Review of "Direct Plate" Processes & Assessment Of the Impact on Primary Imaging of Printed Wiring Boards

By Karl H. Dietz

Environmental, cost, and performance criteria are providing the impetus for printed wiring board (PWB) fabricators to evaluate and adopt direct plate processes as replacement for the traditional electroless copper metallization of conductor vias. This paper surveys direct plate processes and their advantages and disadvantages compared to the electroless copper process. Special emphasis is given to the impact of direct plate processes on the application and processing of photoresists. Surface preparation and other processing requirements are discussed.

The initial metallization of the non-conductive dielectric in the conductor via holes of double-sided and multilayer printed wiring boards (PWBs) has been traditionally accomplished with a catalyzed chemical process called "electroless copper." This process, originally borrowed from the decorative plating industry, has seen many significant improvements over the last 30 years, mainly in the metallurgical properties of the deposit, deposition speed, and process controls.[1,2] In recent years, however, pressures have been mounting to seek alternative through-hole metallization techniques:

- The electroless copper process uses, with few exceptions, formaldehyde, a suspected carcinogen, as the reducing agent.
- The process is inherently unstable, requiring stabilizing additives and frequent bath analyses to avoid copper precipitation.
- Environmentally undesirable complexing agents, such as EDTA, are used to keep copper in solution in the strongly alkaline electroless medium.
- The process consists of a relatively large number of chemical processing and rinsing steps, resulting in high water consumption.
- Board throughput per unit of floor space and time remains low.

Accordingly, replacement technologies have concentrated on elimination of formaldehyde, ease of control, high processing speed, compactness of the process line, conveyorized horizontal processing, and reduced water use, while maintaining or improving through-hole reliability.

Alternative Processes
Several families of replacement technologies have emerged over the last few years and are gaining momentum.[3-18] Based on the chemical principle, these processes can be grouped as follows:

1. Palladium-based systems
2. Carbon/graphite-based systems
3. Conductive polymers
4. Non-formaldehyde-based electroless processes

Palladium-based Systems
In 1963, Radovski patented a "direct plate" process. He had found that, under certain conditions, a board that had gone through all the preparations preceding the electroless copper bath, could go "directly" into an acid copper electroplating bath, obtaining electrodeposition of copper on the dielectric through-hole wall surface of drilled boards. This discovery did not immediately lead to a commercial application. In the mid 1980s, the first commercial application appeared in the form of vertical panel plating.[19,20] A special, single-component organic additive copper electroplating bath had to be used. Because it yielded a copper deposit of inferior metallurgical properties, only a thin copper strike was applied, followed by a standard acid copper bath to build up to the full desired 25 μm (1 mil) metal thickness in the via hole.

In such a process, copper accretion in the hole begins at the copper surface on the rim of the through-hole on both sides and slowly proceeds to the center of the hole, where the two plating fronts merge. This process inevitably leads to some "dog-boning" of the deposit, an undesirable thickening of the copper near the hole entrances and a thinner deposit in the center. Consequently, improvements of this process have focused on enhancing the plating speed, through better through-hole coverage of the palladium and/or improving the conductivity of the deposit, as well as making the process work in standard acid copper baths.[21-23]

Systems Based on Palladium & a Second Metal[24]
To improve the conductivity of the palladium colloid, some systems have modified the acceleration step (*i.e.,* the step in which tin is removed from the palladium in such a way that, in a chemical exchange reaction, another metal, typically copper, is deposited on the palladium, taking the place of tin). These deposits show improved conductivity, speed up the through-hole metallization, and minimize dog-boning.

Polymer-stabilized Palladium Colloids[25]
One commercial system uses an organic polymer to stabilize the palladium colloid. This polymer has chemical affinity with the conditioner chemistry covering the hole wall, assuring good adsorption of the palladium particles and resulting in more complete wall coverage and faster plating. There is a polymer-removal step prior to electroplating.

Palladium Sulfide Coatings[26-28]
This process relies on conversion of the discrete palladium particles to a continuous palladium sulfide film for better hole wall coverage, better conductivity, and plating speed. Palladium sulfide is removed from the copper surfaces prior to dry film resist lamination and plating to assure good copper/copper bond integrity.

Very Small Palladium Colloids[29,30]

Several systems claim the use of superfine palladium colloids for better hole wall coverage and improved conductivity. Particle size distribution measurements are difficult, and shelf life of the colloid and bath life may be a concern.

Dry Film Resist Processing Considerations

In case the palladium catalyzed board is panel-plated, dry film resist processing is not different from the conventional process—the relatively smooth copper surface needs to be roughened (R_z = 1.5 to 3 μm, R_a = 0.15 to 0.3 μm) for optimal resist adhesion. A typical process is brush pumicing. This process may be preceded in tent and etch applications by a mechanical de-noduling step. In the traditional pattern plating process on electroless copper surfaces, a concern has been resist adhesion to scrubbed or unscrubbed (anti-tarnished) electroless copper. In the case of palladium-catalyzed direct plating, the resist must adhere to the catalyzed vendor copper surface. Typically, the palladium is not removed from the vendor copper prior to dry film resist lamination.

The topography of the vendor copper is basically the one created by the mechanical deburring step, modified slightly by the mild microetch preceding the activator step. Deburring might employ a 240-grit brush. Such a surface, although different from electroless copper, normally does not present a problem with dry film adhesion or clean stripping.

It should be noted that the palladium sulfide version of the process warrants special considerations—it is necessary to chemically remove the palladium sulfide from the copper surfaces by under-etching it. This step creates palladium sulfide "skins" that should be filtered out to avoid redeposition on the board, creating interfacial voids between dry film and copper.

In the past, sodium persulfate etchants that yield a relatively rough grain structure, beneficial for dry film adhesion, could not be used, because they chemically destroy (oxidize) the palladium sulfide. Consequently, a hydrogen peroxide/sulfuric acid combination has been in use. This etchant leaves a smoother surface than is desired for most dry film resists. In multilayer production, where palladium sulfide must be removed, not only from the surface copper, but also from the less accessible inner-layer copper in the through-hole, an extra-deep microetch is recommended, which further reduces the original deburring roughness. Therefore, dry film resists with very good adhesion to relatively smooth surfaces work best in this application. Most recently, a special persulfate has been introduced, yielding a rougher microetch without damaging the palladium sulfide film.

Carbon/Graphite-based Systems

In the mid-1980s, the first carbon system was introduced.[31-34] Since then, the carbon system has seen many process improvements, and a graphite system has been available since the early '90s. The carbon/graphite-based systems take advantage of the fact that the chemical element carbon is more or less conductive, depending on its crystal structure. It can be deposited with good adherence to the dielectric in the though-hole; undesirable carbon deposits can be removed from the copper surfaces by under-etching the copper surface on which the carbon particles were deposited.

The graphite process currently uses graphite particles 0.7 to 1.0 μm in size, and is said to provide better adhesion, hole wall coverage, and conductivity than the process employing amorphous carbon black. One pass through the graphite bath suffices, whereas two passes are needed for adequate coverage in the carbon black process. It is also argued that the graphite platelets lie flat on the hole wall surface, resulting in orientation of the conductive electron band, between the honeycomb layers of carbon, in the proper direction for faster plating. Both processes are offered, and preferentially run, in horizontal, conveyorized, wet processing modules. Recently, special modules with enhanced fluid dynamics, not based on the traditional spray action, have become available. They have the advantage of more effective fluid transport, as well as enhanced drying, so that the process line can be shortened substantially, with water consumption reduced.

The carbon-based process cannot tolerate brush-scrubbing, because carbon particles on the dielectric through-hole surface near the board surface may be brushed off, causing slow plating or no plating into the via hole. The graphite-based process[35] apparently can tolerate brush- or pumice-scrubbing without detrimental effect on initiation of the direct plate process; however, most PWB fabricators opt for omission of such a process step for cost or water conservation reasons, as long as good dry film adhesion is warranted. Both carbon and graphite processes don't appear compatible with jet pumice or jet alumina surface structuring because of the abrasive impact of the perpendicularly jetted particles on the catalyst particles in the through-hole.

With regard to the use of organic anti-tarnishes, as in all dry film surface preparations, the compatibility of the anti-tarnish with the dry film resist must be assessed. An increasing number of horizonal, conveyorized, direct plate systems link directly to the automatic cut sheet laminator, with no prelamination hold time of the board and no need to preserve the freshly cleaned surface. In this case, no anti-tarnish is used.

Conductive Polymers[36-41]

Conductive polymers, such as polyacetylene, polypyrrole, polythiaphene or polyanilines have been known for some time, but only polypyrrole has found its way into a commercial application for the initial via hole metallization of PWBs. This technology began in Europe and is gaining acceptance with fabricators who like to apply the direct plate process in a fully conveyorized, horizontal electroplating line for use in flash panel plating. These horizontal, conveyorized electroplating lines work with high current densities to achieve the desired plating thickness over a reasonably short travel time; the conductive polymer apparently can tolerate these conditions.

The polypyrrole conductive polymer process builds on the standard through-hole permanganate desmear chemistry employed by most fabricators of multilayer boards. As the permanganate removes the epoxy smear from the inner-layer copper by oxidation, insoluble manganese dioxide is formed. The board is then treated with a solution of the pyrrole monomer, which is oxidized by the manganese dioxide to form the conductive polymer polypyrrole. The manganese dioxide, in turn, is reduced to soluble manganese salts of valence state +2 and is washed off. The board is then ready for direct metallization. Early versions of the process employed a solvent-based solution of pyrrole that creates volatile organic compounds (VOCs). More recent versions of the process have practically eliminated this solvent altogether.

## Dry Film Resist Processing Considerations

This process has the advantage of depositing the conductive polymer only where it is needed, namely, on the non-conductive surface areas of the via hole wall. Therefore, there is no extra step to remove material from the surface copper that might impact dry film processing. Vendor copper is typically deburred after drilling, followed in many cases by pumice scrubbing.

Non-formaldehyde-based Electroless Processes

One commercial process is not too different from the traditional electroless/electroplate copper plating sequence: Formaldehyde has been replaced by the reducing agent, hypophosphite. The initial electroless deposition is practically self-limiting. The process is, therefore, first run in the electroless mode, then, continuing in the same bath, current is turned on to continue the build-up of copper. From there, the boards are transferred to an acid copper electroplating bath to complete the copper deposition. Not all acid copper plating baths are compatible with this process.

A second process[42] follows the classic pre-electroless step sequence through catalyst application. Then follows dry film lamination, imaging, and development. The catalyzed board with the resist image is then submerged in an electroless copper bath that selectively deposits copper on the copper surface and in the through-hole, but not on the resist. The bath is formaldehyde-free, works at near neutral pH values compatible with aqueous photoresists, and contains only mild, biodegradable complexing agents. A boron compound acts as reducing agent at 60 °C to deposit a 0.1-μm-thick copper layer. Pattern (electro)plating follows.

A third process[43-45] has been commercial in Europe since 1990. The drilled and deburred boards are conditioned in an autoclave with gaseous SO_3 for 1 to 2 min at room temperature. The copper surface is then brush-cleaned, the boards are laminated, exposed, and developed. Several process steps follow that are typical for electroless processing, including activation and electroless nickel deposition. Electroless nickel is selective; that is, it deposits only on the copper and through-hole walls, but not on the dry film resist. The activity of the nickel bath is dependent on the exposed copper surface area. The bath starts slowly if boards show only a few circuit traces. Conversely, the bath becomes very active if boards have large copper areas. Accordingly, bath control is critical.
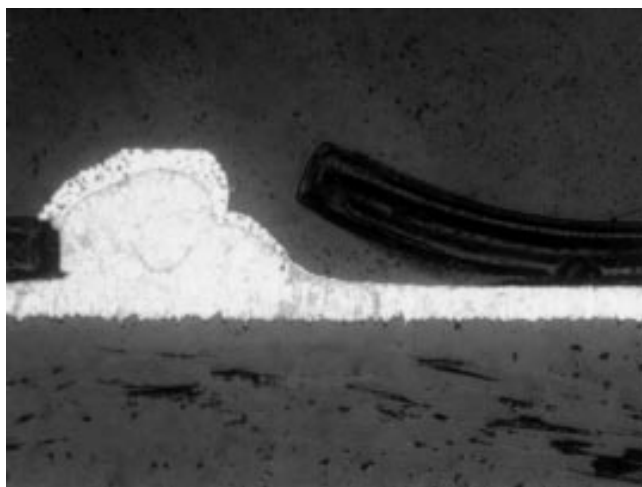
Resist lifting, causing copper and tin-lead underplating.

The pH of the bath is about 5.5; nickel deposit thickness is about 0.5 μm. The electroless nickel bath is followed by a rinse, sulfuric acid dip, and electrodeposition of copper. The nickel deposit (NiB from a boronate bath, not the more common NiP) does not deactivate rapidly as most nickel deposits do, and it is etchable with the common etching chemistries. The process therefore lends itself also to panel plating processes.

Dry Film Resist Processing

In the case of the electroless process based on hypophosphite, there are no special dry film resist processing considerations. Dry film resist is applied to the panel-electroplated surface. A mechanical surface structuring step to enhance mechanical adhesion is desirable before dry film lamination.

In the second process (selective deposition of copper on a board already covered with the developed resist image) the dry film resist is laminated to a drilled, deburred board that has been microetched after conditioner/cleaner steps, and before catalyzing. As a result, the dry film is applied directly to the catalyzed surface. The combination of deburr and microetch should yield the desired surface roughness discussed earlier. There is, however, a new consideration whenever dry film resist is in contact with the plating bath—the resist should be tested for compatibility with the plating chemistry (*e.g.,* in a leaching study, in which effects of resist leachants on the bath performance and the quality of the metal deposit are investigated).

The third process, also a selective process, in which electroless nickel plates on copper and dielectric, but not on dry film resist, presents the following special dry film resist processing considerations:

- Occasionally, the conditioning step can leave smear or crystalline residues on the copper surface that are difficult to remove by scrubbing. A dilute sulfuric acid rinse, followed by a water rinse preceding the scrubbing, can help remove such residues.
- The failure mode observed with dry film resists is usually lifting, as illustrated in the figure. The lifting occurs in large areas and the dry film forms bubbles. A UV bump after development helps with this problem. If the UV bump is too strong, however, nickel plating on the resist sidewall has been observed.
- When checking resist compatibility (*e.g.,* in leaching studies), criteria for compatibility should be the potential interference with a good nickel deposition, especially near the resist traces, plus any indications of resist lifting.

Summary and Conclusions

Several viable alternatives to the traditional formaldehyde-based electroless process are gaining commercial acceptance. These processes offer a combination of environmental, economic, and performance improvements. Dry film resist processing may or may not be affected by these new processes. Special considerations may be required with respect to surface preparation and adhesion. In the case of selective metallization in the presence of the dry film resist, resist and plating chemistry compatibility must be verified.

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