Direct Metallization for Printed Circuit Board Manufacturing

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ABSTRACT
Since Multi-Layer Printed Circuit Boards (MLB) with holes appeared in the market, the processes making holes conductive (MHC) have played critical roles to achieve MLB's function. Current trend of technology requires much lighter, thinner, smaller parts and this trend brings the market lots of technical challenges which we need to overcome. The reliability of Laser drilled Micro Via Hole (MVH) is getting more critical.

Electroless Copper process is a Copper plating by chemical reaction (oxidation-reduction reaction) to provide conductive layer between layers of the PCB. It is composed of 6 steps such as conditioning, micro etching, Pre-dip, Palladium activation, acceleration, Copper plating and generates Palladium/Copper layer on the overall surface. Because Electroless Copper plating is also occurred on base Copper area, there still can be interfacial defects like D-Sep and ICD for Though Hole and Nano/Micro-Void, Separation at the target pad of MVH. The factors causing these defects are internal stress of Electroless plated Copper, H^2 gas generated during reaction in the Copper bath and excessive activation, etc. Specially for MVH, while hole size goes smaller, these defects come more.

Direct Metallization (DM) is another MHC process which is an alternative process and mainly represented by colloidal conductive carbon-base process (Carbon black or Graphite). DM is composed of simple 3 steps including conditioning, conductive colloid adsorption and micro-etch removing carbon particles from the Copper area including target pad. Because DM provides direct bonding between Base Copper and Electro plated Copper without additional layer, it can dramatically reduce interfacial defects commented above. DM enables a simpler MVH structure with only one interface while removing the chance for Electroless Copper's signature nano/micro voiding to promote more reliable electronics even with smaller MVH size. Additionally, non-dynamic conductive colloid bath brings us stable performance and quality of product without side effect like cannizzaro reaction of Electroless Copper process.

Key words: Direct metallization, DM, MHC, Carbon-base process

INTRODUCTION
Direct plating of the nonconductor part is a technique to perform MHC without using electroless copper plating.

There are several types of Direct Plating processes in production such as Carbon based (Carbon Black or Graphite), Conductive Polymer based, Palladium based DM. Current major DM process is Carbon-based DM and its share in DM market is about 90%. In the past, electronics manufacturers have chosen carbon-based DM systems over electroless copper processes due to lower cost of ownership and significant reduction on water, waste treatment, capital cost, energy usage and easier-to-maintain equipment, but as the holes are getting smaller and the area at the target pad of micro-via hole is being smaller, the reliability of this process is becoming the reason why PCB manufacturers are choosing DM recently.

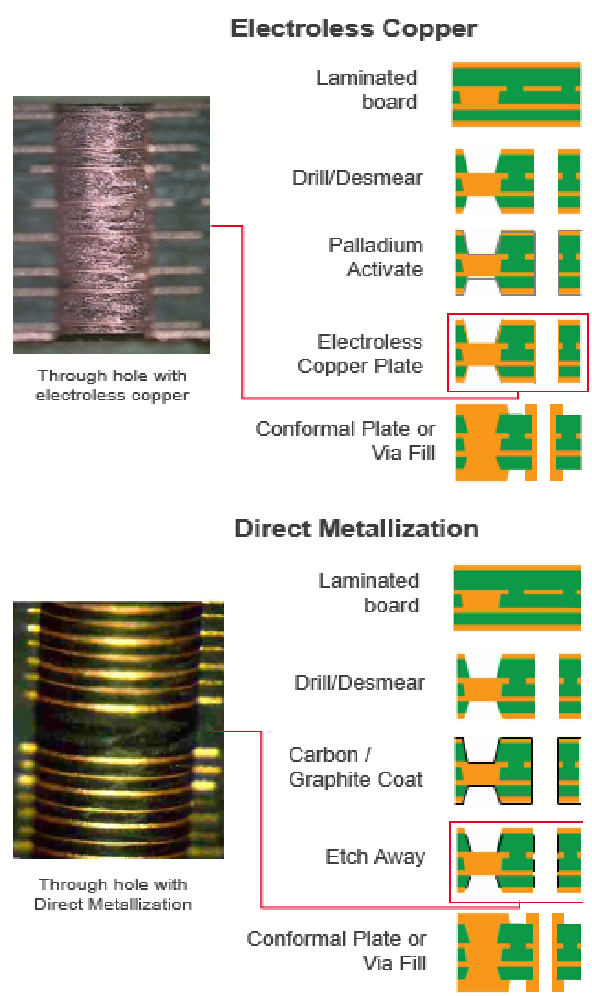


Figure 1. Electroless Cu and Direct Metallization Process Steps comparison

The History of Direct Metallization Technology

Table 1. The emergence of technology and utilization

Year	Technology Application
1963	Colloidal Palladium PTH - Colloidal Palladium / Electroless Copper utilized in first high volume multilayer PCBs.
1984	Carbon Black PTH - Released and utilized for multilayer boards as replacement for electroless copper.
1987	Conductive Polymer PTH - Patented for usage as environmentally friendly PTH alternative.
1993	Colloidal Graphite PTH - A graphite coating with similar properties to carbon black is released and begins high volume production for PCBs
1995	Microvia PCBs / DM Flexible Expansion - The microvia PCB ushers in a new era of circuit density and direct metallization becomes a preferred primary metallization for flex circuits.
2000	Direct Metallization for HDI - Equipment / Chemical optimization of direct metallization enables usage in microvia formation. Vias found to be highly reliable.
2017	Modified-Semi Additive Process - Advanced HDI technologies utilized in semiconductors begin to be applied in PCB mfg. to enable extremely high component densities.
2020	Low Etch Direct Metallization - Low etch technology for direct metallization developed to meet the needs for mSAP, making carbon and graphite-based DM the optimal choice for any kind of HDI.

TOP REASONS FOR DIRECT METALLIZATION

DM has been being used globally for over 35 years and more than 5 million SSF panels are running through DM with proven reliability for HDI and Through Holes as tested by IST, Stimulated convention reflow, OM testing, Hot oil, Pressure cooker test, Thermal cycling test and so on. Carbon and Graphite are like a conductive paint base that is not sensitive to the dielectric, meaning no adjustment for FR-4 epoxy to exotics like PTFE, and composite designs with mix materials for rigid-flex and high speed-low loss signal integrity. These carbon-based DM are compatible with all electrolytic Cu plating systems including DC, PPR, Cu ViaFill, VCP lines without Flash plating with a pure copper to copper bond between the CCL foil or parent Cu and Electrolytic plated Cu. Additionally, DM is a green technology which consumes less water, less electrical power, less waste, no copper and no precious metal like palladium.

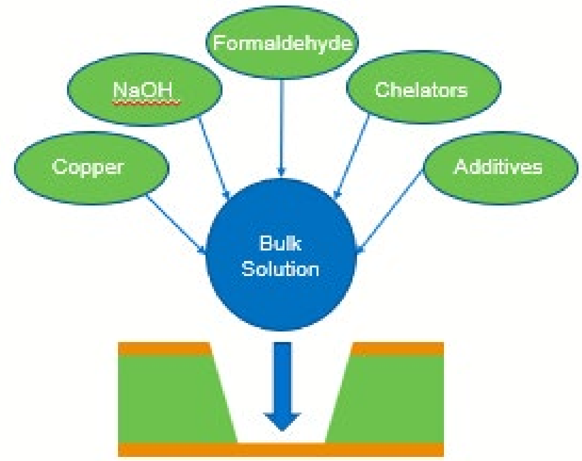
COMPARISON BETWEEN ELECTROLESS CU AND DIRECT METALLIZATION

There are big differences between Electroless Cu and DM from the process sequence to bonding mechanism of plated Cu on inner layer Cu of through hole and target pad for MVH.

Process Concept

Traditional Electroless Cu plating is achieved by complicated chemical red-ox reaction with various chemical components such as NaOH, formaldehyde, Cu, chelator and several additives. DM is by simple colloid coating-etching process.

(a)



(b)

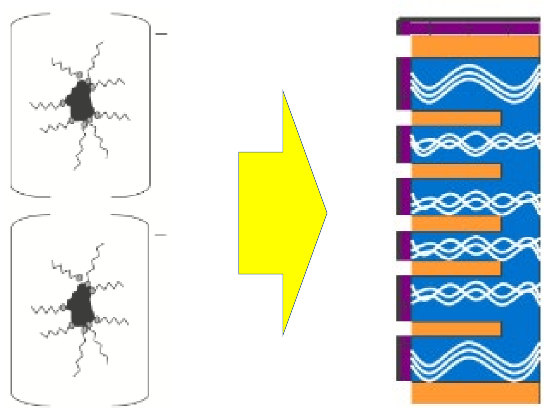


Figure 2. Concept of Electroless Cu and DM

Process Sequence

DM has simpler process steps than Electroless Cu process and it allows smaller space, fewer rinses between chemical steps and saving water and power. Figure 2 shows process sequences of traditional Electroless Cu process and DM including carbon black and colloidal graphite-based DM. When traditional Electroless Cu needs the conditioning, micro etch, activation and acceleration to make the proper environment for Electroless Cu deposition, DM has only conditioning, conductive carbon coating and micro-etch to make hole conductive.

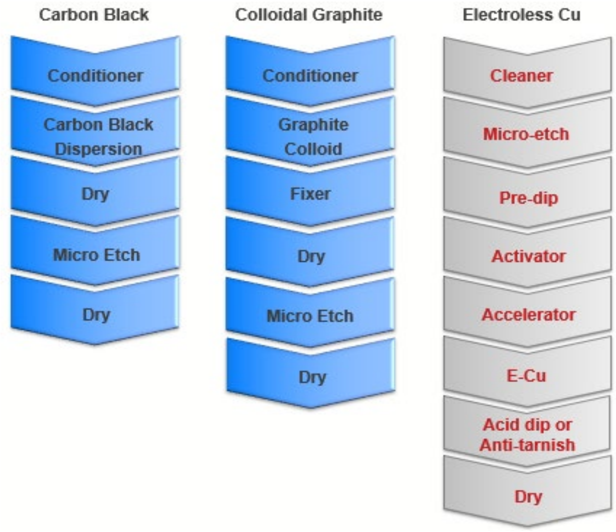
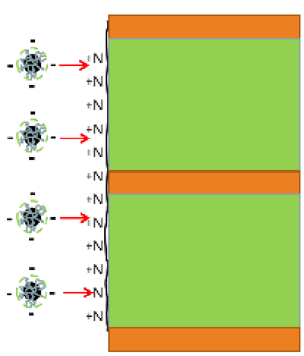


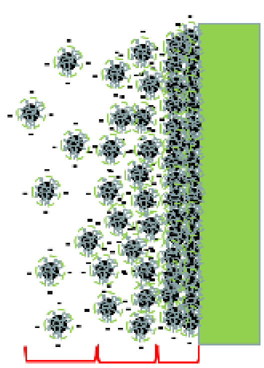
Figure 3. Process Sequences

Mechanism of Colloid Graphite process

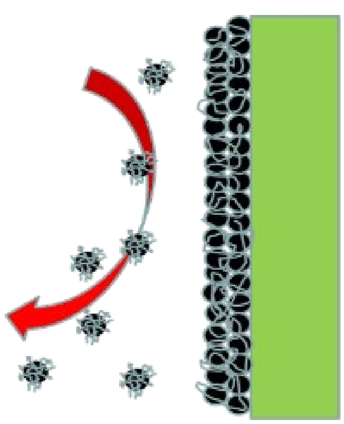
Figure 3 illustrates mechanism of graphite colloid process which is the major DM.

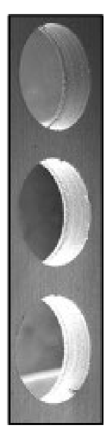
(a) (b)





(c)





(d) (e)

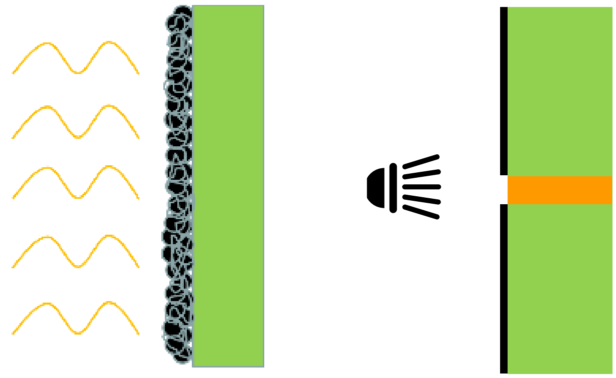


Figure 4. (a) Cleaner/Conditioner (b) Adsorption of colloid graphite (c) Fixer (d) Dry (e) Micro etch

Cleaner conditioner renders the surface with cationic charge to attract negative charged graphite colloids [Figure 3(a)]. In the graphite colloid bath, there are 3 zones as graphite colloids status around panel surface. Zone 1 is the layer graphite colloids are tightly packed, Zone 2 is the one that colloids are packed loosely and the layer has no interaction between colloids and surface is Zone 3 [Figure 3(b)]. Fixer protonates the colloid to adhere the resin/glass surface and remove excessive and loosely packed graphite colloids from the surface [Figure 3(c)]. Adsorbed colloids are dried and packed tighter and have better conductivity and stronger adhesion [Figure 3(d)]. Micro-etch undercuts the remained colloid on the Cu and remove it from the Cu surface leaving pink Cu [Figure 3(e)].

Defect of Electroless Cu process

Even with long history of Electroless Cu plating process, there are still several reliability issues as the hole size is getting smaller with its mechanism of process. The main issues concerned are ICD (InterConnect Defect) in through hole, Nano void or micro void and separation at the interface of MVH.

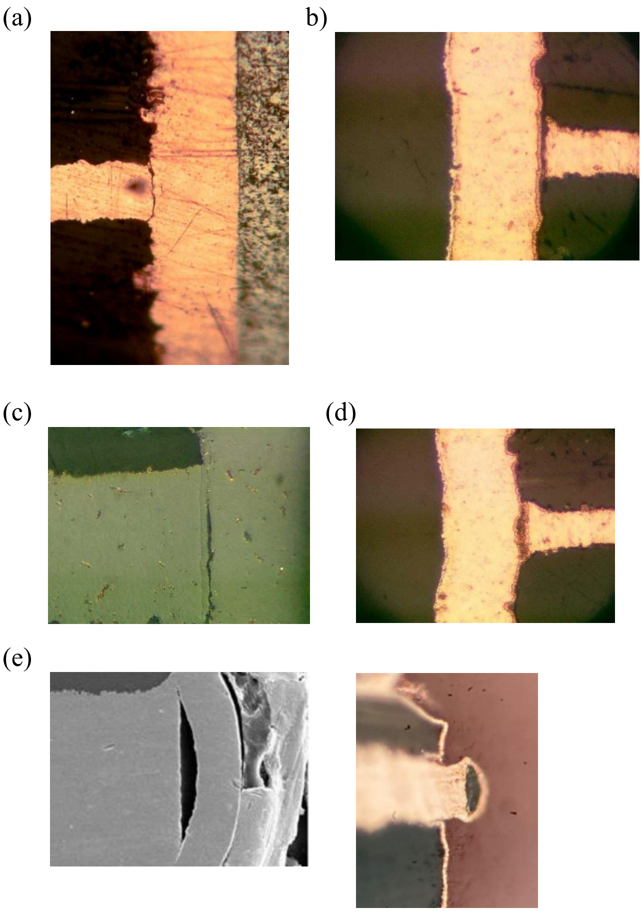


Figure 5. Types of Inter-Connect Defect
(a) ICD (b) ICD Type I (c) ICD Type II (d) ICD Type III (e) D-Sep

Figure 5. shows several examples of ICD including type 1,2,3 and D-Sep. ICD Type I is that the Electroless and Electrolytic plated Cu are separated from the interlayer post. Its main causes are smear, glass or filler on innerlayer, recrystallization of innerlayer Cu, oxidation, excessive Pd, remained conditioner and so on. Type II is between Electroless plated Cu and electrolytic plated Cu deposit on the post. This can be occurred by oxidation of electroless Cu, Dry film residue, high current density at the initial stage of electrolytic Cu plating, etc. Type III is cohesive failure of the electroless Cu and it can be from the poor condition of electroless Cu plating including higher SP.GR, low caustic concentration, poor solution movement in holes, by-product such as formate. D-sep is one of Type IV with all other ICDs including fold-over and foil crack and it's occurred by internal stress and poor adhesion of electroless Cu and it can be observed after electroless Cu process.

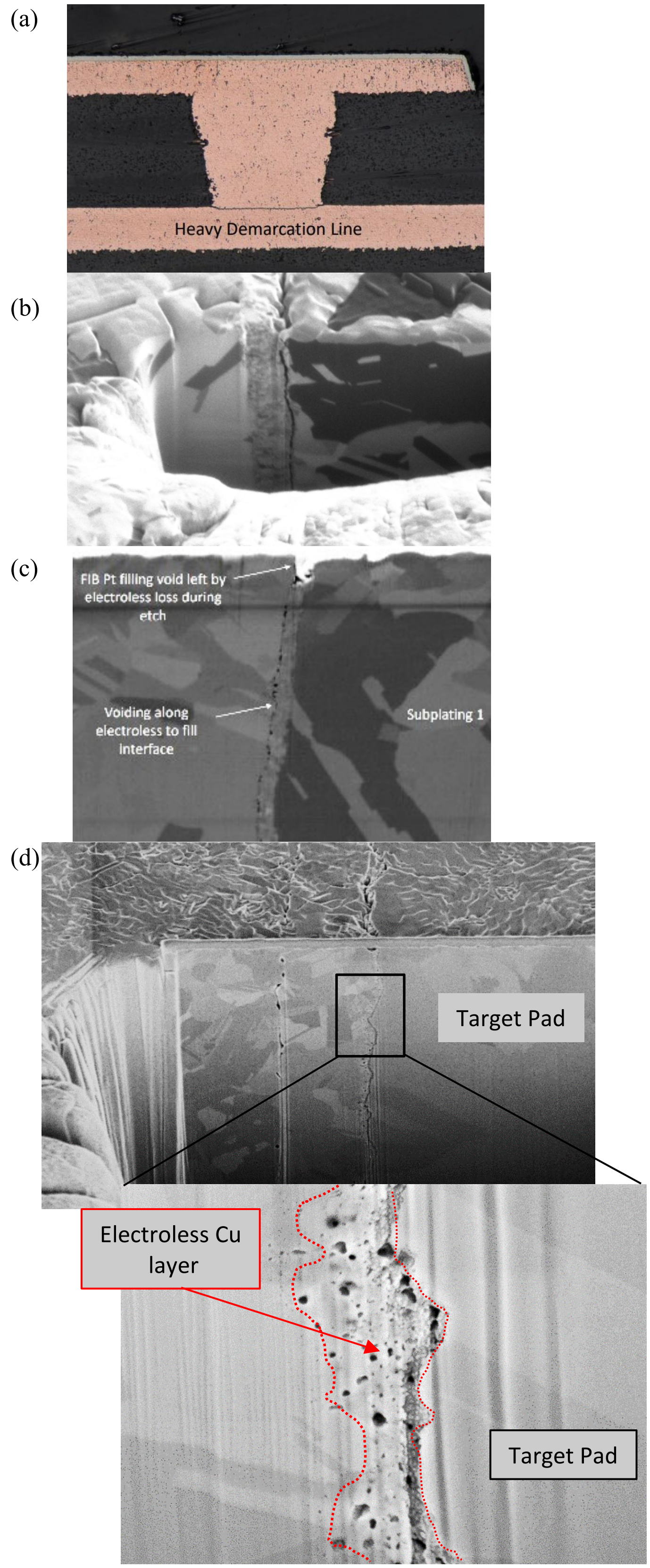


Figure 6. Types of MVH interface defect
(a) MVH showing demarcation line
(b) FIB - Separation and micro voids at electroless Cu layer
(c) FIB - Voiding along electroless to fill interface
(d) FIB - Voiding in the electroless Cu layer

Figure 6. is the examples related to the separation, nano/micro voids at the interface between electroless Cu and plated Cu or target pad, voiding in the electroless Cu layer. These defects are caused by many factors like ICD. Main concerns of nano or micro voids are oxidation, excessive Pd, impurity co-deposited into Cu, hydrogen gas co-deposited into Cu, grain morphology, grain size, recrystallization and so on. Complexed Red-Ox reaction in the hole wall requires high impingement of solution in the small micro via hole and if it is not enough, plated Cu grain structure is not dense and angular. This poor grain structure can generate voids in the electroless Cu layer.

Preferred angular grain structure eliminates nano-voiding and proper additives and diffusion layer creates uniform grain structure equal to the electro-plated Cu. But poor chemical control, bath maintenance and weak solution movement can prevent the ordered deposition of the electroless Cu and lead micro voids in electroless Cu deposit and entrapment of hydrogen gas causing nano voids.
Figure 7 is the comparison between preferred angular grain structure and poor grain structure of electroless plated Cu.

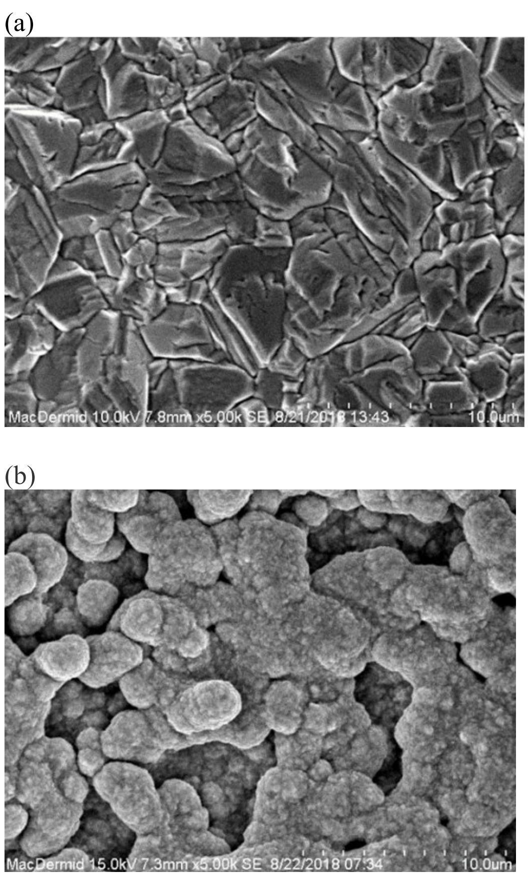


Figure 7. Electroless Cu grain structure comparison
(a) Angular grain structure of electroless Cu
(b) Poor cauliflower grain structure

All defects mentioned above are related to electroless Cu process itself and its pre- and post- steps including the working environment and condition. They are not always occurred, but there are a lot more chances of defects with this additional layer between target pad and electrolytic plated Cu.

Direct Metallization – No layer between target pad and electrolytic plated Cu
Direct Metallization is simple, but reliable process composed of coating and etching which doesn't make any additional layer on Cu surface including target pad of the microvia hole. This direct Cu to Cu bonding is one of the most important features of direct metallization.

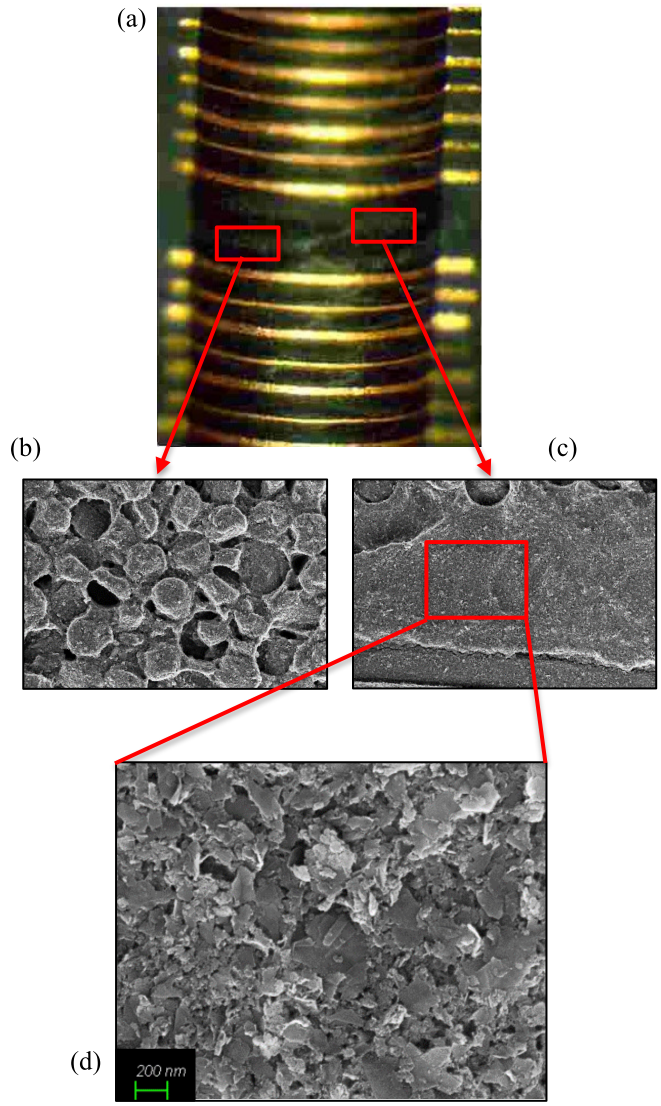


Figure 8. (a) Carbon coated hole wall (b) Uniform graphite coating on glass (c) Uniform graphite coating on resin (d) Uniform graphite coating higher magnification

Uniform graphite coating on the resin and glass in the hole is shown while the innerlayer Cu has clean surface. (Figure 8) This uniform coating provides excellent propagation of plating on the hole wall and Figure 9 shows that overall surface was fully covered by electro-plated Cu in a very short time period.

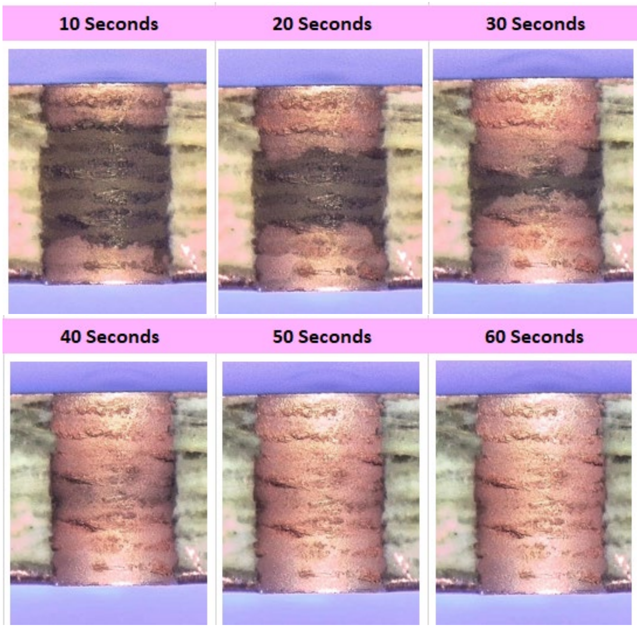


Figure 9. Propagation on conductive graphite coated hole wall. Board thickness : 1.5mm, Hole diameter : 1.0mm.

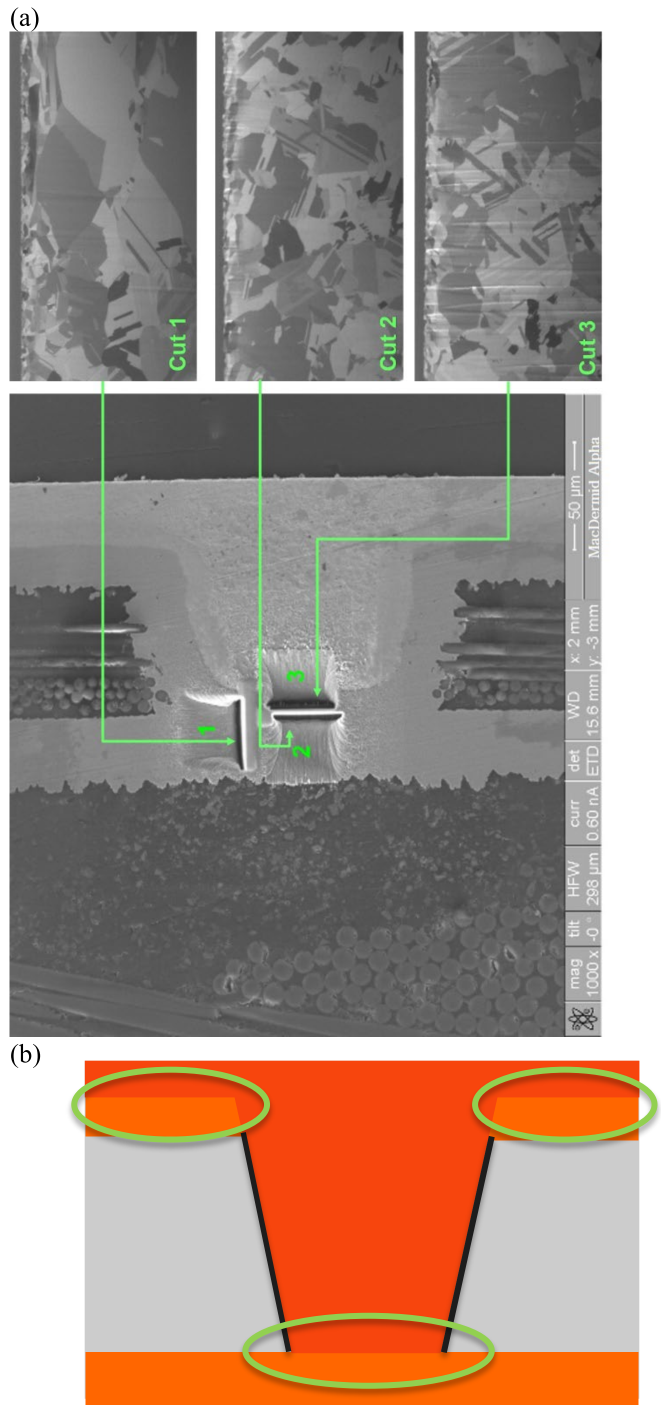


Figure 10. (a) Direct Metallization – Carbon coating remains only on hole wall. No layer on target pad and Cu surface (b) FIB imaging of the interface between the electrolytic Cu plating and the target pad.

Leading edge direct metallization technology allows for strong Cu-to-Cu bonding that performs excellent under thermal stressors.

Micro via reliability is enhanced with a single interface of direct Cu to Cu bonding forming a continuous metallurgical structure. The etch chemistry prepares the target pad with an ideal Cu topography as the base for Cu via fill plating. This promotes the well-defined grain growth of the electrolytic Cu on the target pad. With normal thermo-mechanical cycling, the recrystallization of the copper grain orientation further promotes the desirable continuous metallurgical structure.

Studies with FIB using lamella cuts show the interface line to be uniform in grain size and structure. After thermal shock or cycling, the line between the target pad and electrolytic Cu can be difficult to find. Nano voiding is not present except for instances where it would be due to factors like oxidization or contamination. With only one interface and no physically weaker additional layer, there are much less chances of defects like nano voiding, micro voiding and separations.

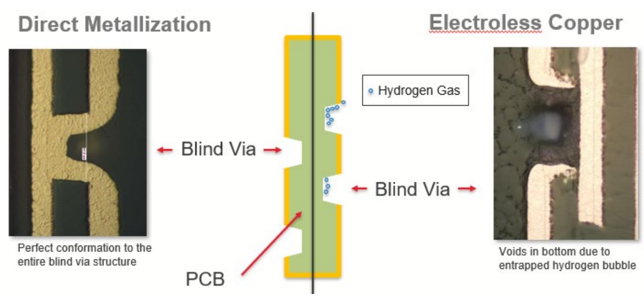


Figure 11. There is no hydrogen gas generation causing voids

Electroless Cu process has red-ox (reduction-oxidation) chemical reaction generating hydrogen gas. These hydrogen bubbles can be entrapped in the holes and cause the voids and it also can be entrapped even in the plated Cu crystals and cause nano voids. Direct metallization coating is occurred on the conditioned (negative charged by conditioner) surface and there is no hydrogen gas generation.

Because direct metallization is the simple process with conditioning and adsorption of carbon/graphite colloid, there is no side reaction, called "Cannizzaro reaction" from electroless Cu process, it is the reaction occurring with NaOH and HCHO in the electroless Cu plating bath. Because it is occurring all the time and consume these chemicals even during the idle time, bath condition changes and it is needed to be well-maintained.

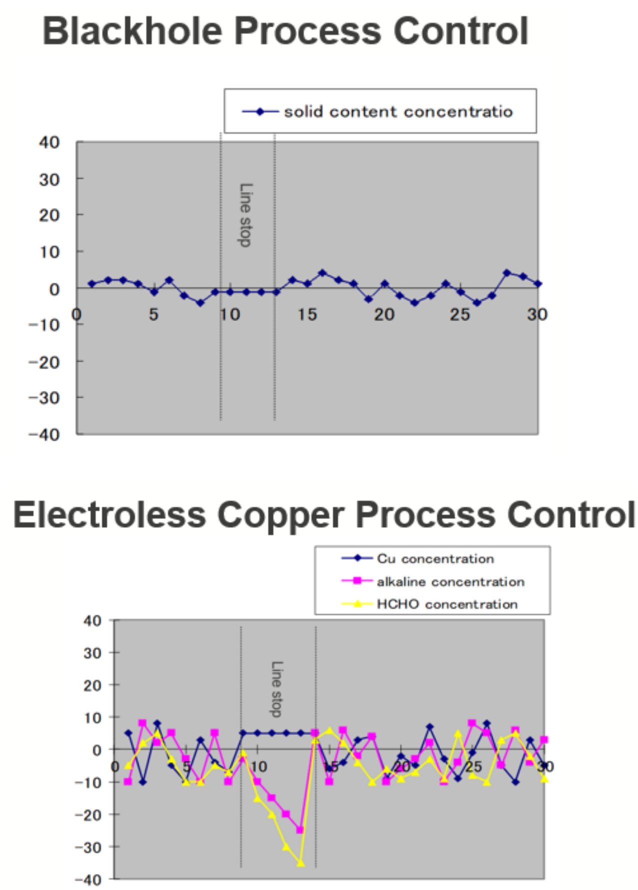


Figure 12. Bath condition comparison during production and idle time

For HDI products, poor laser drilling with inefficient desmear process can remain smear on the target pad and conductive carbon/graphite will be absorbed these remained materials. Because this carbon coating is visible, AOI inspection is a good method to filter the issued panels having defects such as remained smear or debris on the target pad before proceeding further post processes. Electroless Cu just covers those remained smear and not easy to detect the defects before real problem like interface separation occurs.

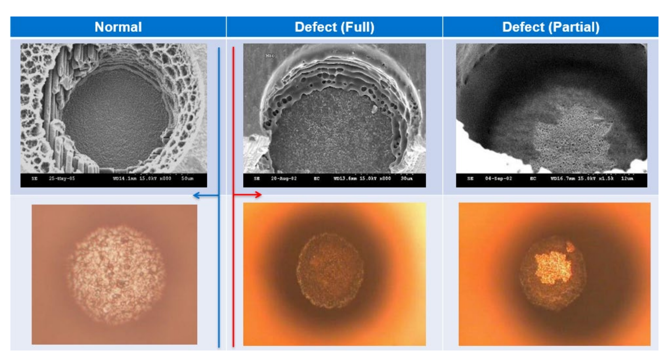


Figure 13. Residue on target pad with direct metallization. Defected products can be filtered before running post processes after metallization

Summary and Conclusion

The microvia has been the primary enabler of high-density interconnect since its inception but concerns over weak via target pad interfaces have so far limited the usage of this design feature in devices that require very high reliability. As HDI designs are becoming more widely utilized in mission-critical and safety-oriented applications, the reliability of the microvia hole is getting more critical. There are many factors related to the microvia reliability such as excessive Pd, oxidation of the target pad, control of hydrogen gas during plating of copper, electroless Cu grain refiner concentration, SPGR of electroless Cu bath solution, chemical etching treatments, rinsing, solution movement, the condition of the copper at the target pad before plating begins including the presence of recast copper, surface roughness, etc., but many of these factors can be removed with direct metallization and it provides strong Cu(base Cu)-to-Cu(electro-plated Cu) direct bonding with no additional weak layer between them and it allows to move forward to apply more HDI technology to the wider market.

Additionally, direct metallization is a green technology with no use of precious metal like Pd and harmful components like cyanide and formaldehyde. Water usage, power usage, waste treatment also much lower than electroless Cu and these contribute to its sustainability.

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