PD• 6NH3• 2RX: NEW PALLADIUM ELECTROLYTE FORMULATION ENABLING THINNER METAL OPTIMUM DEPOSITION

Mharpee T. Gonzales
Jeffrey S. Solas
Michael L. Pangilinan

Texas Instruments Inc.
TI Clark, Clark Freeport Zone, Angeles City, Pampanga
m-gonzales1@ti.com , j-solas@ti.com , m-pangilinan@ti.com

ABSTRACT

Electroplating efficiency is defined in terms of anode (ion) to cathode (metal) conversion. This study maps-out factors contributing to low plating efficiency of Palladium (Pd) being the top cost electrolyte for wet chemicals. The existing bleed-feed system and unoptimized ion concentrate conversion are the main sources of low ion-to-metal conversion with 27% and 38% contribution respectively. Nernst and Mass-balance applications were used to derive new formulation of Pd electrolyte containing C* gpL of Pd concentrate optimal for X Å /ft^2 current density. The new formulation also addresses other challenges including (1) yield loss due to metal surface dents solved by lowering heat of formation (ΔH) of H_2 gas (2) early pump failures solved by lowering bath viscosity thru salt recalculations and (3) thickness uniformity issues solved by chiller system modification for tighter temperature control. New formulation also has 4x longer life than baseline with good metal quality, reliability and passing wire bonding assessments. This study enables qualification of Thinner Y-*um* Pd of BOAC Technologies packages and implementation of electrolyte auto-dosing system which can be benchmark to other metal chemistries including Copper, Nickel and Tin-silver towards optimum plating-efficiency covering all devices and technologies.

1. 0 INTRODUCTION

Palladium (Pd) is one of the most stable but expensive metals of semiconductor today. It serves as a protective layer for BOAC (Bond Over Active Circuit) technologies including automotive devices inhibiting penetration of corrosion due to its metallic structure stability. It also prevents diffusion [1] of other metals such as Copper migration which may result lifted ball during wire bonding similar to *Figure 1*.

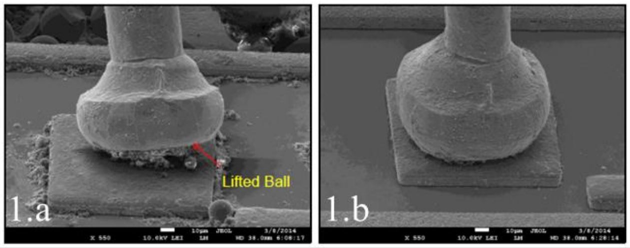


Figure 1:
(1-a) shows lifted ball due to Cu migration; (1-b) baseline

Throughout the year, the demand for Palladium (Pd) metals manufacturability and the cost of its raw materials have vastly increased. The cost per pattern (CPP) has become a constant challenge to all Fab and Bump sites making Palladium electrolyte as the most expensive chemical for wet process and second to *Polyimide resist* across all bump sites.

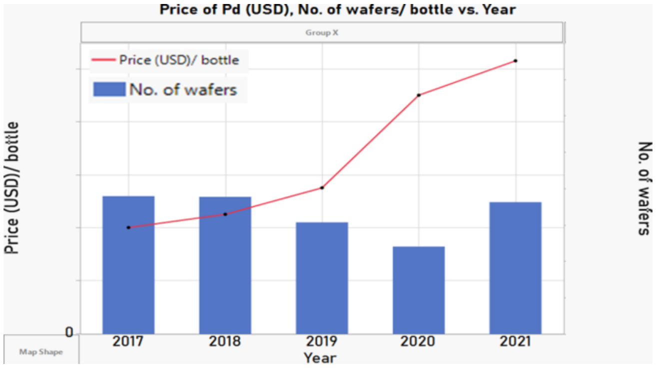


Figure 2:
Trend for cost of Pd ion chemical increases over the years vs. the number of wafers processed.

This paper combines multiple studies towards understanding Palladium (Pd) metal deposition from source (anode) to surface (cathode) towards achieving product, process and system efficiency to drive for continues improvement in reducing cost of manufacturability.

1.1 Electroplating: Metal deposition

Electroplating is a widely use wet process technique of depositing metals on wafer surface. Plate process chamber shown in *Figure 3* is mainly composed of 4 key components: (1) Anode –ion source (2) Cathode – substrate to be plated (3) Power supply and (4) Electrolyte- chemical solution medium. This study centers on plating chemistry of Palladium metals using a Electro Chemical Deposition (ECD) plater *Model SS* utilizing X Å /ft^2 current density.

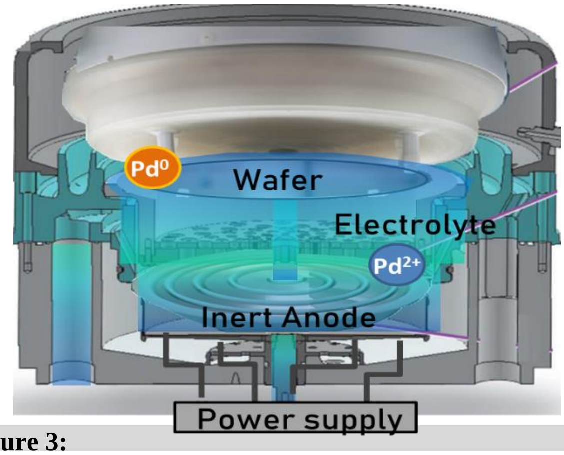


Figure 3:
Cross section of plating chamber where inert anode and wafer (cathode) are submerged in electrolyte solution (life of plating)

Metal deposition occurs inside a process chamber where wafer is submerged in an electrolyte or bath facing the anode. Palladium plating makes use of A/B inert anode which serves as positive (+) contact and direct passage of current while the negative (-) contact is found on chamber head connected to the ring assembly holding the wafer.

Unlike other metal chemistry, Pd ion primary source originate from the electrolyte solution *per se*. This makes its base chemical, additives and pure concentrate required to build the electrolytic bath more and more expensive. One Pd chamber bath build has a cost of >$35K. Based on 2017 data, additional 150% cost per chamber is needed to sustain desired x gpL concentration of Palladium per month and additional 80% cost per chamber in a year for bath life maintenance once max wafer count or *Amp.min*. value count was reached. As seen on *Figure 2*, the current cost of palladium electrolyte increased by as much as 3x and is expected to increase for the incoming years.

1.1.1 Anode: The source

Palladium electrolyte is composed of 3 main components serving their own individual functions vital for metal quality and reliability. Each of these components are being consumed as metals are deposited on wafers hence must be maintained with their desired concentration range.

Table 1: Palladium bath components with their corresponding concentration limits and functions

Component	Concentration	Function
Pd (ion)	cc-CC gpL	Main Pd ion source
Ammonia	pp-PP (pH)	Buffer
Ammonium salt	dd-DD gpmL	Conductivity

Critical properties of bath known for Pd plating include pH and viscosity. Ideal Palladium plating occurs at basic pH but pH becomes acidic in continues processing. Buildup of hydronium (H^+) ions occurs from anodic-cell reaction inherent to plating process is what causes pH shift.

Resist leaching can also contributes to excessive build-up of H^+ especially the operating temperature for Pd is at T °C. Resist leaching occurs when the organic materials of photomasks (**α**) react to corrosive plating bath (β) affecting the activity of ions presented as **α** > β which is usually occur at higher temperature [2]. Organic resist leaching affects metal quality (Carbon traces on Pd surface) and is mitigated by monitoring viscosity of Pd bath during bath maintenance and performing bath change thru complete electrolyte dumping once bath life was reached. Bath maintenance plays big role in ensuring bath integrity.

A. Bath maintenance

Each bath component concentration is being checked and sustained daily. During maintenance, tool is being placed to maintenance state to (1) Obtain sample, (2) Titrate or analyzed, (3) Calculate required replenishments, (4) Actual dosing and (5) Tank stabilization. 20% of tool overall availability is loss due to these activities adding up to cases for action.

Ion loss from maintenance:

(1) During sample obtainment from the tank, approximately 0.6% of total volume per analysis is loss which is equivalent to 40% of tank loss in a month. Once low level of tank is triggered, deionized (DI) water make-up will replenish causing bath dilution, lowering concentration of components hence ions are loss.

(2) Titration analysis for Pd ions make use of AA Spectrometer where Pd ions from bath are ionized into gasses and the absorbed ionization energy was read thru Pd spectrum. Precision of metrology is greatly affected by unfiltered Pd spectrum creating false concentration detections affecting bath analysis results.

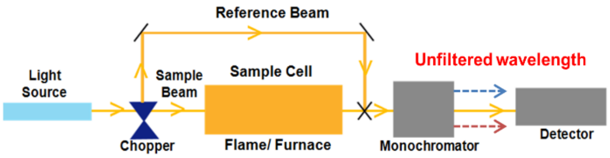


Figure 4:
AA spectrometer process of detection diagram

(3-4) Based on titration results, required replenishment is calculated thru dilution formula (CxVx=CyVy where (x) is original concentration (C) and original volume (V) and (y) is the aftermath. This method which makes use of single volume-based component calculation contribute to other components ion loss during maintenance resulting to excessive bleeding as presented on Table 2.

Table 2: Palladium bath components calculation for method of replenishment where Feed>Bleed

Component	Calculation	Bleed/Dumping
Pd (ion)	$C_1V_1=C_2V_2$	Yes, excessive
Ammonia	$C_3V_3=C_4V_4$	Yes, excessive
Ammonium salt	$C_5V_5=C_6V_6$	Yes, excessive

(5) Pd chemistry is working at elevated temperature of T °C. Loss in evaporation during tool idle triggering DI make-up replenishment resulting to dilution and loss of ions. This need further study and actions to mitigate.

1.1.2 Cathode: The Surface

The direction of Palladium metal thickness on BOAC and similar packages is going thinner. From 2017, Pd thickness moved from YYY um to YY um and since 2021, *Worldwide Bumping* is currently qualifying Y um Thinner Pd thickness on packages with no lifted ball issue.

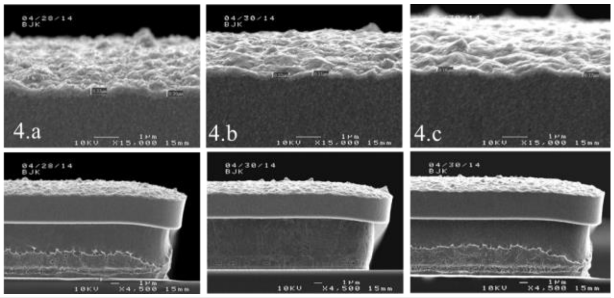


Figure 5:
(4.a) is high magnification and cross section of BOAC metal with YYY um Pd (4.b) is for YY um Pd and (4.c) is for Y um Pd

As industry moves to thinner Pd, several challenges on Pd metal quality need solving. These challenges involve yield loss and thickness non-uniformity across the wafer which factors originating from electrolytic bath. These issues are expected to be magnified as we move to thinner Pd metals.

A. Yield loss

One of the top defect contributors for BOAC and similar technology is "Dimple". As shown in *Figure 6*, it is a white metal abrasion or dent manifesting on the surface of Pd layer. This defect originates from the excessive bubbling of Pd bath due to evolution of hydrogen gas which is inherent to Pd plating process and is aggravated by acid formation.

$$2\,H^+(if\ too\ acidic) + 2e^- \rightarrow H_2(gas\ evolution)$$

The bubbles pop during plating creates a dent on metal surface (missing Pd). As BOAC technology moves to thinner Pd thickness, there is a high risk to induce a No-Pd coating on surface which may result to lifted ball.

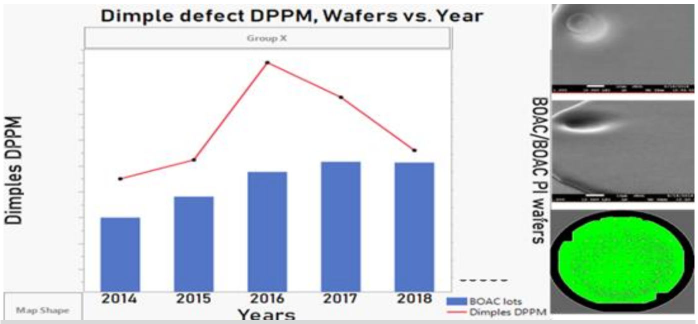


Figure 6:
Defect trend of "dimples" on Pd surface vs. BOAC wafers processed

B. Uniformity challenge

Top Risk based on Failure Mode and Effect Analysis (FMEA) for Pd plating is "Dual-tone" defect. As shown in *Figure 7*, it is characterized by two- metal colors caused by huge differences on uniformity of Pd thickness within the die and across the wafer.

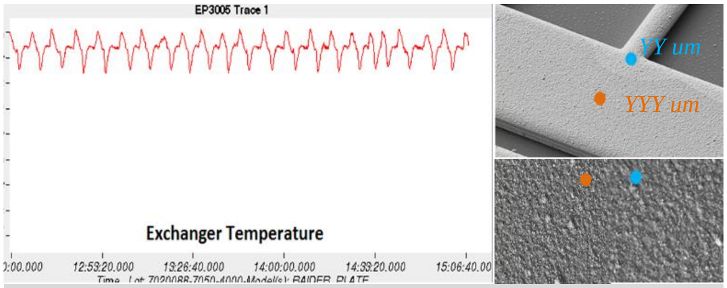


Figure 7:
"Dual tome" defect originates from uncontrolled temperature of tank due limitations of refrigerant chiller design causing high standard deviation (0.76) on tank temperature.

Uncontrolled uniformity is critical as we move to thinner Pd. Previous study also points uncontrolled bath temperature [3] and ageing bath life [4] contributing to challenges in uniformity hence must be considered in implementing controls and actions.

This paper integrates and improves cathode (Source) to anode (Surface) efficiency in terms of (1) Minimum ion loss on bath for process efficiency (2) Optimum Pd metal thickness, yield and uniformity for product quality and (3) Lowering overall BOAC manufacturability cost thru improvement programs.

2.0 EXPERIMENTAL SECTION

2.1 Materials

This study centers on ion speciation of Palladium in ammonia and ammonium salt only as basis of new electrolyte formulation in X $/ft^2$ (ASF) current density. Other Pd-X chemistry and plating ASF may require different calculations and study but similar concepts may apply.

This study makes use of *Plater SS* utilizing upgraded Process Cooling Water (PCW) chiller system to maintain tt-TT °C temperature. Metrology used to get responses were *AA* spectrometer, *DD* densitometer and *MM* pH meter for bath component analysis, *FF* XRAY for Pd thickness, *CK* Automatic Visual Inspection (AVI) for Grayscale value (GSV) response and yield, *SMS YY* texture/stress analyzer, *AEYY* Auger's analyzer and *AS* ToF-SIMS imaging for metal quality check.

Packages and technology cover all BOAC technologies including automotive with open area ranging from >10%. Both Bumping and Assembly risk assessments were covered.

2.2 Procedure

This study made use of Enhanced Fault Tree analysis (EFTA) in identifying all possible causes of ion-to-metal loss in Palladium plating system. The causes were categorized as (1) From the source which centers on mapping out where ions are loss during plating maintenance and process and (2) From the Surface from which inefficiency and inconsistency of Pd metal thickness deposited on substrate or wafers. Heat map was generated to identify high risk factors and different programs were generated to mitigate each risk.

The center of the study is the formulation of new electrolyte solution. Thru the use of manipulated Nernst law and Mass balance equations and utilizing process operating parameters, optimum component concentrations and combinations were derived using equation 1:

$$Ecell = E°cell - \frac{RT}{zF}\ln\frac{[\,Oxidized\ component\ 1{,}2{,}3\ \ldots]}{[Reduced\ component\ 1{,}2{,}3\ \ldots]}$$

where E/Eº is potential of cell, RT/zF is constant and [oxidized & reduced component] were calculated

This was done to re-define component concentrations minimizing side chain reactions on bath contributing to ion loss in plating system. Process margin was then defined thru actual design of experiments (DOE) and risk assessments. Further adjustments were made on concentration combinations to address other challenges originating from Pd electrolyte bath including dimples and nonuniformity. Life of newly formulated bath was also defined after achieving lower variation on tank temperature thru chiller system upgrades.

New method of tracking behavior of bath components in a continues wafer processing was also done thru Statistical Process Controls or SPC. This is thru setting up new Delta charts for concentration over *Amp.min*. which corresponds to products process. DI fill occurrence tracking thru Tools Realtime automated detection was also set-up to record dilution occurrence.

Combining all actions at one, new bleed and feed auto-dosing system was generated to address ion loss on Palladium plating improving overall efficiency.

To support risk assessments of new formulated bath, multiple wire bonding and reliability tests were performed including ball shear, wire pull, CSAM (0-3), MSL2A, HTSL (150 °C/1000 hr.), Autoclave (121 °C/168 hr.), TC500 (-65 to 150 °C) and also high-level surface analysis including Auger Test and Time-of-flight (TOF) analysis for possible cation/anion contamination- Carbon, Oxygen, Chlorine etc.

3.0 RESULTS AND DISCUSSION

3.1 EFTA Results

High risk factors based on EFTA in terms of Risk priority number (RPN) were (1) Ion concentrate conversion-240 RPN, (2) Bleed Feed system-180 RPN (3) AAS Analysis loss- systematic error –160 RPN (4) Evaporation loss-90 RPN.

3.1.1 AAS analysis

Systemic error from titration analysis was addressed first to ensure repeatability of concentration results throughout the study.

Based on review of titration results of Pd metals using AA spectrometer, wide variability was observed parallel to scheduled lamp alignment and zero offset which was part of tool maintenance. This activity creates uncontrolled wavelength scattering which need 1-2 days conditioning prior stabilization.

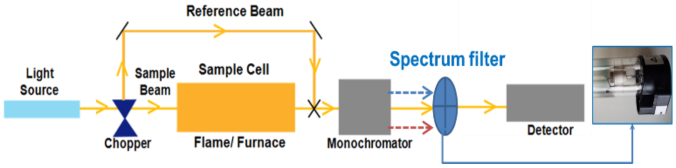


Figure 8:
Improved AA spectrometer diagram after installation of spectrum filter- innovation is 1^{st} to TI

Installation of spectrum filters was implemented during the conditioning to screen out spectrometer noises. Use of standard solutions plot thru SPC were used to validate effectiveness of actions. cpK improved from 1.01 to 2.43 ensuring repeatability of analysis by 96%.

3.1.2 Ion concentrate conversion

Based on equation 1 calculation, cc gpL concentrate of Pd ion was derived vs. CC gpL (baseline) in X ASF plating operating specification. This is still within technical specification of supplier which is x-cc gpL in well agitated bath.

DOE was performed to measure responses such as thickness, visual results, weight, shear, and yield. As shown on *Table 3*, the GSV response is showing Conditional range upon approaching xcc gpL and below (p-values =0.051) for open area >50%. From there, new target of c* gpL was defined with specification of ± 1 gpL. Data was replicated on multiple open areas and on different bath life.

Table 3: Summary of experimental results supporting calculations where in passing risk assessment is between C-CC (P=passed; C=conditional; F=Fail)

	200 mm			300 mm			
x-cc	Thick	GSV	Yield	Thick	GSV	Yield	
cc	P	F	P	P	F	P	
c	P	C	P	P	C	P	
C	P	P	P	P	P	P	L-spec
C*	P	P	P	P	P	P	Target
CC	P	P	P	P	P	P	U-spec

This result supports that optimum plating can be done at lower concentration- C* gpL vs. CC gpL (baseline) to minimize larger loss of ions brought by side chain reactions. Higher Pd concentrate may precipitate as $PdCl_2$ and $Pd_2(OH)$ which are non-free ions hence not convertible to metals [4]. High organic material leaching activity is also an indication of high side chain reactions hence it is best to run on optimum/minimum concentration value to minimize this phenomenon.

The new formulation containing new Pd ion concentration improves efficiency by 8% and has annual savings of USD >20K.

3.2 New formulation: The Source

As the new target concentration for Pd change, other components including pH additive (ammonium hydroxide) and conductivity salt (ammonium salt) were also revisited using the same concept of mass balance calculations seen on *Table 4* with verified responses thru DOE seen on *Figure 9*.

Table 4: Summary of speciation and calculation results defining new limits requiring response validation/assessment

Component	**Pd ion (Pd)**	**Ammonia (•6 NH_3)**	**Salt (•2 RX)**
Limiting reagent	$Pd(OH)_2$	OH^-	PdO
Calculated concentration	cc gpL	m.m $x10^{-m}$ M or pH= PP	d.d M or dd gpmL
Specification	C*- CC gpL Target: C*	pp -PP pH Target: P*	dd-DD Target: D*
DOE required	Yes, OOS	Yes, OOS	Yes, OOS
New specification	C-CC gpL	P*-PP pH	dd-D*

RX= *inorganic* salt

Based on the results of DOE, increasing the ammonia level by 3% improved yield by 1-2% for non-automotive and 3-6% for automotive devices as shown on *Figure 9*.

By means of increasing the ammonia content, hydronium ions are controlled hence the heat of formation of hydrogen gas was also lowered mitigating evolution of hydrogen gas during plating: $\downarrow 2\,H^{+} + 2e^{-} \rightarrow \downarrow H_2$.
In addition, since evolution of H_2 gas is inherent to the process, installation of de-bubbler on pipelines was also done as a proactive action.

Low counts of tool down time originating from early pump failures was also lessen by 60%. This is after implementation of lower conductivity salt of bath reducing viscosity of liquid by 8% avoiding excessive clogging of pump and pipes.

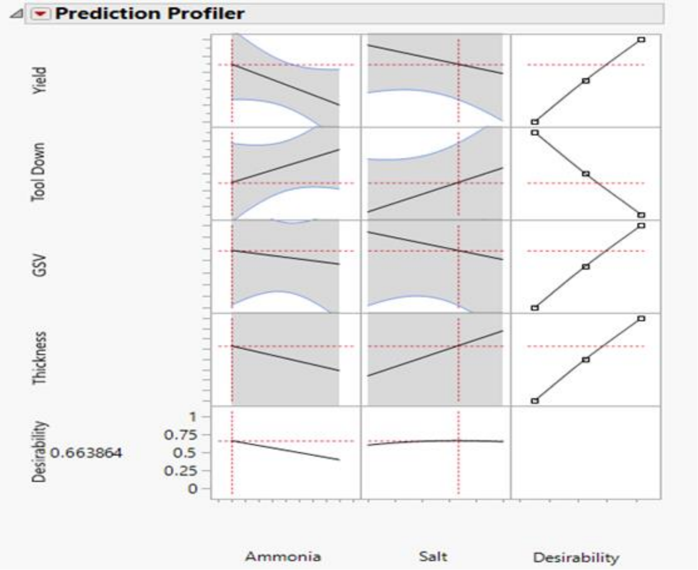


Figure 9:
Predicted profiler to define maximum desirability of Ammonia and salt concentration vs. responses

3.3 New Pd thickness: The surface

Table 5: Summary of stress test done on different packages with varying Pd thickness. YY um was qualified for BOAC packages with supporting risk assessments.

Cu + Ni + Pd µm	**Pd stress (Z-5Z mPa)**	**Remarks**
C + N + Y	Z*	Passed- New Qual
C + N + 1.5Y	Z*	Passed- Qualified
C + N + YY	Z*	Passed- Qualified
C + N + YYY	Z	Passed- Baseline
1.5C +N + YY	Z*	Passed
2.0C+ N + YY	Z*	Passed

To enable further reduction of Pd thickness on packages as shown in feasibility study of *Table 5*, Pd thickness uniformity must improve [4]. This was achieved by converting current chiller system from refrigerant based cooling system to Process Cooling Water (PCW). Upgraded PCW chiller which make used of fix input setpoint of 10-12 ºC versus variable setpoint of previous chiller which has system-based adjustments on cooling set-point. Chiller system upgrade cut down standard deviation of tank temperature from 0.76 to 0.48 sigma. The PCW chiller is also made of stainless materials which eliminated frequent down time due to damaged copper steel of refrigerant system. Realtime auto-detection was also activated for real time detections of failure and fixing contributing to heat gain or loss.

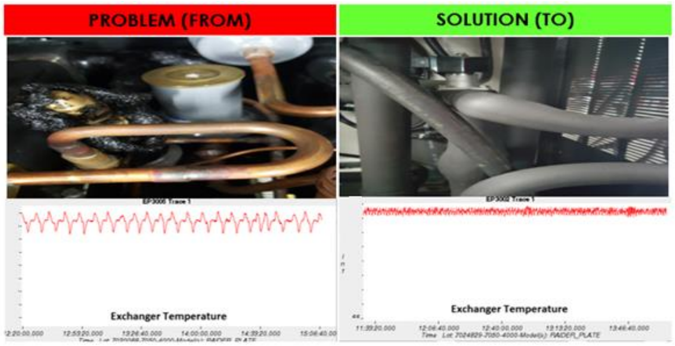
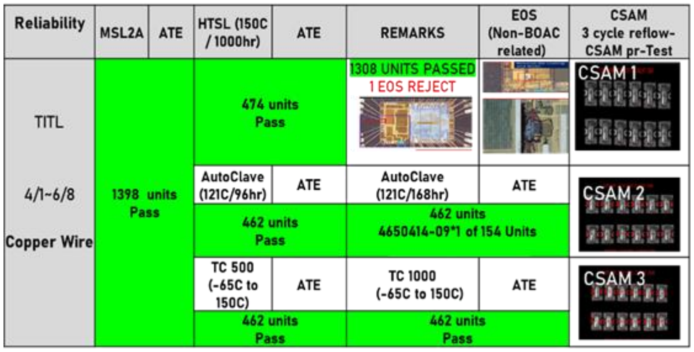


Figure 10:

Upgrade from refrigerant based system (problematic) to PCW chiller showring improvement on chiller/tank temperature by 36%.

With improved chiller system and temperature operating range, new bath life and bath change maintenance method was also implemented in 2020. From KK *Amp.min* value for 200 and 300 mm, Pd life is now operating at 2x longer life for 300 mm and 3x longer for 200 mm. Maintenance was changed from complete bath dumping to 50% dumping which adds up to the total savings.



Reliability	MSL2A	ATE	HTSL (150C / 1000hr)	ATE	REMARKS	EOS (Non-BOAC related)	CSAM 3 cycle reflow-CSAM pr-Test
TITL 4/1~6/8 Copper Wire	1398 units Pass		474 units Pass		1308 UNITS PASSED 1 EOS REJECT		CSAM 1
			AutoClave (121C/96hr)	ATE	AutoClave (121C/168hr)	ATE	CSAM 2
			462 units Pass		462 units 4650414-09*1 of 154 Units		
			TC 500 (-65C to 150C)	ATE	TC 1000 (-65C to 150C)	ATE	CSAM 3
			462 units Pass		462 units Pass		

Figure 11:

Complete wire bond and reliability assessment conducted at Assembly Site

Plated metals using the newly formulated Pd electrolyte and new Pd thickness showed passing wire bonding and reliability test. 1 EOS reject seen after Autoclave at 121 ºC/168 hr. but was nullified as EOS was observed after removing BOAC and die coating layers from which located far from plated BOAC metals.

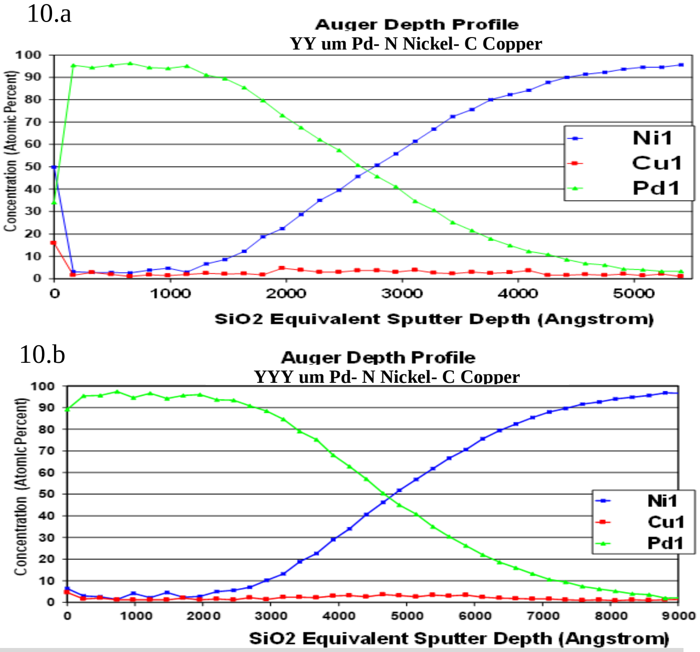


Figure 12:

Auger depth analyses profile for 10.a - YY um Pd using newly formulated electrolyte vs. 10.b YYY um Pd (baseline solution)- comparable

Auger surface analyses showed YY um Pd deposits processed using the newly formulated electrolyte has the same registry of %elemental composition and metal purity compared to baseline (YYY um Pd) with p-value of 0.541 which means that quality of metals produced by the study did not change.

ToF SIMS results also showed no traces of unknown positive (Li, Ti, C^+) and negative ions (O, F, Cl) induced on the surface of metals run at 10 Å depth and 20 Å depth removal. As shown on *Figure 13*, Traces of Carbon negative (C^-) showed higher peak registry of 82 amu vs 22 amu of baseline at 10 Å depth removal. However, increasing removal rate to 20 Å and curing samples at 380 ºC did not manifest trace of Carbon hence possible traces of C^- can be treatment related. Nevertheless, the metal quality and reliability remain pure and unchanged throughout the study.

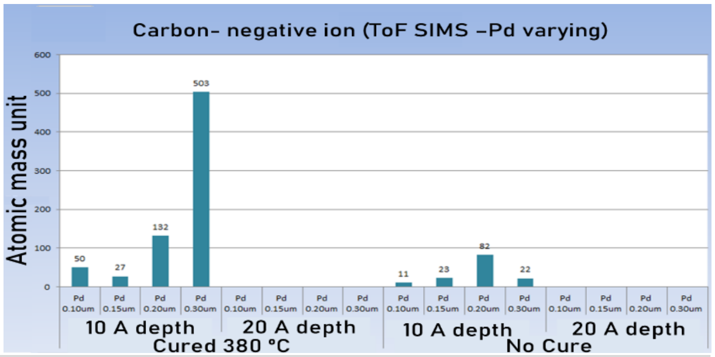


Figure 13:

ToF SIMS result for Carbon elements- critical to check if resist leaching made of Organic carbon can contaminate metal deposits.

3. Auto-Dosing Capabilities

Through the use of newly defined optimum concentration, high process capability values (SPC) of concentration drop over *Amp. min.* (wafer processed) and predictable DI Fill occurrence over time, Pd plating auto-dosing is now ready for implementation. The new system will make use of pre-formulated concentrated bath as source of Automatic chemical fill. The new dosing system eliminates tool down time from bath maintenance and is expected to impact tool overall availability to 95% and IDL productivity by 80%.

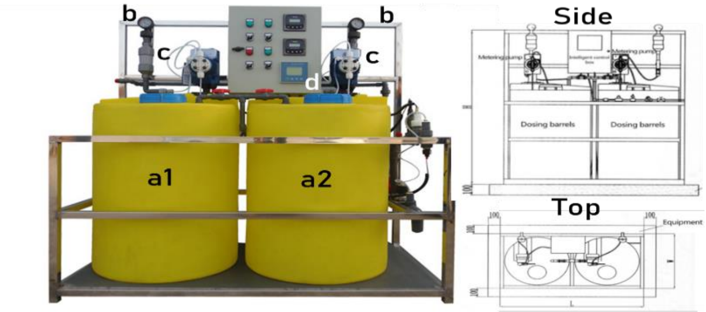


Figure 14:

Sample model for new auto dosing units made of a1= main tank, a2= back up tank, b= flow gauge, c= actuator valves, d= main control

4.0 CONCLUSION

Other Site copied bath specification were challenged. Enabling lower thickness YY um Pd with optimum uniformity can be achieved by optimizing concentration of ions. The newly formulated Pd electrolyte was adapted to achieve high metal-to-ion efficiency. Loss of Pd ions originates from bath analysis maintenance from which 8% systematic error affecting titration repeatability was eliminated after spectrum filter installation. Unwanted side chain reactions of bath components were also solved by lowering Pd ion concentrate from CC gpL to C* gpL. Increasing ammonium hydroxide content by 3% also improved dimple defect DPPM by 82% and lowering conductivity salt improved bath viscosity eliminating early pump failures and clogged pipelines. In addition, uniformity was also achieved by minimizing temperature tolerance from ±1 ºC to ± 0.5 ºC through PCW chiller system upgrade. Consequently, prolonged the bath life of new formulated bath by 60% for 200 mm and 50% for 300 mm. In terms of bath life maintenance, qualification of 50% bath dumping (instead of 100%) was also implemented to further cut down the cost of bath maintenance by 55%. These improvements have paved way to Y um Pd packages qualification at 93% plating efficiency. Quality and reliability tests of plated metals utilizing new Pd bath formulation passed risk assessments covering Bump, A/T and Advance surface analysis and assessments.

This project has been shared and implemented to all other sites with an overall cost savings equivalent more 250% improvement from forecast. This project supports continues CPP reduction of Bump with ensuring Quality as the top priority.

5.0 RECOMMENDATIONS

It is recommended to implement auto dosing capabilities to all plating chemistry including SnAg, Copper, Nickel which will further improve tool productivity by 10%.

The use of mass balance calculations as basis for stoichiometry can be used for optimum material or chemical to process efficiency. This is applicable to any organic or inorganic solutions, mixtures or solvents from which analytes are known. For example, the concept can be used to define wet etchants mixture concentrations of acid and oxidizers for optimum removal of known seed layers. This concept is also applicable for calculation of minimum volume and solvation of photoresist, developer, stripper and flux that will zero out resist or flux residue applicable to sites using chemical-to-materials assessment.

All major projects such as calculations of new target concentration, new bath life maintenance and longer bath life has been fan-out to other sites. Two sites have completed fan-in of new concentrate in first quarter of 2021.

6.0 ACKNOWLEDGMENT

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8.0 ABOUT THE AUTHORS

MHARPEE GONZALES, Resident Chemist at Texas Instruments Clark since 2013 with Masters in Pure and Applied Chemistry. He was recently elected as member of Technical Staff (MGTS) in 2023.

MICHAEL PANGILINAN, Computer Engineer. Joins Clark Equipment Engineering in 2010 and has been a member of Technical Staff (MGTS) since 2022

JEFFREY SOLAS, Chemical Engineer. Joins Clark in 2006. Elected as MGTS in 2016 and SMTS in 2020.