Reengineered Conductive Polymers – The PTH Alternative to Electroless Copper for HDI Mass Production

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Abstract

In many areas conductive polymers have already gained full acceptance as a reliable and qualitatively outstanding metallization process and as a true competitor for electroless Cu. In the paper presented the entire process sequence is explained, with the process not being a series of individual steps with individual functions, but a rather logical and most elegant sequence of interrelating chemical systems.

Process details down to a molecular level are being revealed, information necessary to grasp the full meaning of each physical or chemical reaction occurring. Various process options are being discussed with a particular focus on the selection of monomers, acids in the polymerisation step and buffer systems for the preceding MnO2 formation, knowledge which formed the basis for a recent process reengineering.

Finally a series of HDI production results will be shown, demonstrating why conductive polymers are already the most successful PTH alternative to electroless Copper.

Introduction

Due to reduced investment and running costs, their environmental friendliness and the low space requirements, direct metallization (DM) processes have become very popular in the 1990s. The DM sequences itself can be divided into three subgroups, the conductive polymer based, the Carbon based and the Pd colloid based DM processes. While the latter two at some stage require an etch cleaning step, the conductive polymer (CP) sequences are highly selective by nature. With microvia plating and the global penetration of HDI mass production new limitations for some DM processes have been encountered. The CP versions however proved to give excellent, persistent and high yield results.

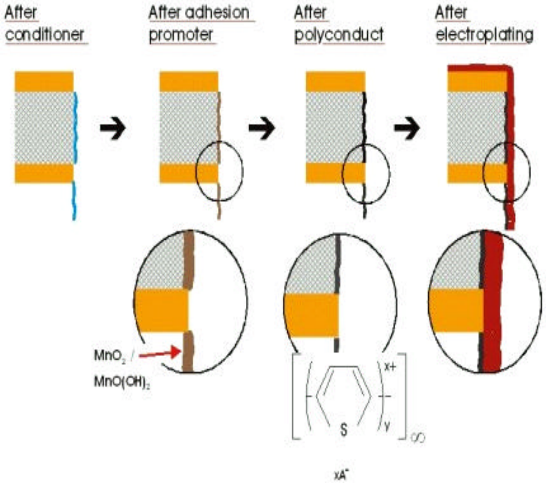


Figure 1 – Overview Process Sequence Conductive Polymer

The Special Requirements for HDI Microvia Production

In order to be successful in plating vias smaller than 250 µm in diameter two main criteria have to be fulfilled. Each and every single entity has to be wetted and the deposited metallization layer should be deposited with sufficient throw to keep dwell times in normal ranges. With conductive polymers wetting is excellent partly due to the fact that most of the process electrolytes are run at high temperatures. The conductive layer is very thin, satisfying all throwing power requirements. The disadvantage of several DM methods in particular with blind microvia plating are due to missing wet ability or required excessive etching, both leading to voids of folding.

The Secrets of the Conductive Polymer Sequence

The CP sequence basically consists of a step in which all organic material (base material and conditioned glass fibres) is oxidised by Permanganate, followed by the polymerisation reaction which is induced by the MnO_2 formed in the preceding reaction.

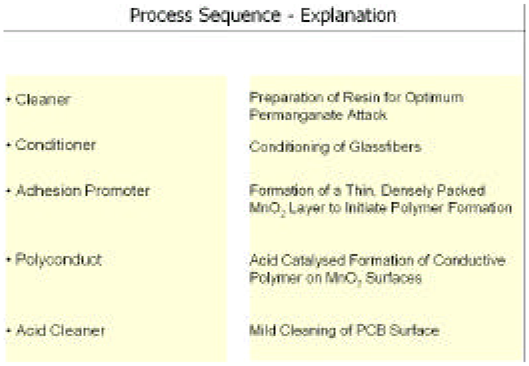
The resulting conductivity however depends on many factors, which shows that the reactions and the mechanism involved are not as simple as one would imagine. Contrary to the Permanganate electrolytes used in the desmear process the adhesion promoter (name of the electrolyte in the CP process) is run at acidic pH. This guarantees a fine, dense and relatively thin layer of MnO_2, required for a controlled formation of the conductive polymer. Furthermore no MnO_2 will remain after the polymerisation, which is the basis for the excellent Cu to base material adhesion found with acidic permanganate adhesion promoters.

Also owing to this, electrolytes of reducing nature (i.e. H_2O_2) can be used in post treatment step, since no danger for oxygen evolution exists (through the reaction of remaining MnO_2 with H_2O_2), which would decrease the conductivity of the metallization. On top of all that no Manganate is created at acidic pH, thus no regeneration unit is required.

Equally decisive for a low resistivity is the buffer system used to maintain the pH in the adhesion promoter electrolyte. Even though not present in the polymerisation step the concentration and the kind of buffer have to be carefully selected to achieve excellent results.

The polymerisation step (Polyconduct bath) requires a careful balance between temperature, pH and electrolyte components to fulfill highest conductivity demands. The acid used for pH adjustment to the low working value is most important for stability and lifetime, and last but not least for the conductivity result.

In Figure 3, you will see a comparison of different acids being used in the Polyconduct and the differences in conductivity resulting. The test vehicle to be seen is uncladded on one side and after CP treatment plated for 2 min at 2 Adm-2. The distance of Cu growth relates to the conductivity of the CP layer.



Process Sequence - Explanation

• Cleaner	Preparation of Resin for Optimum Permanganate Attack
• Conditioner	Conditioning of Glassfibers
• Adhesion Promoter	Formation of a Thin, Densely Packed MnO_2 Layer to Initiate Polymer Formation
• Polyconduct	Acid Catalysed Formation of Conductive Polymer on MnO_2 Surfaces
• Acid Cleaner	Mild Cleaning of PCB Surface

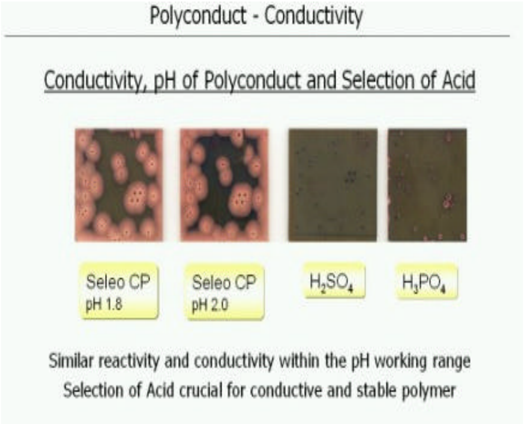
Figure 2 - Explanation of Process Steps

Reengineered Conductive Polymer Sequence

The new development on the Conductive Polymer segment (Name Seleo CP) to be described is the combination of acidic permanganate chemistry with a Thiophene Polyconduct. This combination requires a complete new chemical design of the two electrolytes involved.

A special buffer system had to be created which provides the necessary acidity and at the same time, the chemical characteristics to provoke the demanded conductivity. Unlike non-acidic Permanganate systems the pH of the newly created adhesion promoter is stable at 3.5 with the lifetime of the bath.

For the polymerisation a Thiophene derivate was selected. The solubility of the species in aqueous solutions is low; therefore a microemulsion is used to dissolve the required amount of monomer. The emulsions temperature stability for transport and storage is an important feature, because at values strongly deviating from ambient temperature two phases will separate. The bipolar polymer chosen for the formation of the microemulsion effects at stability range between –5 and +50 °C.



Polyconduct - Conductivity

Conductivity, pH of Polyconduct and Selection of Acid

Similar reactivity and conductivity within the pH working range

Selection of Acid crucial for conductive and stable polymer

Figure 3 - Conductivity and Selection of Acid

Conductivity

As described above the conductivity obtained for a polymer formed under these conditions is a function of many variables, the most important being (other than concentrations):

Adhesion Promoter
  pH and its stability
  chemical characteristics of buffer and electrolyte

Polyconduct
  pH
  Selection of Acid

Combination of Chemistry – Adhesion Promoter and Polyconduct

With the options of Thiophene or Pyrrole as monomers and acidic or neutral/basic Permanganate one obtains various conductivities/resistivities on standard FR4 base material.

With the newly created system the conductivity directly after formation is around 5 kO/cm. Other combinations in its best setting are above this figure, as is displayed in Figure 4.

Once formed the conductivity of the polymer is stable with time, unlike obtained with the currently used Pyrrole systems. The combination of acidic adhesion promoter with Thiophene creates a polymer whose resistivity increases from 5 to max 10 kO/cm within the next five days. With the change to an alkaline Permanganate the resistivity increases to > 25 kO/cm. Changing the acid in the Polyconduct can create a further increase up to values >130 kO/cm.

Storage, hot air drying and developer solutions have no negative impact on the conductivity.

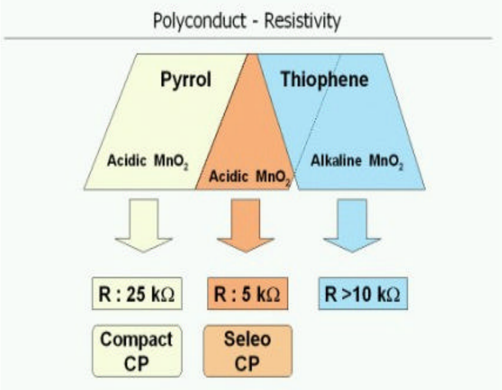


Figure 4 – Different Combinations of Monomers and pH of Adhesion Promoter

Summary

The newly designed Conductive polymer direct metallization process Seleo CP is based on an acidic permanganate step in combination with a Thiophene derivate as monomer. It affects highest conductivity, while exhibiting unsurpassed selectivity. Due to its excellent wetting characteristics the process is – unlike other DM sequences – suitable for HDI and microvia production with highest yields. Together with the general economical and ecological advantages of a direct metallization, this conductive polymer development, it is the alternative to electroless copper for high tech applications (See Figure 5.)

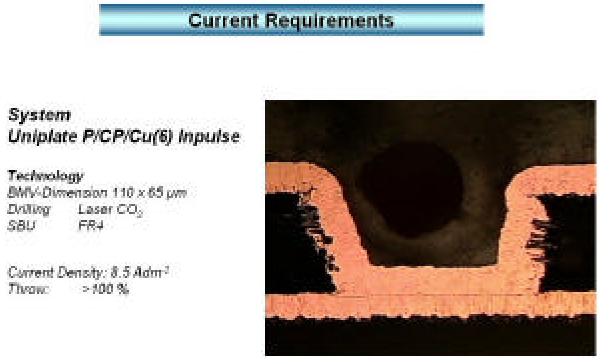


Figure 5 – Production Experience – High Current Density