 700ppm Ni and 6ppm Cu.

Solder Joint Strength

The strength of solder joints formed on the ENIG deposits was evaluated using normal speed ball shear test. The shear forces and failure modes of the ENIG process with the Cyanide-free immersion gold bath was compared to ENIG process with conventional cyanide-containing immersion gold bath. Samples included as-plated samples, samples after 1x OSP simulation and after heat treatment at 150°C for 4 hours and the results were showed Fig. 7.



(a) Shear Force and Failure mode of the ENIG deposit of Cyanide-free immersion gold



(b) Shear Force and Failure mode of the ENIG deposit of Conventional cyanide-containing immersion gold



Figure 7: Ball shear test result comparison of the ENIG deposit: (a) the Cyanide-free immersion gold bath and (b) Conventional cyanide-containing immersion gold bath.

The shear force reported in Fig. 7 showed that the ENIG deposit from both baths had similar shear force which was exceeded 1100g under the three different conditions. More important is the shear failure mode of the solder joint was ductile. It was the most desirable failure mode. It indicated that the failure occurs within the bulk solder rather than along the intermetallic region and the bonding provided from the intermetallic layer was very strong. The findings were applicable to both fresh bath and aged bath of the Cyanide-free immersion gold and Conventional cyanide-containing immersion gold chemistry.

CONCLUSION

A high performance Cyanide-free immersion gold process has been developed. The plating behavior and performance results in this paper shown the newly developed chemistry is suitable for ENIG application. The process has been optimized to have stable plating rate, deposit with excellent uniformity, good corrosion resistance, pure Au layer formed in IG process and stable solderability performances.

Elimination of cyanide from the ENIG process makes the process more environmental friendly and safe from toxic chemicals. Also, the low operating temperature gives another advantage for energy saving.

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