Printoganth FF – The Formaldehyde Free Electroless Copper Process

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1. Introduction

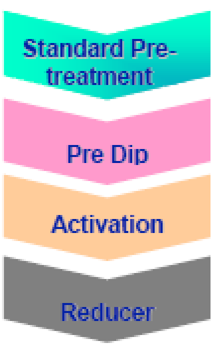
The most commonly known and used metallization technique in PCB manufacturing – electroless copper – will have to meet modern ecological requirements. The main concern is the use of toxic formaldehyde as reducing agent. The Printoganth FF process uses the much more friendly alternative hypophosphite for the reduction of copper ions.

Even though many theoretical and applied investigations have already been published, the final realization for a process that is suitable for continuous mass production has turned out to be difficult. Besides finding the optimum process conditions, the determination of the metallization mechanism is most critical. One of the key factors for a suitable process is the control of deposition speed and deposit structure, which requires the correct formulation of the stabilising system.

2. General Process

Upcoming demands on the PCB industry to implement environmentally friendly processes with the same quality as currently used proven systems, requires a short term realization. Even so meeting the demands of high density technologies, such as fine line developments requires a non conducting dielectric surface to avoid electrical failures like high resistance shorts. Alkaline ionic palladium activation has proven to give a fine homogenous palladium layer for superb electroless copper adhesion whilst after the copper removal by etching there is no or negligible conductivity due to palladium particles on the surface.

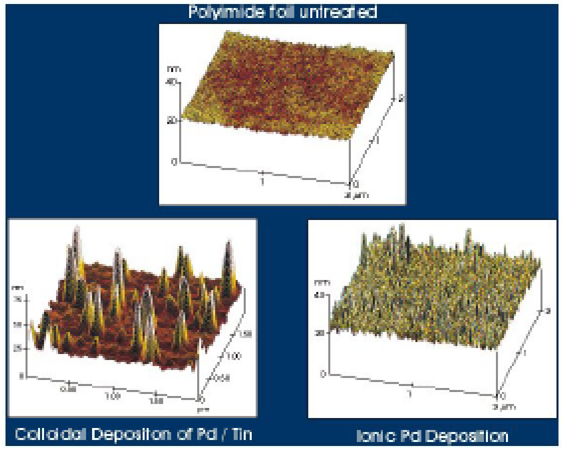
2.1. The Activation Process



Alkaline ionic palladium activation :

- Uniform palladium deposition
- More bath stability without tin oxidation issue
- Reduced residual conductivity beneficial for subsequent fine line technology

The combination of alkaline ionic activation and formaldehyde free electroless copper demonstrates clearly its suitability for HDI technologies with its uniform copper growth. As visualized in picture 1 clearly a difference can be seen between several activation systems. The colloidal deposition of tin stabilized palladium significantly forms cluster while the ionic system creates a uniform palladium layer for the following electroless copper process.



Pictures 1: Different deposition characteristics depending on metal stabilizing system

2.2. The Electroless Copper Process

The electroless copper process with hypophosphite as the reducing agent is largely described in combination with copper sulfate, sodium citrate, boric acid and nickel sulfate as the catalytic part. The most critical and important parts of this process are the choice of stabilizer and of course the process parameters.

Printoganth FF Basic Solution

Is a buffered NaOH system containing citrate as the complexing agent. This is of course biodegradable and a lot more environmentally friendly than using EDTA or Quadrol.

Printoganth FF Reduction Solution

Is based around sodium hypophosphite. This gives handling and health benefits to operators as opposed to formaldehyde that is usually used for electroless copper systems. The reducing agent also does not undergo the Cannizaro reaction during le periods like the formaldehyde system.

Printoganth FF Copper Solution

Contains copper and nickel.

Printoganth FF Stabiliser

Is designed to be measured. The usual request from customers is to be able to measure all components of a process and now we have an analyzable stabilizer system.

The main reaction mechanism is widely described in several publications. Even though that the process is not fully auto catalytic and requires catalytic activities for the reaction to start and run this process continuously. The alkaline ionic palladium activation provides the best performance due to its uniform layer. For continuous running a certain amount of nickel ions will be co-deposited. The anodic decomposition of hypophosphite on palladium and nickel deposits to orthophosphite provides the necessary electrons for the reduction of complexed copper ions to create finally a homogenous electroless copper layer.

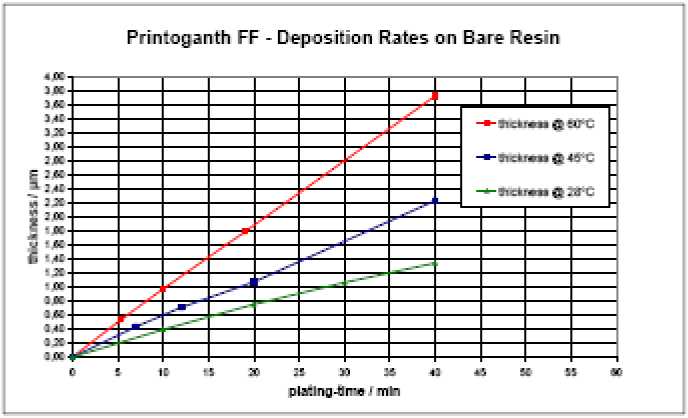
3. Advantages in Detail

1. **Low internal stress deposition**
   Even in high Tg and SAP application several studies confirm the blister free deposition, making it suitable not only for conformal mask application.
2. **High stability**
   Reflecting the stable bath conditions there is no need for air agitation. Based on its chemical nature there is no self decomposition of the reducing agent during low or idle times which leads to economical advantages.
3. **Plate-out characteristics**
   As observed for conventional systems, in less stabilised electrolytes copper deposition occurs. Complete and rapid precipitation has never been observed during monitoring.
4. **High and constant deposition speed**
   The electrolyte can be stably operated over 60 °C with a naturally increased deposition speed.
5. **Simple Process running**
   Temperature controlled, the deposition speed can be varied and adjusted to suit different base materials. This leads to economical advantages.
6. **Improved process control**
   a) Reducer and NaOH
      Effectively hypophosphite doesn't react with NaOH resulting in stable reducer concentrations and pH value. Almost immediate process ramp up can be realized after break down times improves the line utilization.
   b) Stabiliser
      Can be analyzed electrochemically
   c) pH Control
      It is less alkaline and will be operated via pH control.
   d) Cu Controller
      The copper concentration will be measured with colorimeter. No changing's have to be done.
7. **Formaldehyde free**
   With reference to toxicology the reducing agent is only an irritant as compared to formaldehyde which is toxic.

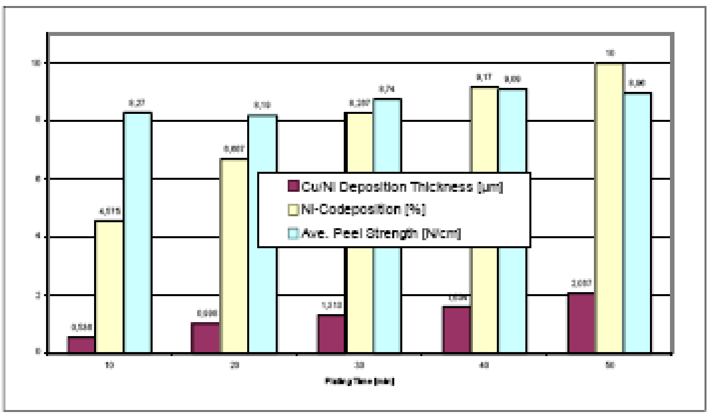
4. Chemical Influences and resulting Practical Experience

Various investigations have been undertaken to monitor and investigate the plating behaviour and appearance. Most interesting were studies related to the morphology echnologies requiring fast eposition speeds, such as horizontal metallization techniques as well as low eposition speeds preferred in some vertical applications.
of the deposit which was examined by etch rate comparisons, temperature influence on nickel co-deposition or electrical resistance measurements. The stable deposition characteristics were heavily investigated as one can see in picture 2. Out of the results a nickel co-deposition of about 10 % bestow the best mechanical properties. Average peel strength results of 9 N/cm were obtained with a deposition temperature of 45 °C with constant desmear conditions and after electrolytic plating giving a total copper thickness of 25 µm on Ajinomoto GX bare dielectric (picture 3). Constant deposition speed could be obtained up to 60 °C as well as for a long time period of 40 min. Depending on the process parameter adjustments this electroless copper bath

is suitable for technologies requiring fast eposition speeds, such as horizontal metallization techniques as well as low eposition speeds preferred in some vertical applications.



Picture 2 : Plating speed of Printoganth FF with various temperatures



Pictures 3 : Influence of co deposed nickel on the peel strength investigation

4.1. IST Reliability

To meet current quality requirements a detailed investigation is in progress and first results demonstrate 1000 cycles passed under following conditions:

1000 cycles passed

Desmear Conditions

- Vertical Desmear

Printoganth FF Conditions

- 7 min (approx. 0,4 µm)
- 7 min (approx. 0,4 µm) + Copper strike (approx. 2,5 µm)
- 12 min+ Copper strike (approx. 5 µm)

Inpulse Copper Conditions

- Inpulse Plating

    1 x 1.0 m/min @ 10 ASD (40 ASD rev)
    1 x 0.8 m/min @ 8 ASD (40 ASD r ev)
    80/2-39/4-180 °C
    Total Cu thickness approx. 25 µm

4.2. Solder shock Reliability

Solder shock test: 6 x 288 °C (acc. IPC-TM-650 #2.6.7.1) passed.

4.3. Blind Micro Via, Inner Layer and Through Hole Appearance