Direct Plating for Flex and Rigid-Flex Boards

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Abstract

In manufacturing flexible and rigid-flex boards, the metallization step using electroless copper poses a major challenge, namely the leaching of polyimide base material into the plating bath. Leaching is exacerbated by the combination of high alkalinity and extended dwell time in the bath during the plating cycle. The result of excessive leaching is the degradation of the quality of the plated deposit leading to compromised adhesion. This is presently overcome by increasing the renewal frequency of the electroless copper plating solution, increasing the demands on bath control as well as the overall cost.

Our process introduced in this paper forms a thin conductive Palladium film on the dielectric, eliminating the need for electroless copper deposition step. The conductive film readily accepts copper electro-plating and yields an adherent deposit.

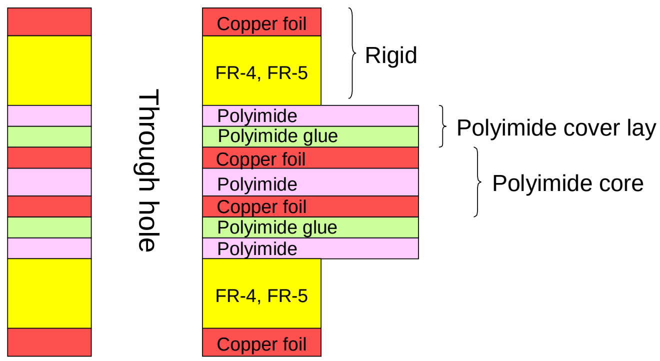
The process requires a short immersion time in an alkaline solution, alleviating any damage to the resin and minimizing the accumulation of leached byproducts. The palladium is specific to the dielectric resin and does not adsorb to the copper surface eliminating the need for copper etching before electroplating. The treatment time is short leading to improved productivity. The process is stable and easy to control, resulting in enhanced adhesion and increased inner layer connection reliability.

Introduction

As hand held electronic devices take hold in all phases of business, there is a continuous need to reduce weight and size. The demand for flex and rigid flex circuit boards continues to grow. Flex offers advantages in weight as well as form to fit in constricted dimensions, like cell phones, video cameras, bar code readers etc.

The most popular material used in flex and rigid-flex boards is polyimide resin. It provides good thermal resistance, outstanding electrical properties as well as dimensional stability. However conventional plating methods are being stretched to their limits to attain the required reliability of the finished product.

Fig.1 Typical rigid-flex substrate



A rigid flex stack-up (Figure 1) is normally composed of a multitude of materials; copper, epoxy resin (FR4 or FR5), glass fiber and polyimide. Two types of polyimide products are used, one is the core material and the other is an adhesive layer which covers the copper in the core material.

In general, adhesive layers have inferior chemical resistance as compared to that of thermoplastic polyimide resin, which is used for core and cover-lay. Excessive leaching from the adhesive layer will contaminate the plating solution as well as create a dent/wedge between copper and the laminate, thus compromising the laminate strength.

It is difficult for electro-less copper plating process to provide satisfactory electric conductivity to four dissimilar materials of copper, glass, epoxy, and polyimide. Accumulation of leach byproducts has an adverse effect on adhesion and connection reliability. Leach byproducts are usually controlled by accelerating the solution renewal cycle, at the expense of bath life.

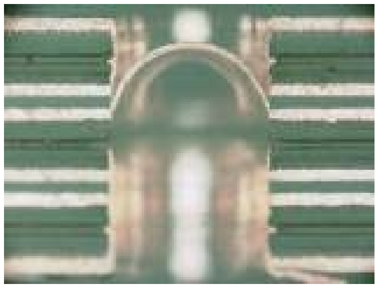
In this paper, the “Palladigm® process” is introduced, which is presently under development as a direct plating process that is assumed best to manufacture flexible and rigid-flex substrates in which various polyimide materials are used.

Problems of flexible and rigid-flex substrates in conventional process

To date, electroless copper plating is the most popular method for metallization of through holes (TH) and blind via holes (BVD). However, almost all the electroless copper plating baths are very high in alkalinity (pH of 13 or higher), and require a prolonged dwell time. For flexible and rigid-flex substrates, which use polyimide, this leads to nonconformity to adhesion and reliability specifications.

Prolonged dwell time may result in the opening of the imide ring due to its hydrophilicity in aqueous alkaline solutions, giving rise to leaching of byproducts, as well as the possibility of moisture adsorption at the copper polyimide interface giving rise to occasional blistering (refer to

Fig.2 Erroneous cases of electro-less copper plating process in rigid-flex substrates



Abnormal plating by glue of polyimide cover lay

Week plating adhesion on polyimide surface with electro-less copper plating

Fig 2). At Uyemura, "EE-1" has been introduced as a direct plating process which does not use electroless copper plating, and sales promotion has been implemented with flexible substrates set as a target. This direct plating process allows Sn/Pd colloids to adhere to resin. The conductivity is then gradually enhanced by plating a coating of electroplated brightener free acid copper.

However, this is not suitable for substrates of a large area or high aspect ratio because the electric resistance of catalyst is too high and the initial electroplated deposit is time consuming. Since polyimide of a large area exists on the copper laminate side in rigid-flex substrates, treatment by this process requires a restriction to the polyimide area. In the plating field, a large number of processes called direct plating exist. Examples of catalysts include Sn/Pd colloid, Pd colloid, carbon, conductive polymer, and others they provide reduced process steps which lead to shorter treatment times. These are very desirable aspects that make the use of horizontal continuous conveying equipment possible.

One common aspect of all these direct metallization processes is the controlled etching of the copper surface. This is designed to remove any metallization film or residues from the surface, to ensure excellent adhesion between the laminate copper and the electroplated copper, and to achieve a robust inner layer interconnect. Under etching leads to interconnect failures and over etching leads to wedge voids at the inner connect.

In developing a direct plating process, our key targets were set to solve the foregoing uncertainty factors. The development concepts of our process are shown as follows:

- Not to use an electroless copper plating bath
- To shorten treatment time
- To minimize time in an alkaline bath.
- To selectively impart the catalyst only to the resin
- To use a tin free palladium colloid
- Environmentally friendly chemical composition.

Process Mechanism

Table 1 Palladigm® treatment process

Steps	Chemicals	Temp. (℃)	Time (min.)
Cleaner	WCD	50	5
Soft etch	SPS	25	1
Acid rinse	H2SO4	RT	1
Activator	WAT	40	5
Accelerator	WPD	50	3
Alkali rinse	WMA	35	2
Acid rinse	H2SO4	RT	1

Table 1 shows the treatment steps in the process. There are 3 basic steps in the process namely cleaner, activator and accelerator

Fig.3 Comparison of pH variations and treatment time

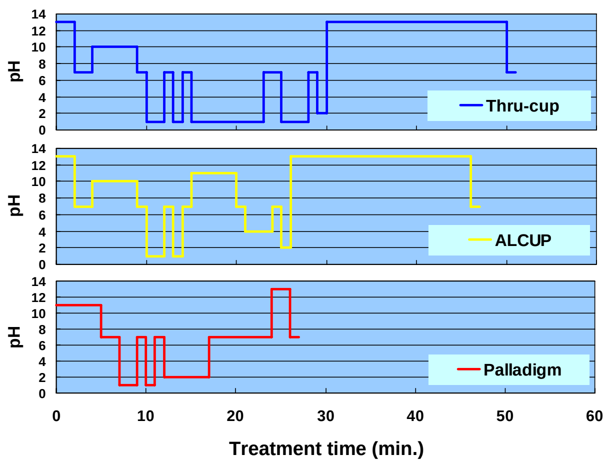


Fig. 3 compares pH variations and treatment time of our process with two conventional electrless copper deposition processes. In contrast to the conventional electroless copper plating treatment e.g. Thru-cup: Sn/Pd colloid, and ALCUP: alkaline Pd complex,, full conductivity of the substrate film, for acid copper plating, is achieved in about half the treatment time.

Our process only forms a Pd thin film on the dielectric substrate in the TH the BVH and any polyimide exposed on the copper laminate surface, as shown in Fig. 4. Thereafter, complete electroplated coverage is achieved.

Fig.4 Treatment of rigid-flex substrate

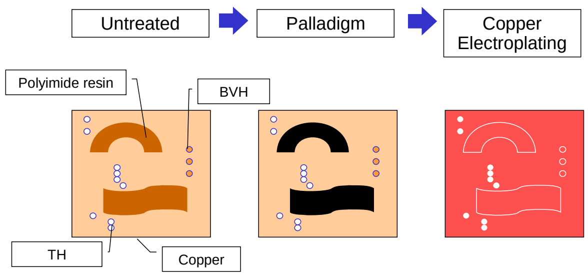
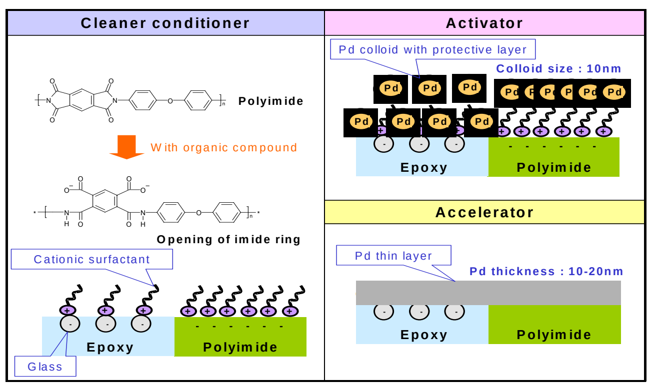


Fig. 5 shows a graphic presentation of the process mechanism.

Fig.5 Image of process mechanism



Cleaner Conditioner WCD

As a cleaner it is capable of removing soils, oil films and stains from both the copper and the resin surfaces. It also contains a nonionic surfactant that lowers the surface tension and improves the wettability and liquid permeability into high aspect through holes and blind vias

Surface conditioning is achieved by first opening the polyimide ring forming hydrophilic groups that in turn would adsorb the cationic surfactant.

The cationic surfactant is adsorbed directly on the glass fibers.

Activator WAT

In the activator bath, Pd is adsorbed to the hydrophobic group of the neutralized cationic surfactant on the polyimide and fiber glass surfaces, as well as adsorb on epoxy surfaces. Pd does not adsorb on the copper surface.

Accelerator WPD

Excess Pd is removed and the Pd forms a thin continuous film that is highly conductive.

Process Features

Catalyst adsorption

Fig.6 Pd catalyst adsorption rate to each material

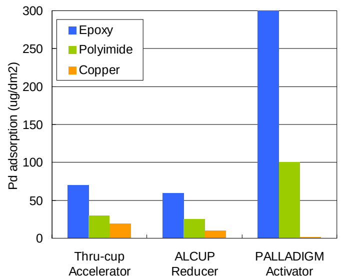
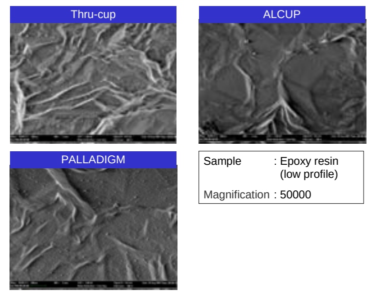


Fig.7 Pd catalyst observation by FE-SEM



As shown in Fig. 6, the catalyst adsorption rate of our process is remarkably greater compared to that of the pretreatment of the conventional electro-less copper plating process. It is assumed that this increase of the catalyst adsorption rate instantaneously starts the formation of a thin film on the dielectric resin. In addition, since no catalyst is adsorbed onto the copper laminates and inner layer copper, no dissimilar metals exist at the interface between coppers, and connection reliability between the inner copper layer and plating films can be expected.

Using FE-SEM, the Pd catalyst condition onto the epoxy resin was observed (Fig. 7). Fig. 7 indicates that as compared to Thru-cup and ALCUP® processes, which are pretreatment process of electro-less copper plating, our process imparts the Pd catalyst at higher density. The Pd catalyst size is about 10 nm at maximum.

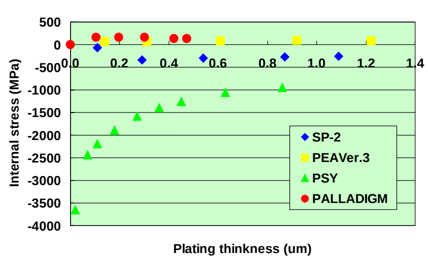
Internal Stress

Fig 8 shows internal stress of the process's Pd thin film. It is confirmed that the process's Pd thin film provides lower internal stress than general elcectroless copper plating films. The Pd thin film is free of blisters on the most demanding larger smooth surfaces and has excellent adhesion characteristics.

Plating deposition capacity

In the event that the polyimide material is treated by electro-less copper plating process without

Fig.8 Internal stress



Electro-less Copper	Chelate	Application
SP-2	EDTA	Full Additive
PEA Ver.3	Rochelle S.	Build-up
PSY	EDTA	MLB

Measurement equipment : Spiral contract meter
Sample : Stainless steel

desmear treatment, seepage of the electro-less copper plating chemical is observed on the film in the polyimide core and cover-lay as shown in Fig. 9, but this kind of phenomenon never occurs with our process. One reason for this can be attributed to reduced treatment time in an alkaline medium.

Fig.9 Effects on polyimide material

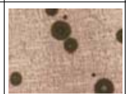
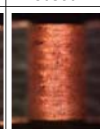
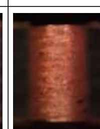
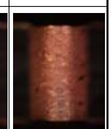
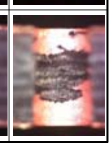
Process	Core	Cover lay	Cover lay glue
Electro-less Copper Plating			
Palladigm			

Fig. 10 shows the acid copper plating deposition capacity after the process. It indicates that our direct plating process, achieves deposition in which plating film gradually grows from the TH copper laminates towards the center portion.

Fig.10 Electroplating deposition capacity

Process	Acid copper plating time			
	0min.	30sec.	1min.	2min.
PALLADIGM ↓ ETN				
Conventional				

Sample	: FR-4 (1.6mmt-1.0mm)
Current density	: 2.5ASD

As compared to this, the superior conductivity of our Palladium deposition process allows the whole TH to be covered with electroplated copper in the first 30 seconds of plating. By this, the characteristics equivalent to those of substrate plating by electroless copper plating are achieved

Conclusion

Our process is now in the final stages of development and at present, it is subject to various tests in the laboratory pilot line in order to establish commercial production control conditions. In addition to this, efforts are being devoted to fitting the process to horizontal continuous conveying equipment in order to provide an inexpensive process with high reliability for flexible substrates.

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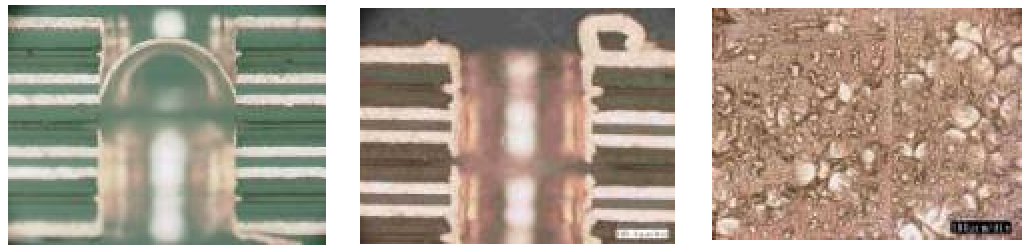
Existing Limitations for Rigid-Flex Processing

Electro-less copper plating

- Too many process steps and high alkali process
- Dissolution of polyimide material in electro-less copper plating bath
- Weak adhesion between electro-less copper deposited film and polyimide



EE-1 process

- Need flash acid copper plating
- It can not cover on the big area of polyimide in rigid flex board
- Difficult to use the horizontal equipment

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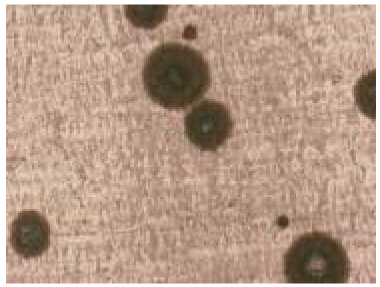
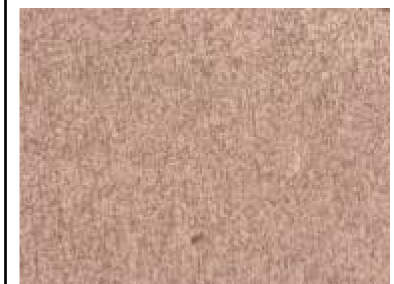
Process Limitations Leaching

Process	PI core	PI cover layer	PI glue layer
Conventional (after ELC)			
PALLADIGM process (after Accelerator)			

Sample: No Desmear

- **Exude liquid from between plating film and PI resin after Electro-less copper plating**
- **New DMT process is not exuded liquid after Accelerator**

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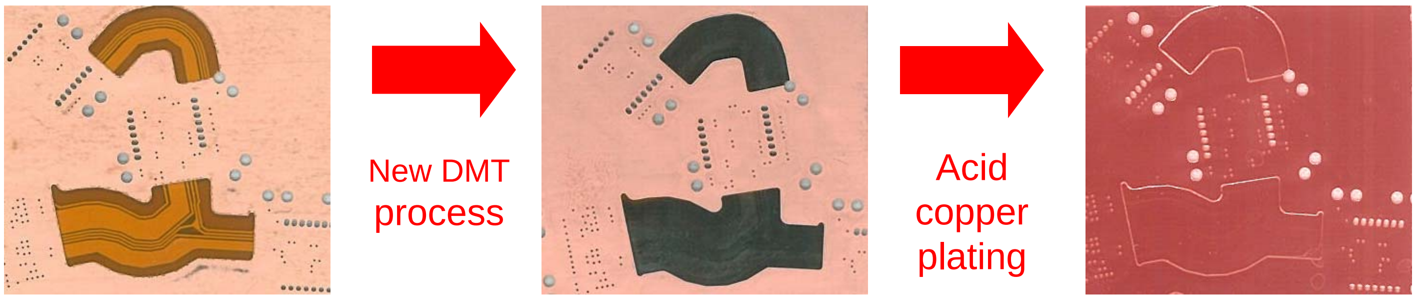
Feature: Large Area Coverage



- Copper Electroplating without electro-less copper
- Catalyst is adsorbed only on the resin.
- Treatment time is shorter than electro-less copper process.
- Same connected reliability as electro-less copper
- Tin free
- Simple process steps with alkali
- Most material can be treated (FR-4, FR-5, Flex, Rigid flex and ……….)
- Lower cost

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Direct Metallization processes

Name	A	B	C	D	E	F	G	H
Process	Etch Cleaner	Conditioner	Cleaner	Primer	Sensitizer	Micro-etch	Cleaner	Conditioner
	Conditioner	Promoter	Starter C	Etching	Pre-Activator	Conditioner	Shadow	Soft Etch
	Pre-dip	Poly-conduct	Dry	Pre-dip	Activator	Oxidation	Micro-etch	Acid Rinse
	Conductor		Conditioner	Activator	Converter	Catalyst	Anti-tarnish	Pre-dip
	Post Dip		Starter C	Post Dip	Enhancer	Fixing		Activator
			Heat Dry	Accelerator	Stabilizer	Post Dip		Accelerator
			Micro-cleaner	ELC/EC	Micro-etch			Flash EC
			Anti-tarnish					
Catalyst	Pd Colloid	Polymer	C	Pd/Sn	Pd/Sn	Monomer	C	Pd/Sn
Flash EC				Need				Need
Horizontal line	○	○	○	×	○	○	○	×
Feature	Pd Colloid	MnO_2 3 steps	Dry step	ELC&EC (Same bath)	Vulcanization	$KMnO_4$	Graphite 4 steps	Flash EC : Polymer
Patentability	○	○	○	○	○	○	○	

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New DMT Process

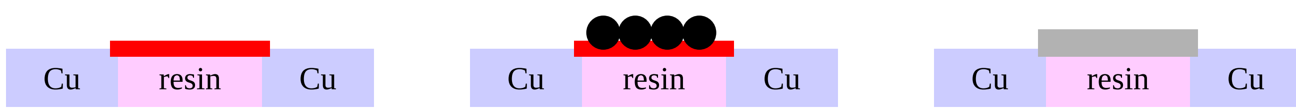
Process	Cleaner
	Etching
	Acid rinse
	Activator
	Accelerator
Catalyst	Pd
Flash EC	
Horizontal line	○
Feature	Catalyst is adsorbed only on the resin
Patentability	PATPEND

Process

Steps	Cleaner	Etching	Acid rinse	Activator	Accelerator
Temp.	50	40	R.T.	40	50
Time	5	2	1	5	3
pH	12	1 >	1 >	1.5	7 - 8
Product	WCD	H_2O_2 H_2SO_4 MSE-7	H_2SO_4	WAT WHP	Palla Assist WPD WHP

Model

Cleaner	Activator	Accelerator
Modified resin	Pd colloid	Pd Thin film



Thickness : 10 - 20nm

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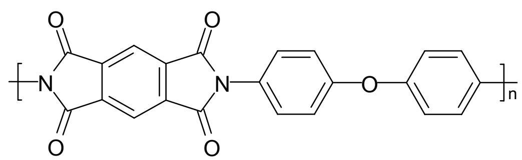
Catalyst Adsorption Mechanism

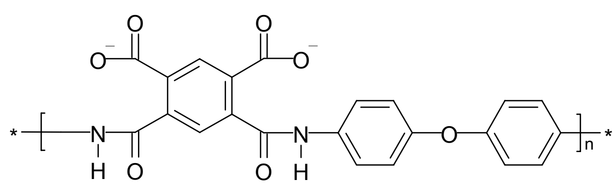
Cleaner conditioner

The surface of the polyimide is open imide ring with organic compound. The cationic surfactant adsorbs the functional group, and the adsorption of Pd catalyst becomes possible. In the glass cloth of the negative electrification, the cationic surfactant is made to neutralize.

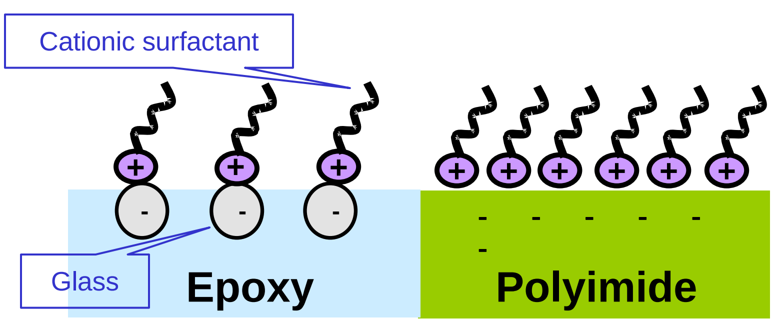


Polyimide

With organic compound

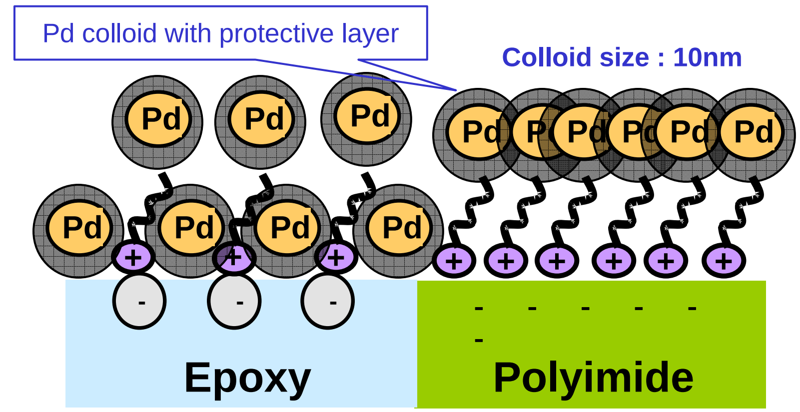


Opening of imide ring



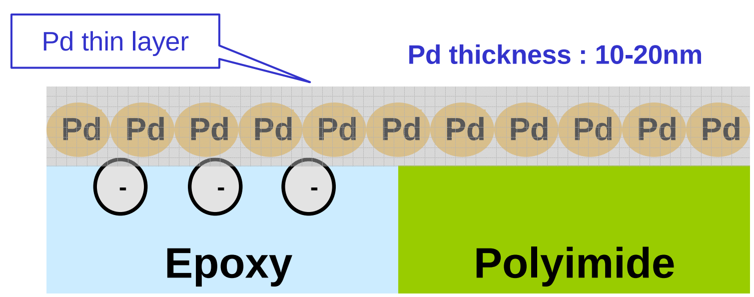
Activator

The Pd colloid with protective layer is bonded on to the neutralized glass, polyimide resin, and the epoxy resin by Van der Waal's attraction forces.



Accelerator

After the protective layer of the Pd colloid is removed in Accelerator, Pd re-adsorbs on the resin again. And the thin dense Pd film is formed.



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Palladigm Process

Steps	Temp. (deg.C)	Chemicals	Conc. (ml/L)	Time (min.)
Cleaner	60	WCD	50	5
Hot water rinse	40			1
Water rinse	RT			1
Soft etch	25	SPS 62.5%H2SO4	200 20	1
Water rinse	RT			1
Acid rinse	RT	62.5%H2SO4	100	1
Water rinse x 2	RT			1
Activator	40	WAT WHP	5 20	5
Water rinse x 3	RT			1
Accelerator	50	Palla Assist WPD WHP	1 50 4	3
Water rinse	RT			1
Alkali rinse	50	WMA	100	2
Water rinse	RT			1
Acid rinse	RT	62.5%H2SO4	100	1
Water rinse	RT			1

Continuous

Steps	Temp. (deg.C)	Chemicals	Conc. (ml/L)	Time (min.)
Acid copper plating	25	ETN1A ETN1B	1 10	Optional
Water rinse	RT			1

Dry

Steps	Temp. (deg.C)	Chemicals	Conc. (ml/L)	Time (min.)
Acid cleaner	40	MSC-3-A	100	5
Hot water rinse	40			1
Water rinse	RT			1
Acid rinse	RT	62.5%H2SO4	100	1
Water rinse	RT			1
Acid copper plating	25	ETN1A ETN1B	1 10	Optional
Water rinse	RT			1

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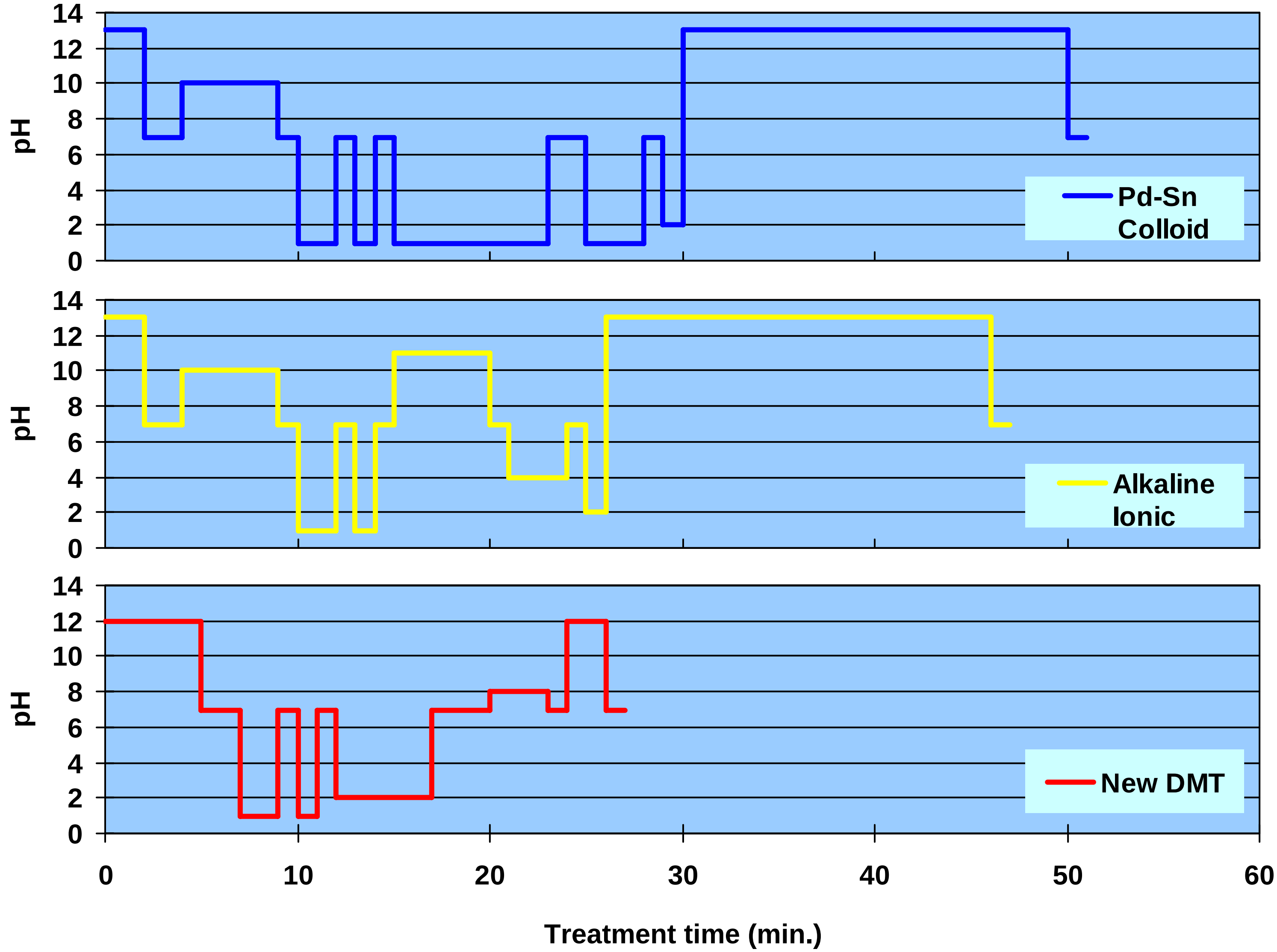
Comparison of Exposure to Alkalinity



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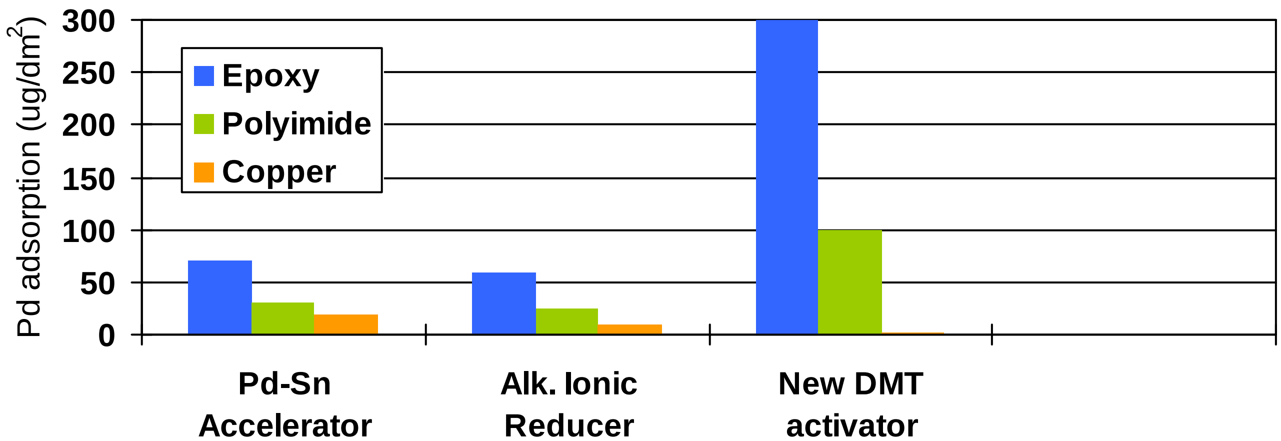
Pd Adsorption and Adhesion

Items		Pd-Sn	Alk. Ionic	New DMT	
				Activator	Accelerator
Pd adsorption (ug/dm^2)	Epoxy(FR-4)	70	60	300	1800
	PI(Kapton)	30	25	100	1700
	Copper	20	10	0 – 3	0 – 3
Electrically conductive (100mm space)	Epoxy(FR-4)	∞	∞	∞	< 1KΩ
Adhesion on PI (Before Electroplating)	Tape test (No Desmear)	NG	NG	OK	



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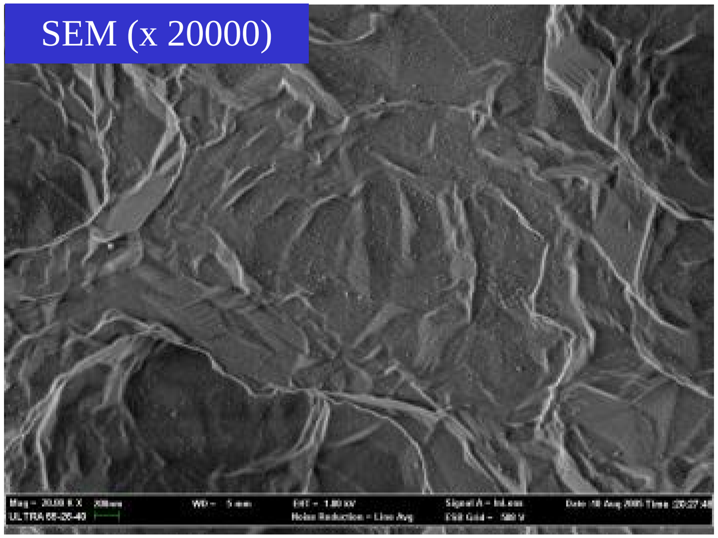
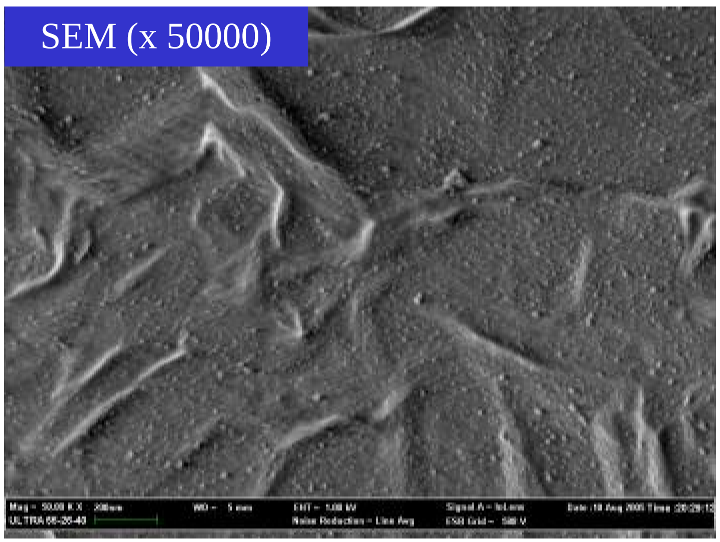
New DMT by FE-SEM

New DMT (Pd colloid) after Activator

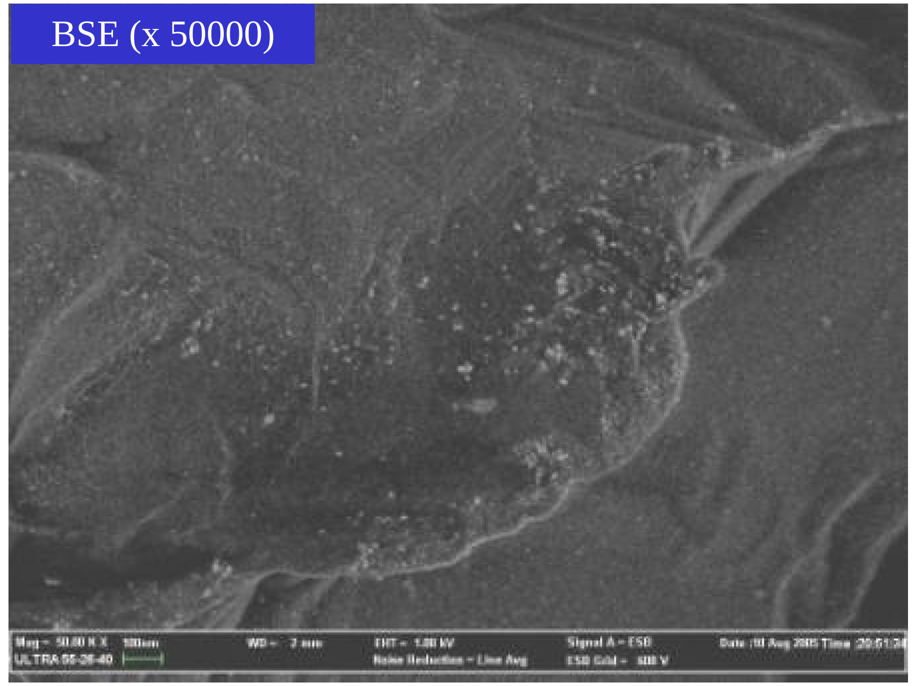
SEM (x 20000)



SEM (x 50000)



BSE (x 50000)



- Size of Pd colloid is less than 10nm.

Sample: Epoxy resin (Low profile)

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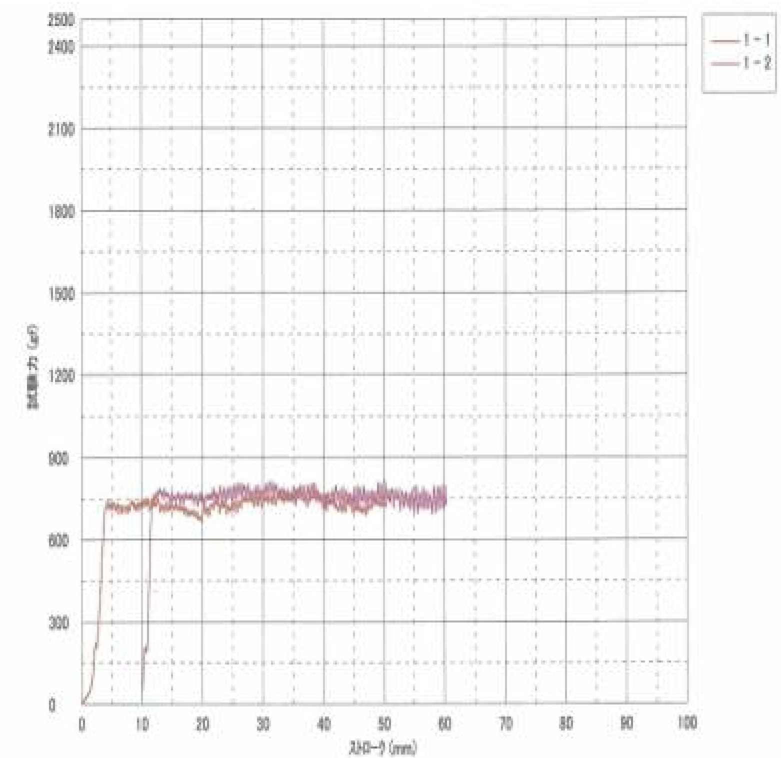
Peel strength on epoxy resin (Low profile)

New DMT process

Av.: 750g/cm



Cu electroplating thickness: 25um

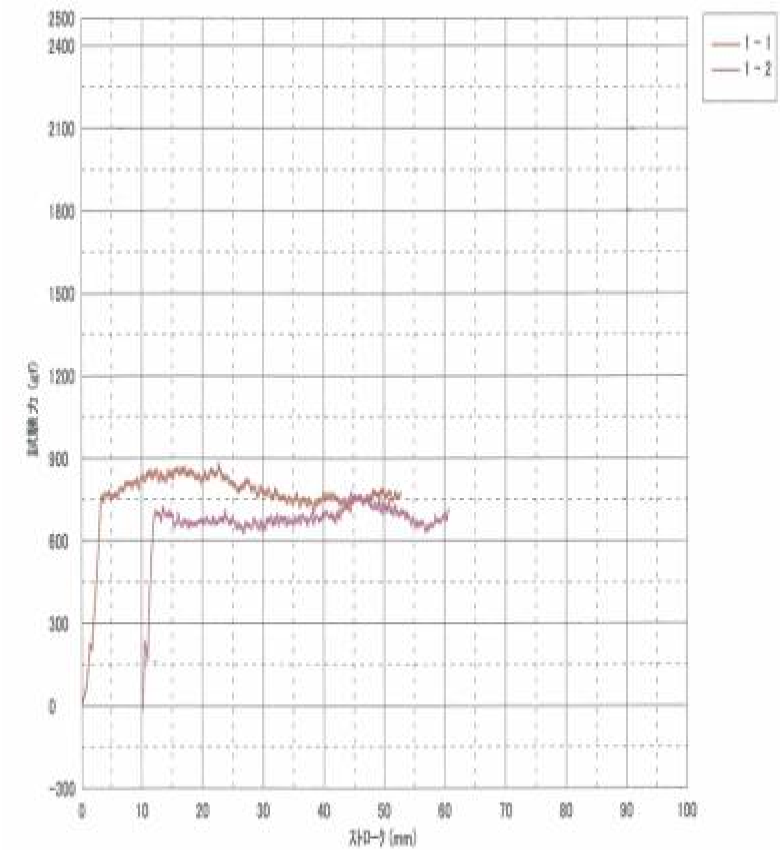
Cu electroplating Dk: 2.5ASD

Measure width: 10mm

Peeling speed: 50mm/min.

Electro-less copper

Av.: 750g/cm



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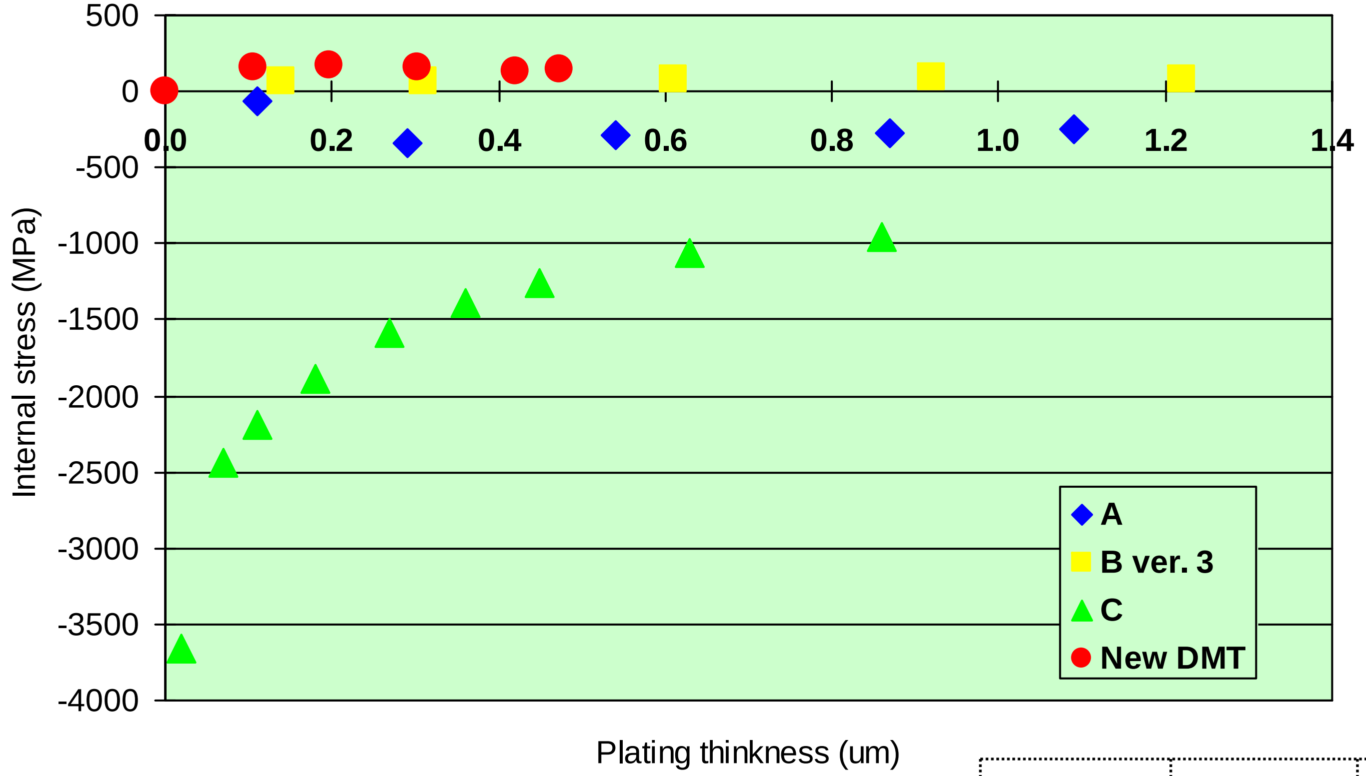
Internal Stress Comparison



E'less Copper	Chelate	Application
A	EDTA	Full Additive
B ver. 3	Rochelle S.	Build-up
C	EDTA	MLB

Measurement equipment: Spiral contract meter

Sample: Stainless steel

New DMT process has Low internal stress and tensile stress.

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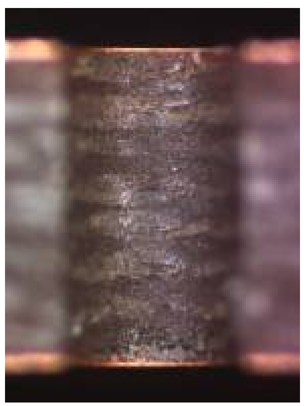
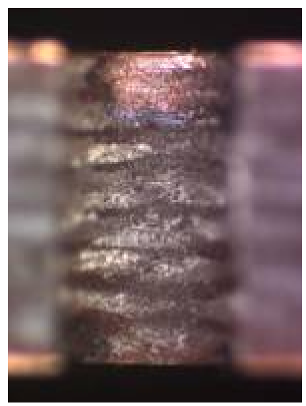
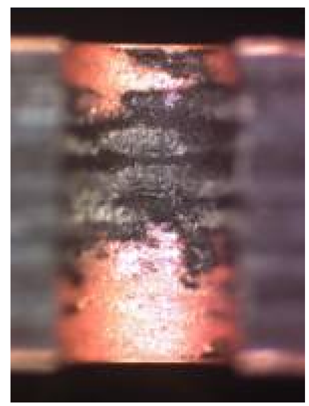
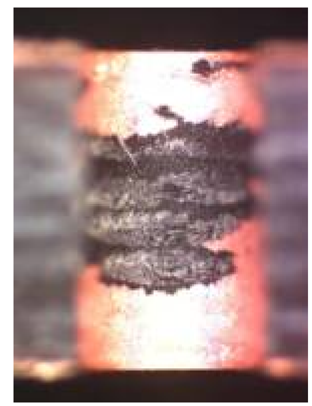
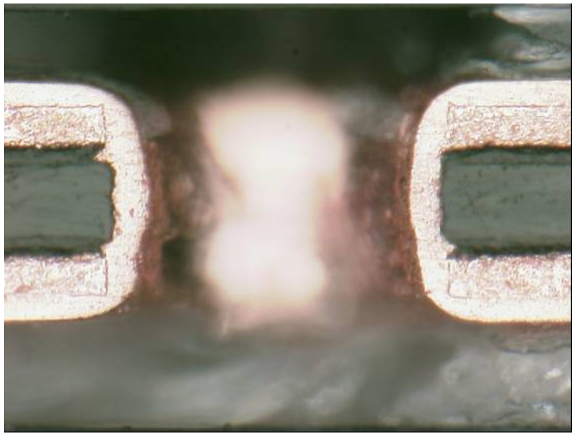
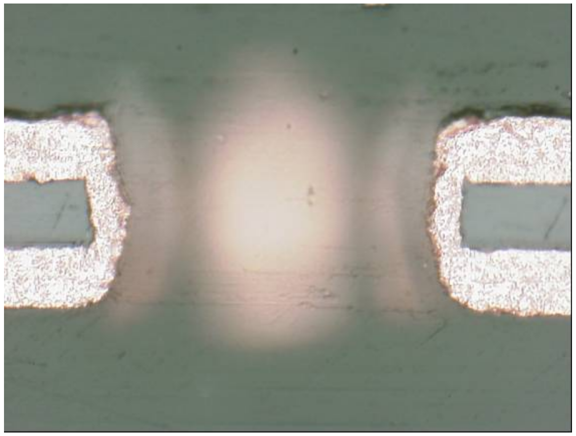
Conductivity/Plating in TH

Process	Acid copper plating time			
	0min.	30sec.	1min.	2min.
New DMT process + Acid Copper				
EE-1				

Sample: FR-4 (1.6mmt-1.0mm)

Current density of acid copper plating: 2.5ASD

Cross Section of Flex board's TH

3 layer (Kapton)	2 layer (Upilex)
	

Acid copper plating: Thru-cup® EPL

Current density: 2.5ASD

Plating thickness: 10um

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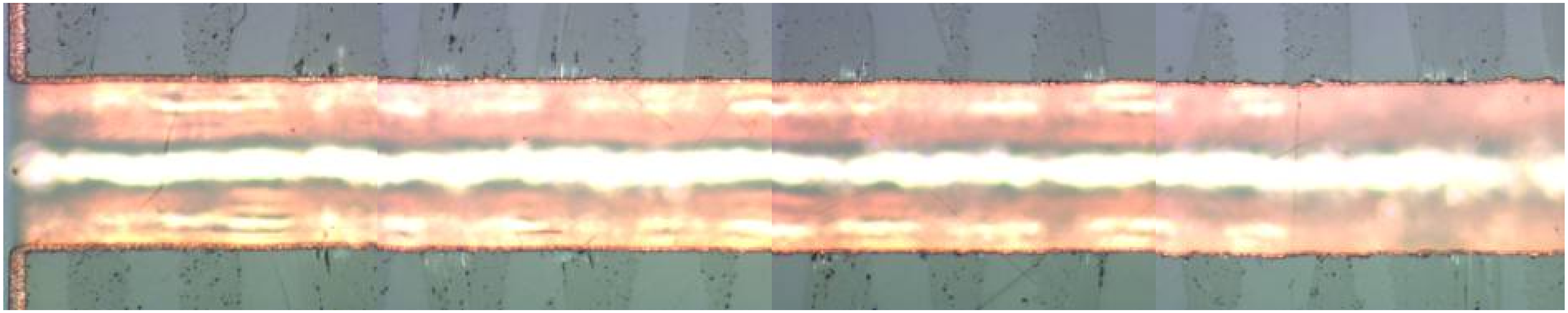
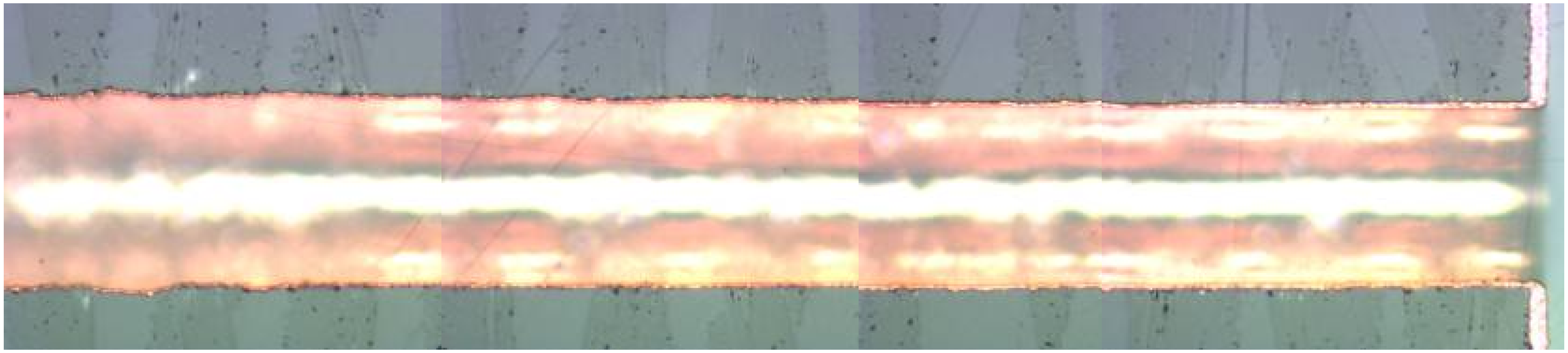
Plating Deposition of High Aspect PTH

FR-4 (**5mmt-0.3mmΦ**)





Cu electroplating: Thru-cup® ETN

Current density: 2.5ASD

Plating thickness: 10um

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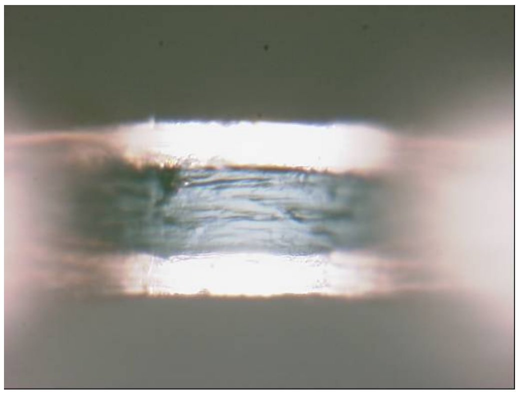
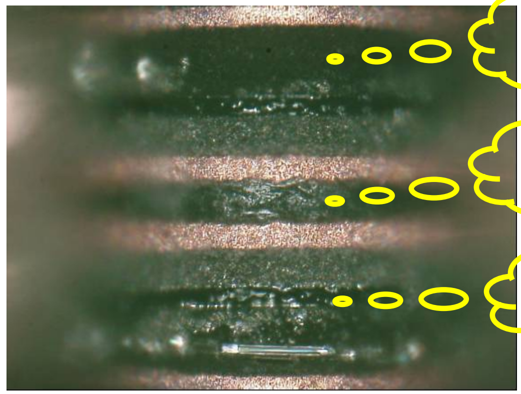
Plating Deposition in TH and BVH

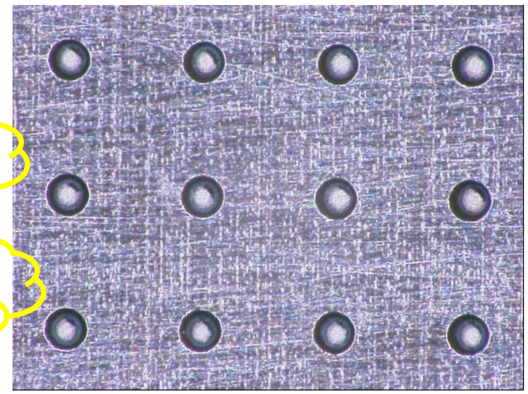
Flexible TH
(0.04mmt-0.15mmφ)

Rigid Flex TH
(0.25mmt-0.3mmφ)

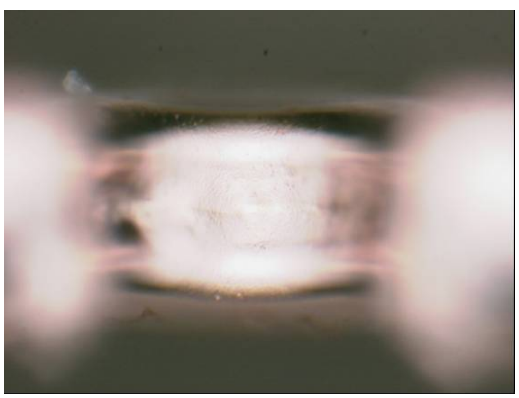
Rigid Flex BVH
(90umφ-100umh)

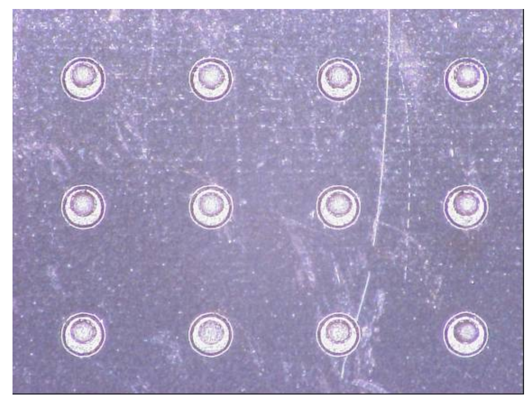






New DMT process ⇒ EPL 2.5ASD (10um thickness)





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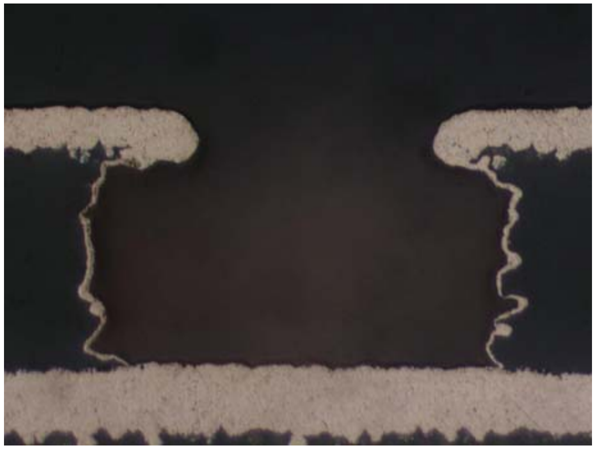
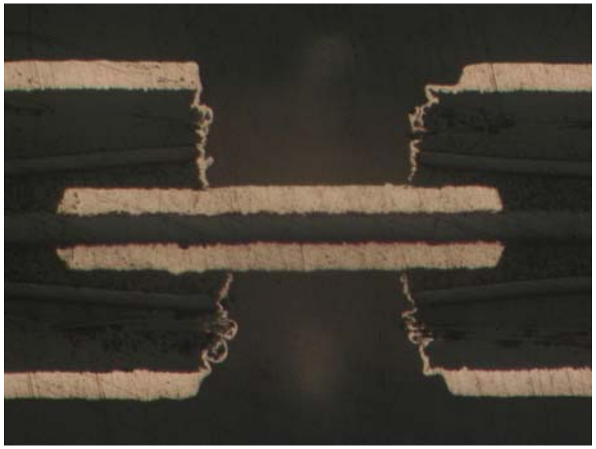
Plating Deposition in BVH

RCC ：90umΦ-70umh

Rigid Flex ：120umΦ-





Acid copper plating: Thru-cup® EPL

Current density: 2.5ASD

Plating thickness: 2um

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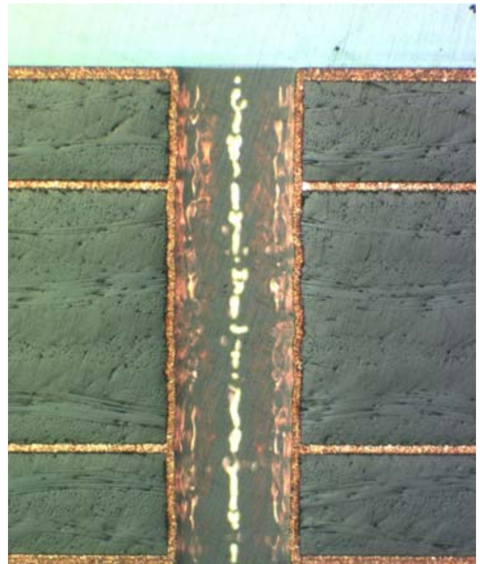
Throwing Power

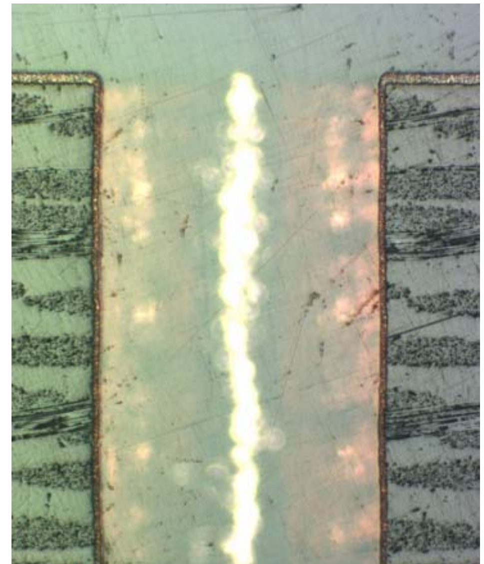
Board	Thickness (um)	T.P. (%)		
		Max.	Av.	Min.
MLB	25	101	**95**	88
FR4	25	114	**108**	103
FR5	25	107	**105**	103
R.F.	25	94	**91**	85
Flex	10	132	**127**	121

Cu electroplating: Thru-cup® ETN

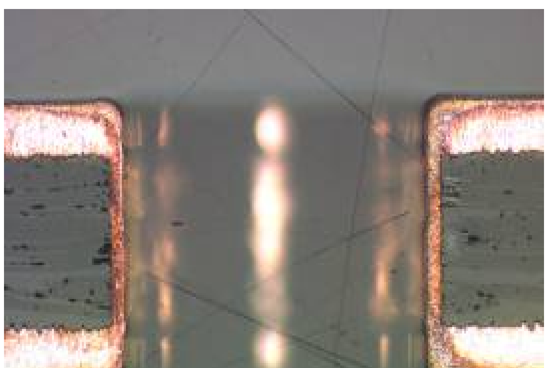
Current density: 2.5ASD



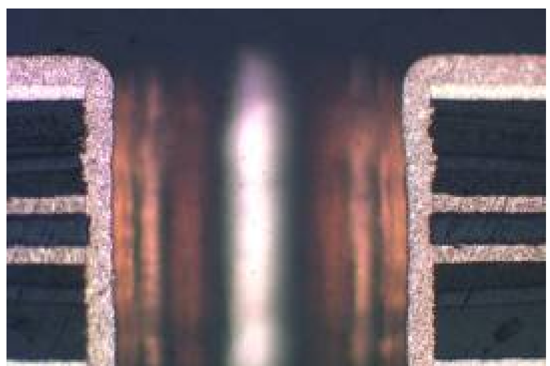
MLB (**1.6mmt-0.4mmΦ**)



FR4 (1.6mmt-1.0mmΦ)



FR5 (**0.4mmt-0.6mmΦ**)



R.F. (**0.25mmt-0.3mmΦ**)

Flex (**0.07mmt-0.15mmΦ**)

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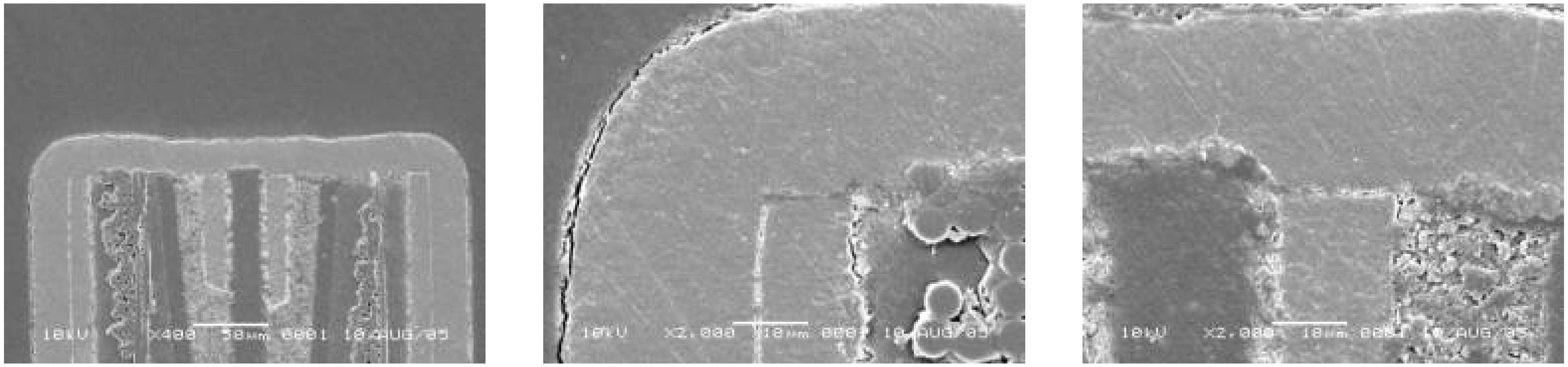
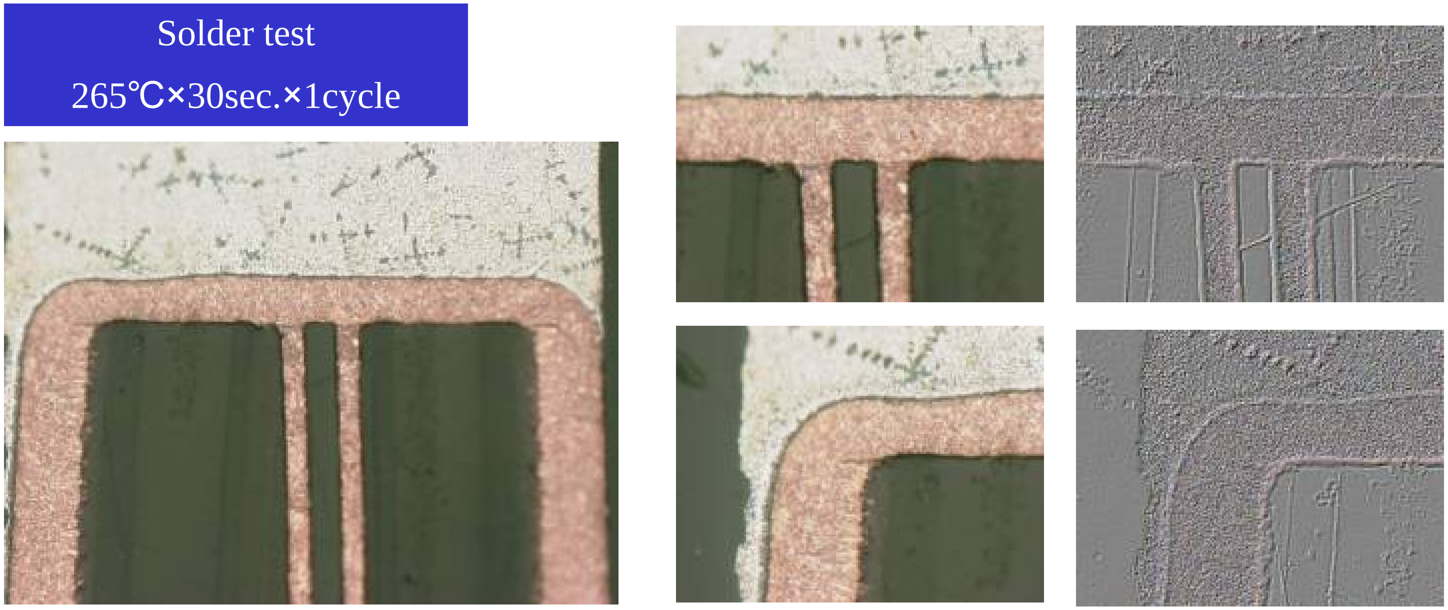
Reliability Testing of Rigid Flex

as plate



Solder test

265℃×30sec.×1cycle

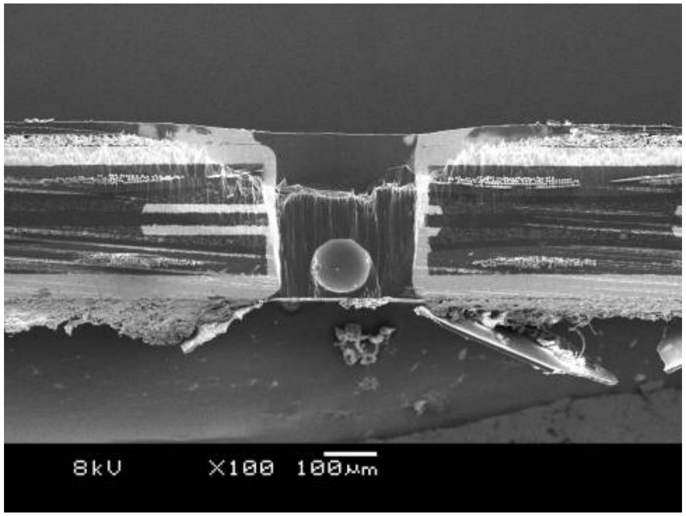


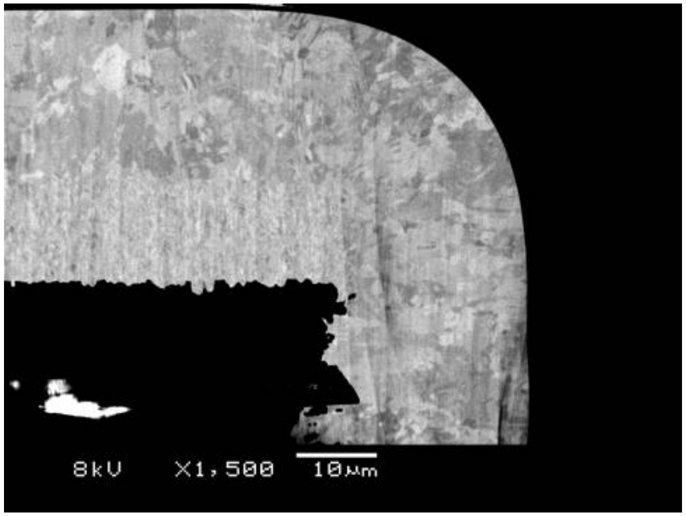
Cu electroplating: ETN (Thickness : 25um)

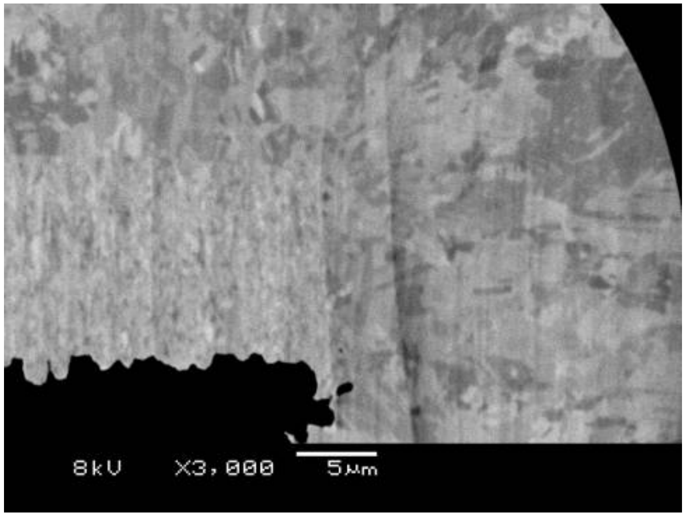
Current density: 2.5ASD

Cross section by CP after Electroplating

as plate







Surface polish: Cross section polisher SM-09010 (JEOL)

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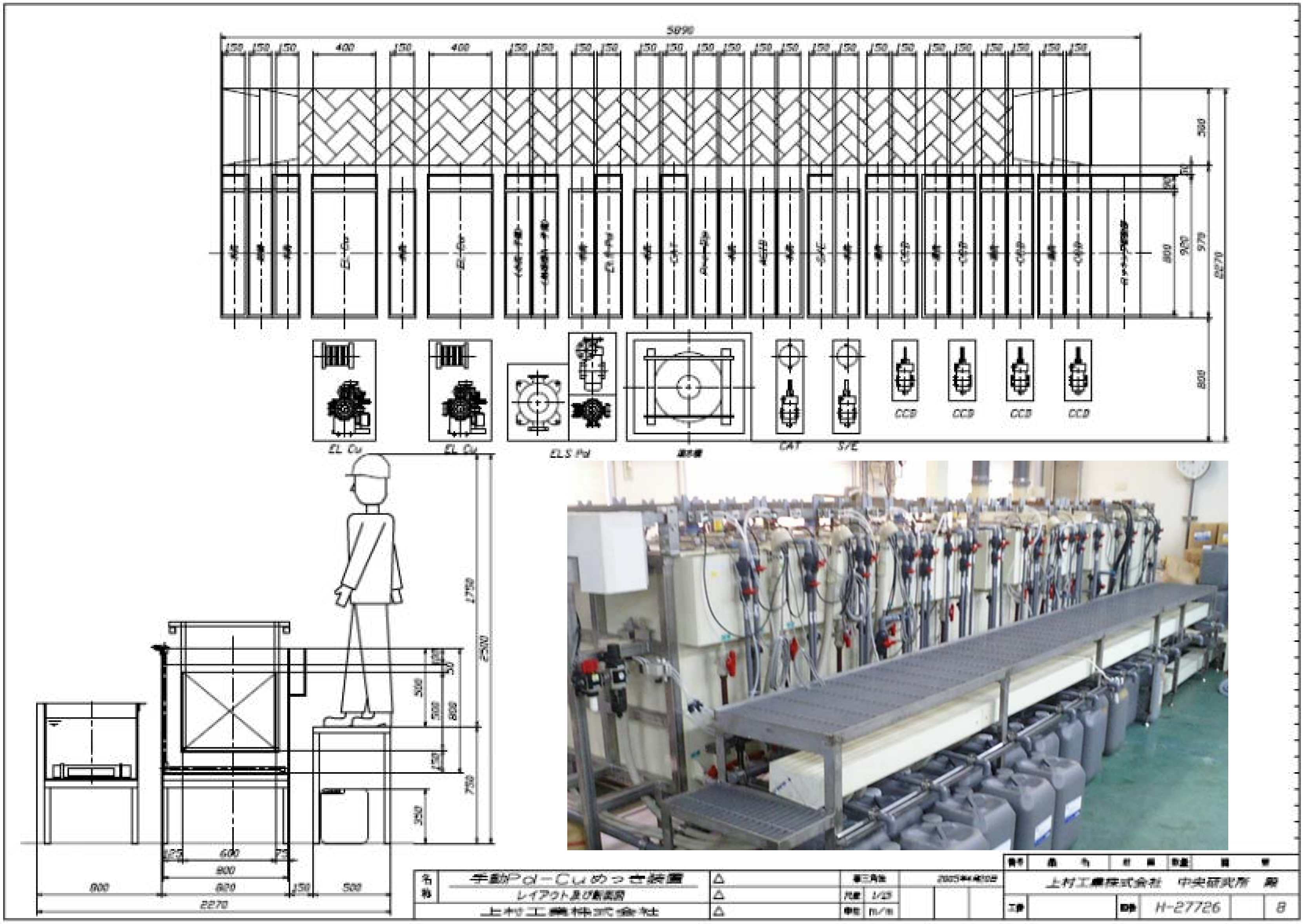
Pilot Line for DMT Process



Horizontal Line for DMT Process

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